Journal Pre-proofs

Synthesis of novel LaCoO$_3$/graphene catalysts as highly efficient peroxymonosulfate activator for the degradation of organic pollutants

Mohaned Hammad, Steven Angel, Ahmed K. Al-kamal, Anam Asghar, Amin Said Amin, Mena-Alexander Kräenbring, Haakon T. A. Wiedemann, Vineetha Vinayakumar, Md Yusuf Ali, Paolo Fortugno, Cheolyong Kim, Torsten C. Schmidt, Christopher W. M. Kay, Christof Schulz, Doris Segets, Hartmut Wiggers

Please cite this article as: M. Hammad, S. Angel, A.K. Al-kamal, A. Asghar, A. Said Amin, M-A. Kräenbring, H. T. A. Wiedemann, V. Vinayakumar, M. Yusuf Ali, P. Fortugno, C. Kim, T.C. Schmidt, C. W. M. Kay, C. Schulz, D. Segets, H. Wiggers, Synthesis of novel LaCoO$_3$/graphene catalysts as highly efficient peroxymonosulfate activator for the degradation of organic pollutants, *Chemical Engineering Journal* (2022), doi: https://doi.org/10.1016/j.cej.2022.139900

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

1　**Title page**

2　**Synthesis of novel LaCoO$_3$/graphene catalysts as highly efficient**

3　**peroxymonosulfate activator for the degradation of organic pollutants**

4　Mohaned Hammad[a]*, Steven Angel[c], Ahmed K. Al-kamal[c,g], Anam Asghar[b], Amin Said Amin[a], Mena-

5　Alexander Kräenbring[a], Haakon T. A. Wiedemann[d], Vineetha Vinayakumar[a], Md Yusuf Ali[c], Paolo

6　Fortugno[c], Cheolyong Kim[b], Torsten C. Schmidt[b], Christopher W. M. Kay[d,f], Christof Schulz[c,e], Doris

7　Segets[a,e]*, Hartmut Wiggers[c,e]*

8　[a] Institute for Combustion and Gas Dynamics – Particle Science and Technology (IVG-PST), University

9　　of Duisburg-Essen, Duisburg, Germany

10　[b] Instrumental Analytical Chemistry and Centre for Water and Environmental Research, University of

11　　Duisburg-Essen, Essen, Germany

12　[c] Institute for Combustion and Gas Dynamics – Reactive Fluids (IVG-RF), University of Duisburg-

13　　Essen, Duisburg, Germany

14　[d] Department of Chemistry, Saarland University, Saarbrücken, Germany

15　[e] Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Duisburg,

16　　Germany

17　[f] London Centre for Nanotechnology, University College London, 17-19 Gordon Street, London WC1H

18　　0AH, United Kingdom

19　[g] Department of Materials Engineering, University of Al-Mustansiriyah, Baghdad, Iraq

20

21　Corresponding authors:

22　Dr. Mohaned Hammad*

23　Prof. Doris Segets*

24　Institute for Combustion and Gas Dynamics – Particle Science and Technology

25   Prof. Hartmut Wiggers*

26   Institute for Combustion and Gas Dynamics – Reactive Fluids

27   University of Duisburg-Essen

28   Carl-Benz-Str. 199

29   47057 Duisburg, Germany

30   mohaned.hammad@uni-due.de

31   doris.segets@uni-due.de

32   hartmut.wiggers@uni-due.de

Prof. Hartmut Wiggers*

Abstract

Metal leaching in perovskite-based catalysts during peroxymonosulfate activation processes can severely restrict their application in wastewater treatment. Therefore, enhancing the stability of perovskite nanostructures is crucial to improve catalytic performance and broaden applications but has been rarely achieved so far. We developed a scalable method to synthesize novel stable and environmentally-friendly nanocomposites of $LaCoO_3$ and few-layer graphene (consisting of roughly nine layers) for the removal of organic pollutants from wastewater. With abundant oxygen vacancies and synergistic effects between $LaCoO_3$ (LCO) and few-layer graphene, the novel $LaCoO_3$/graphene catalyst exhibits outstanding catalytic degradation (>99 %) of diclofenac, metoprolol, carbamazepine, and bisphenol A at a high concentration (40 mg/l) in less than 10 minutes in the peroxymonosulfate activation system, with mineralization of 57, 55, 61, and 62 %, respectively. The $LaCoO_3$/graphene catalyst exhibited excellent reusability and high catalytic performance within a wide pH range (3–11). The formation of $LaCoO_3$/graphene composites prevents cobalt leaching (0.004 mg/l), stabilizes sub-stoichiometric LCO and thus increases the content of Co^{2+} in the structure, leading to much higher catalytic activity than that of pure $LaCoO_3$. Electron paramagnetic resonance and radical quenching experiments revealed that both radical pathways ($SO_4^{\bullet-}$, $^\bullet OH$, and $O_2^{\bullet-}$) and non-radical pathways ($^1O_2$) contribute to bisphenol A degradation and the relative contributions of $^\bullet OH$, $SO_4^{\bullet-}$, and $^1O_2/O_2^{\bullet-}$ were determined to 13.4, 32.6, and 54 % for BPA removal, respectively. Overall, our results indicate that $LaCoO_3$/graphene is a promising material towards peroxymonosulfate activation for environmental remediation.

Keywords: Bisphenol A, gas-phase synthesis, graphene, heterogeneous catalysis, peroxymonosulfate.

1 Introduction

Trace organic pollutants such as industrial chemicals and personal care and pharmaceutical products discharged into the environment have brought serious threats to nature and humans due to their persistence, toxicity, and bioaccumulation [1,2]. Advanced oxidation processes (AOPs) are considered a promising technology to degrade organic pollutants [3]. The Fenton reaction is a classical AOP method that utilizes iron ions/salts to activate hydrogen peroxide (H_2O_2) and produce hydroxyl radicals ($^{\bullet}OH$, oxidative potential 1.9–2.7 V) at acidic pH (2.5–3.5) [4]. However, the traditional Fenton reaction is inherently limited by the narrow range of the working pH, metal leaching, and sludge generation during H_2O_2 activation [5]. In the last decade, sulfate radical-based advanced oxidation processes (SR-AOPs) were developed as promising alternatives to the classical Fenton reaction because of their high oxidative potential (2.5–3.1 V), wide pH adaptability (2–9), and long half-life time (30–40 ms) [6]. In order to generate sulfate radicals, peroxymonosulfate (PMS), or peroxydisulfate (PDS) are used most frequently and activated by heat [7], UV or visible light [8], microwave ultrasound [9], electrochemical processes [10], and transition metal ions (e.g., Co, Mn, Cu, and Fe) [11]. In this regard, different transition metal oxide catalysts such as Co_3O_4, $CuFe_2O_4$, $LaCoO_3$, etc. [12–14], zero-valent metal [15], and carbon-based materials [16] are reported to activate peroxymonosulfate (PMS) or peroxydisulfate (PDS) in refractory chemical degradation processes. Among them, transition metal-based perovskites such as $LaCoO_3$ (LCO) nanoparticles have received considerable attention in PMS activation because of their structural flexibility, high electronic conductivity, and their ability to create oxygen vacancies [17,18]. Our recent study reveals that the catalytic activity of $LaCoO_3$ nanomaterials is significantly higher than that of Co_3O_4 nanoparticles towards PMS activation for bisphenol A degradation [19]. Furthermore, a previous report shows also that the cobalt-based perovskite, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, exhibited better redox potential and electrical conductivity than Co_3O_4 nanoparticles for PMS activation [20]. $LaCoO_3$ has been widely used as catalyst in the field of water and ethanol oxidation [21], cyclohexene oxidation [22], catalytic combustion [23], photocatalysis [24], and heterogeneous Fenton reactions [25]. However, the reusability and toxicity of cobalt-based perovskite due to cobalt leaching in aqueous systems severely impeded their practical application in wastewater treatment. Therefore, fabricating stable and

4

85 environmentally-friendly cobalt-based solid-state catalysts has attracted increasing interest for PMS

86 activation.

87 For the synthesis of perovskites, various methods have been explored. These methods are usually

88 grouped into different categories [26,27]. One category is known as solid–solid synthesis, including

89 methods such as microwave, combustion, ceramic, and mechanochemistry synthesis. As these methods

90 are usually followed by extended high-temperature calcination to reach the desired crystallographic

91 phase, the final particles typically provide low specific surface areas – with few exceptions (e.g.,

92 activated reactive synthesis [28]). In the quest of phase-pure perovskites with high specific surface areas,

93 liquid-based or solution-mediated synthesis has been also explored. This category includes methods

94 such as sol-gel or Pechini processes, or nanocasting (e.g., using soft or hard templates). Nevertheless,

95 these methods are also associated with high-temperature calcination and the resulting lack of

96 morphology control [29] (e.g., in sol-gel or Pechini methods) or with the complex removal of templates

97 (e.g., silica in nanocasting methods) and low yields of material [26]. In contrast to these conventional

98 synthesis routes, spray-flame synthesis of perovskites is a method that enables production of phase-pure

99 and high specific surface area materials in a single step [30,31]. Furthermore, this method allows the

100 use of low-cost precursors (e.g., metal nitrates or chlorides) and facilitates the synthesis of high-quality

101 perovskites in a continuous and scalable way [32].

102 Recently, researchers have attempted to improve the catalytic activity and stability of catalysts by

103 incorporating catalysts on carbonaceous materials such as carbon [33], C_3N_4 [34], carbon quantum dots

104 [35], and graphene derivatives [36]. Comparing with the above mentioned carbonaceous materials,

105 single and few-layer graphene provides high electrochemical stability and high surface area that can be

106 used as adsorbent support for the decomposition of organic pollutants [37]. Xu et al. reported that

107 graphene revealed an improved adsorption capacity for bisphenol A (82 mg/g at 302.15 K) compared to

108 other carbonaceous materials [38]. Due to their high electron mobility and unique optical properties,

109 graphene/semiconductor nanoparticles-based composites have also shown to possess a high

110 photocatalytic activity [39–41]. As reported in one of our previous works, the high surface area of few-

111 layer graphene and the presence of unpaired π electrons in the graphene structure facilitate a fast

5

112 transport of the photo-induced electrons between graphene and Fe_3O_4 [42], which improves the

113 degradation efficiency towards methylene blue. Besides, graphene exhibits exciting properties such as

114 mechanical flexibility, chemical stability, and optical transparency [43]. For instance, Wang et al.

115 demonstrated that the catalytic activity of a Co_3O_4/graphene hybrid in terms of Orange II degradation

116 was 2.5 times faster compared to that of pure Co_3O_4. Graphene facilities the electric conductivity of the

117 composite compared to pure Co_3O_4, and therefore promotes electron transfer between the catalyst and

118 PMS, resulting in increased sulfate radical ($SO_4^{\bullet-}$) generation [44]. However, to the best of our

119 knowledge, there is no report on the application of $LaCoO_3$/graphene (LCO/Gr) in PMS activation. This

120 motivates the development of a new strategy for scalable production of LCO/Gr nanostructures for PMS

121 activation. Usually, the incorporation of cobalt-based catalysts in graphene is achieved by hydrothermal

122 [45] or post-impregnating methods [46], which requires additional steps for surface functionalization of

123 nanoparticles and/or graphene-based structures and needs a subsequent chemical reaction step to reduce

124 graphene oxide [47,48]. The hybrids of cobalt-based nanoparticles and graphene can always show low

125 metal leaching [49]. However, the better chemical stability was not based on the low cobalt leaching

126 [50]. In fact, no metal leaching was observed in some metal-free catalysts, but they showed poor

127 chemical stability after PMS activation [51].

128 The aim of this study is to prepare a stable composite of LCO and few-layer graphene (hereafter referred

129 to as graphene for simplicity), to investigate the contribution of $LaCoO_3$ and graphene and in particular

130 their interaction with respect to the degradation of pollutants, to understand the physicochemical

131 properties of the novel $LaCoO_3$/graphene catalyst, and to propose an activation mechanism for

132 peroxymonosulfate. We demonstrate a convenient and scalable method to prepare stable LCO/Gr

133 nanocomposites. LCO nanoparticles synthesized via spray-flame synthesis are bonded to graphene from

134 scalable microwave-plasma synthesis by a simple ultrasonication technique. This approach follows our

135 previous studies showing that the binding of graphene (30 % w/w) to nanoparticles hinders nanoparticle

136 agglomeration as well as restacking of the graphene sheets [42].

2 Materials and methods

2.1 Materials

For the synthesis of LCO, $La(NO_3)_3 \cdot 6\,H_2O$ (AppliChem Panreac, > 99.0 % purity) and $Co(NO_3)_2 \cdot 6\,H_2O$ (Honeywell, > 99.0 % purity) were used as precursors dissolved in a mixture of ethanol (VWR, > 99.9 % purity) and 2-ethylhexanoic acid (2-EHA) (Alfa Aesar, >99 % purity). 5,5-dimethyl-1-pyrroline N-oxide (> 97.0 %; TCI), 2,2,6,6-tetramethyl-4-piperidon (≥ 95 %), bisphenol A (≥ 99 %), diclofenac sodium salt (≥ 98 %), metoprolol tartrate salt (≥ 98 %), carbamazepine (≥ 98 %), potassium peroxymonosulfate (100 %), sodium phosphate monobasic (≥ 99 %), sodium nitrate (≥ 99 %), sodium chloride (≥ 99 %), sodium hydrogencarbonate (≥ 99 %), β-carotene (≥ 95 %), tert-butyl alcohol (≥ 99.5 %), p-benzoquinone (≥ 98 %), potassium bicarbonate (≥ 99.5 %), and potassium iodide (≥ 90 %) were purchased from Sigma Aldrich for the catalysis tests. Sodium hydroxide (≥ 97 %) and nitric acid (> 69 %, both VWR chemical) were used to adjust the pH of the respective solution. All chemicals were used as received without further purification. All gases (argon (Ar), oxygen (O_2), methane (CH_4), hydrogen (H_2), and nitrogen (N_2)) were supplied from Air Liquide with a purity of 99.5 % or higher. Upper Mississippi River NOM (NOM, 1R110N) was received from International Humic Substances Society (IHSS, Saint Paul, MN, USA) as dry solid extract. NOM stock solutions were prepared by mixing the required concentration of NOM in 50 ml of distilled water containing 0.1 mol/l NaOH with shaking overnight. Afterwards, the solutions were filtered through a polypropylene syringe filter (0.22 μm) and the pH was adjusted to 7 using H_3PO_4.

2.2 Synthesis of LCO nanoparticles

The synthesis of LCO nanoparticles was performed using an enclosed spray-flame reactor – described previously [31,52] using the standardized *SpraySyn* burner [53]. For the preparation of the precursor solutions, $La(NO_3)_3 \cdot 6\,H_2O$ and $Co(NO_3)_2 \cdot 6\,H_2O$ in a total concentration of 0.2 mol/l were dissolved in a mixture of ethanol (35 Vol.%) and 2-EHA (65 Vol.%). By using a syringe pump, the precursor solution was supplied to the reactor at a constant flow rate of 2 ml/min via a capillary surrounded by an annular

162   gap through which O_2 was supplied at a flow rate of 10 slm as dispersion gas. The atomization of the

163   solution was done by the shear forces caused by the contact of the high velocity dispersion gas with the

164   solution at the capillary tip. The resulting aerosol was ignited by a premixed flat pilot flame (3 slm CH_4

165   and 20 slm O_2, stabilized on a sintered bronze plate), coaxially surrounding the spray nozzle. The spray

166   flame was shielded from the reactor walls by a surrounding sheath-gas (140 slm, compressed air). To

167   control the temperature of the off-gas and to minimize the sintering of the nanoparticles, an additional

168   quench gas flow – 200 slm compressed air – was supplied downstream of the spray flame. The pressure

169   in the reaction chamber was held constant at 970 mbar and the nanoparticles were collected from the

170   reactor off-gas using a membrane filter.

171 ## 2.3   Synthesis of graphene

172   The synthesis of freestanding few-layer graphene flakes was carried out using a microwave plasma

173   reactor as described before [54]. A microwave antenna (iplas company) was used to focus the

174   microwaves to the center of a quartz tube located in the center of the antenna. Ar (30 slm) and H_2 (1 slm)

175   were used as plasma gases and to stabilize the centrally introduced precursor gas flow. The plasma was

176   ignited using a 2-kW microwave generator (Muegge, Germany) that operates at a frequency of 2.45

177   GHz. Ethanol (0.5 ml/min) used as graphene precursor was vaporized at 180 °C and mixed with argon

178   as carrier gas (5 slm) using a controlled evaporation mixing system (CEM W-209-333-P, Bronkhorst).

179   The mixture was fed through a nozzle into the center of the plasma zone. The resulting graphene flakes

180   were collected from a PTFE-coated filter membrane located downstream the reaction zone. The typical

181   production rate of this process is 200 mg/h.

182   In order to disperse graphene in water and to support the self-assembly with LCO nanoparticles, the

183   graphene surface had to be modified with carboxyl groups. Thus, pristine graphene was stirred in a

184   concentrated mixture of sulfuric and nitric acid (3:1) for a few minutes, collected by centrifugation

185   (12,000 rpm), and washed with de-ionized water for three times. The carboxylated graphene was then

186   dried at 60 °C under vacuum for 24 hours.

2.4 Reproducible fabrication of LCO/Gr

LaCoO$_3$/graphene nanocomposites were prepared via a controllable ultrasonication-assisted self-assembly process. The LCO/Gr nanocomposites were assembled through an electrostatic interaction between the positively charged LCO (+37.4 mV, pH=9) and the negatively charged graphene (−40.6 mV, pH=9). 300 mg carboxylated graphene were dispersed in 60 ml water by sonication (Hielscher UP200S, 60 % amplitude, 60 % cycle duty (0.6 s pulse rate)) for 30 minutes. Subsequently, dispersions of LCO (700 mg particles in 100 ml water by sonication) were added to the graphene dispersion under stirring and the obtained mixtures were further sonicated for another 60 minutes on an ice bath. The final pH of the suspension was 9. The product was collected via centrifugation and dried at 60 °C under vacuum for 24 hours.

2.5 Materials characterization

Characterization by thermal gravimetric analysis (TGA) was performed with a Netzsch 449 F1 Jupiter at temperatures increasing from room temperature to 1000 °C with a heating rate of 10 K/min under the flow of synthetic air (250 ml/min). X-ray diffraction (XRD) patterns were recorded in the 2θ range of 10–80° using a PANalytical X'Pert X-ray diffractometer equipped with a Cu K$_\alpha$ radiation ($\lambda = 1.5406$ Å). The morphology of the synthesized nanoparticles was acquired with a JEOL JEM-2200FS transmission electron microscope (TEM). Raman spectra were collected using a Renishaw inVia Raman microscope with excitation laser wavelengths of 532 nm (1000–1800 cm^{-1}) and 680 nm (100–1000 cm^{-1}). The surface composition of the materials was studied by X-ray photoelectron spectroscopy (XPS) using a VersaProbe II (Ulvac-Phi) with monochromatic Al K$_\alpha$ light at an emission angle of 45°. The specific surface area was analyzed by the Brunauer-Emmett-Teller (BET) method with a Quantachrome NOVA2200 analyzer. The pH point of zero charge (pH$_{pzc}$) of the catalysts' dispersion was determined by a Malvern Zetasizer. In order to evaluate the electrochemical behavior of the catalyst, electrochemical impedance spectroscopy (EIS) was performed using a Solartron 1260 in the frequency range between 0.1 Hz and 1 MHz at an applied AC potential value of 100 mV. To that end, the catalyst powder samples were pressed into pellets (thickness between 0.3 and 0.5 mm) by a 5-

213 mm stainless steel die (force: 15 kN, for 15–30 minutes). Then, the pellets were coated with gold on

214 both sides to improve the contact between the platinum electrodes (size 5 mm). The Hansen solubility

215 (understood here in the context of similarity) parameter (HSP) were determined according to a method

216 reported by Bapat et al. using analytical centrifugation (AC) [55]. Briefly, 1 wt/v% LCO and LCO/Gr

217 dispersions were prepared by 5 minutes sonication of the powder in the respective probe liquids listed

218 in Table S1. The dispersions were filled into cells and then inserted into the rotor and centrifuged at

219 2000 rpm for 20 hours. AC measurements were performed using a LUMiSizer LS 651 (LUM GmbH,

220 Berlin, Germany) with a wavelength of 410 nm. Reactive radicals spectra were obtained using an

221 electron-spin resonance spectrometer (MiniScope MS-5000, Freiberg Instruments, Germany) and

222 recorded using a microwave power of 10 mW and a modulation amplitude of 0.2 G at room temperature.

223 A mercury intrusion porosimeter (PoreMaster-60, Anton Paar) was used to determine the porosity and

224 pore size distribution. The pore radius (r) was determined using the Washburn equation.

225 $$P = \frac{-2\gamma \cos\theta}{r}$$ (Equation 1)

226 Where P is the pressure γ is the interfacial energy (surface tension) of mercury and θ is the contact angle

227 of mercury with the material. The mercury is intruded into the sample at a rate of 7–28 MPa /min and

228 the pressure ranged from 100 Pa to 400 MPa.

229 ## 2.6 Catalysis studies and analyses

230 The degradation performance of the as-prepared LCO catalyst was evaluated for BPA degradation. In a

231 typical run, 6 mg catalyst was initially dispersed into 60 ml BPA aqueous solution (40 mg/l) at 25 °C,

232 and the initial pH was adjusted by H_2SO_4 and NaOH to different pH values (3–11). The resulting

233 suspension was continuously stirred for 30 min to ensure the establishment of an adsorption/desorption

234 equilibrium between BPA molecules and the as-prepared catalyst before a certain amount of PMS was

235 added. During the experiment, 2 ml of the suspension was withdrawn at given time intervals,

236 immediately quenched with 0.5 ml methanol, centrifuged (12,000 rpm, 20 min) to remove the particles,

237 and the supernatant was injected into a HPLC vial. To evaluate the reusability of the catalyst, the as-

238   prepared nanoparticles were recovered by a centrifuge (12,000 rpm, 20 min), washed with de-ionized

239   water three times, and then re-dispersed into 60 mL BPA aqueous solution for the next use.

240   Moreover, degradation of DCF, MTP, and CBZ was also investigated to test the catalytic activity of the

241   as-prepared catalyst. To obtain the degradation reaction kinetics of organic pollutants, pseudo-first-order

242   kinetics reaction rate constants (k_{app}) were determined according to the following equation:

243
$$\ln \left(\frac{C_t}{C_0}\right) = -k_{app}t \qquad \text{(Equation 2)}$$

244   Where C_t depicts the pollutant concentration at time t, C_0 is the initial pollutant concentration, and k_{app}

245   is the reaction rate constant.

246   The concentrations of BPA, DCF, MTP, and CBZ were analyzed by high-performance liquid

247   chromatography (HPLC, Shimadzu LC-10AT) with an EVO C18 column (Kinetex 5μm EVO C18 100

248   Å 100 × 3.0 mm, Phenomenex). The flow rate of the mobile phase consisting of 0.1 % formic acid in

249   water and methanol (60:40, v:v) was 0.5 ml/min. To determine the residual concentration of PMS,

250   100 μl of the suspension was withdrawn at given time intervals, mixed with potassium bicarbonate

251   (5 g/l) and potassium iodide (40 g/l), and then analyzed by UV-Vis spectroscopy (Varian Cary 400) at

252   a wavelength of 352 nm [56]. The mineralization rate was determined using a total organic carbon

253   analyzer (TOC-5000A, Shimadzu). The effects of pH, temperature, and co-existing ions (such as Cl^-,

254   NO_3^- $H_2PO_4^-$, HCO_3^-, etc.) on the PMS activation of LCO/Gr composite catalyst were also investigated.

255   To evaluate the reusability of the LCO/Gr nanoparticles, the LCO/Gr catalysts were collected by

256   centrifugation (Sigma 3-30KS centrifuge, Sigma Laborzentrifugen GmbH, Germany) at 14,000 rpm for

257   10 min, followed by thorough washing with deionized water and re-dispersion into fresh BPA solution

258   for the next experimental run. To identify the dominant reactive radicals in the system, ethanol (EtOH),

259   tert-butyl alcohol (TBA), and β-carotene were used as scavengers for $SO_4^{\cdot-}$ and $\cdot OH$, $\cdot OH$, and $^1O_2$

260   respectively. Furthermore, electron paramagnetic resonance experiments were performed to identify

261      $SO_4^{\cdot-}$ and $\cdot OH$, and $^1O_2$, respectively, using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-

262   tetramethyl-4-piperidon (TEMP) as spin traps. The EPR spectra were measured using a MiniScope MS-

263   5000 electron spin resonance spectrometer (modulation amplitude 0.2 G, microwave power, 10 mW).

The concentration of dissolved metal ions was determined by atomic absorption spectroscopy (AAS, Thermo Electron Corporation, M-Serie).

3 Results and discussion

3.1 Preparation of LCO/Gr nanocomposites

To quantify the amount of adsorbates and carbon in as-synthesized LCO and the LCO/Gr nanocomposites, TGA measurements were performed at up to 1000 °C under synthetic air to decompose residuals on the particle surface as well as graphene (see supplementary material, Figure S1). The weight loss of the pristine LCO is about 19 % and can be ascribed to the loss of adsorbates such as water (3 %, 50–170 °C) and the oxidation of unburned combustion residuals (16 %, 200–600 °C) releasing water and CO_2. Compared to the result of as-synthesized LCO, the additional weight loss for LCO/Gr is 32 %, which can be attributed to the oxidation of graphene (300–750 °C). Accordingly, the observed graphene weight loss value is in good agreement with the intended composition of the LCO/Gr nanocomposite.

3.2 Structural characterization of LCO/Gr nanocomposites

Raman spectroscopy was employed as a qualitative method to evaluate the purity of the synthesized graphene and to identify the phase composition of the LCO and LCO/Gr nanoparticles (Figure 1a). The peak at around 650 cm^{-1} measured for LCO (black graph) matches the Co–O stretching vibration of the $LaCoO_3$ phase [57], whereas the Raman spectrum of graphene (red graph) consists of two peaks. The D (1350 cm^{-1}) and G (1580 cm^{-1}) bands are ascribed to sp^3 defects and the first-order scattering of sp^2 carbon atom domains in a 2D hexagonal carbon lattice, respectively. The intensity ratio between the D and G bands (I_D/I_G) is a measure of the degree of disorder and defects in the graphene structure [58]. The observed I_D/I_G ratio of 0.5 is quite low, indicating a very high quality of the as-synthesized few-layer graphene (see supplementary material, Figure S3a) with a low degree of structural defects. Importantly, there is a significant difference in I_D/I_G values between the pure few-layer graphene and LCO/Gr composite (0.79, green graph in Figure 1a). However, when LCO (0.68 g) and graphene

288   (0.32 g) were mixed without having been processed to the LCO/Gr nanocomposite in advance, there is

289   almost no change in I_D/I_G (0.54, blue graph). This provides strong evidence that the deposition of LCO

290   nanoparticles on the graphene nanosheets did introduce defects in the graphene structure due to strong

291   interaction between LCO nanoparticles and graphene sheets.
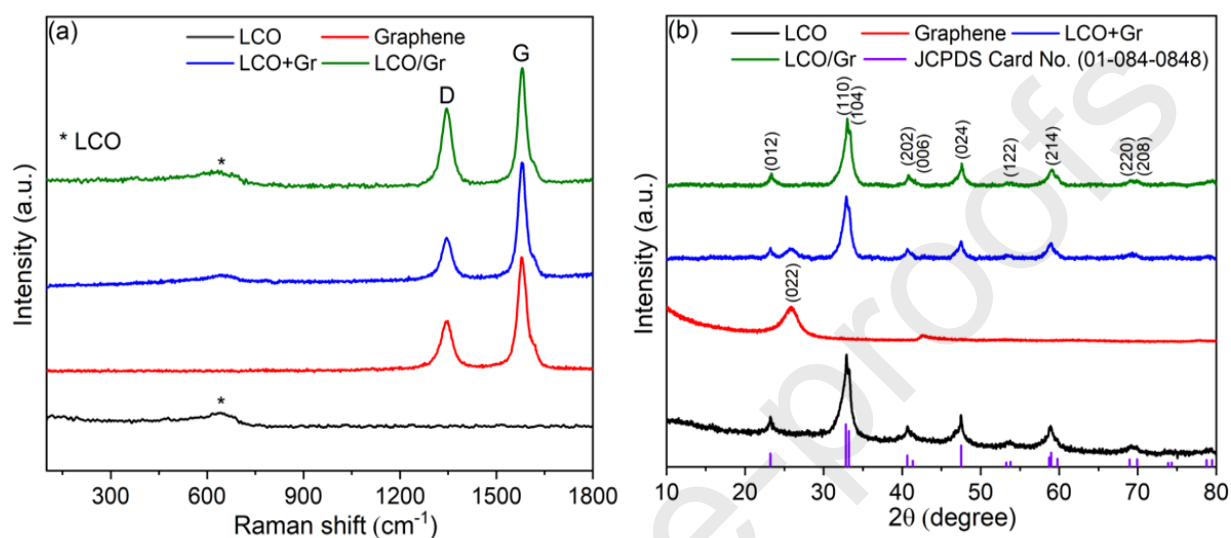
292

293   Figure 1. a) Raman spectra and b) XRD patterns for LCO, graphene, LCO+Gr, and LCO/Gr nanopowders. All

294   Raman spectra were measured with an excitation wavelength of 532 nm (1000–1800 cm^{-1}) and 680 nm (100–

295   1000 cm^{-1}).

296   The crystal structure of LCO, graphene, and LCO/Gr materials was characterized by powder XRD

297   (Figure 1b). The LCO diffraction peaks (black graph) can be indexed to the rhombohedral LaCoO$_3$

298   perovskite phase (JCPDS Card No. 01-084-0848) [59] and the peak shape is characteristic for

299   nanoparticles with high crystallinity. The mean crystallite sizes calculated from the XRD pattern of LCO

300   and LCO/Gr nanoparticles using Rietveld refinement are 9 and 9.3 nm, respectively (see supplementary

301   material, Figure S2), which is within the accuracy of the analysis and confirms that the LCO crystallites

302   do not change in structure and size. However, the lattice constants of LCO derived from Rietveld

303   refinement slightly increase with the introduction of LCO to graphene, whereas in case of the physical

304   mixture (LCO+Gr), there is no significant change (see supplementary material, Table S1). We interpret

305   this as a clear indication of chemical interaction between LCO and graphene in the composite material.

306   The weak expansion in the lattice constant of LCO in LCO/Gr (compared to bulk LCO and pristine LCO

13

307 nanoparticles) can be attributed to the presence of oxygen vacancies as also reported in literature [60,61].

308 The intense and broad peak of graphene at $2\theta = 26.2°$ corresponds to the (002) plane of graphene.

309 Interestingly, the characteristic (002) diffraction peak of graphene has almost disappeared in the LCO/Gr

310 nanocomposite compared to the LCO+Gr nanoparticles mixture. This suggests that reduced graphene

311 stacking occurs, most probably due to the coverage of graphene with LCO nanoparticles [44].

312 The morphology and chemical composition of LCO nanoparticles and LCO/Gr nanocomposites were

313 characterized by TEM and elemental mapping. The sphere-like LCO nanoparticles (mean diameter

314 about 7 nm, see supplementary material, Figure S3b) are uniformly distributed, covering almost the

315 entire surface of the graphene sheets in LCO/Gr nanocomposite (Figure 2a). The high-magnification

316 TEM image (Figure 2b) reveals that all LCO nanoparticles are connected to graphene. The chemical

317 homogeneity of the LCO was evidenced by SEM energy-dispersive X-ray elemental mapping of

318 LCO/Gr (Figure 2c–g). The EDX analysis was performed to further confirm the composition of the

319 LCO/Gr material and showed that the La/Co ratio is about unity (see supplementary material, Figure

320 S3e). Moreover, the high-resolution TEM (HRTEM) image of LCO/Gr further shows the crystal lattice

321 fringes with an interlayer spacing of 0.26 and 0.34 nm, corresponding to the (104) and (002) planes of

322 the rhombohedral $LaCoO_3$ perovskite phase and highly crystalline graphene, respectively. This result is

323 consistent with the XRD analysis.
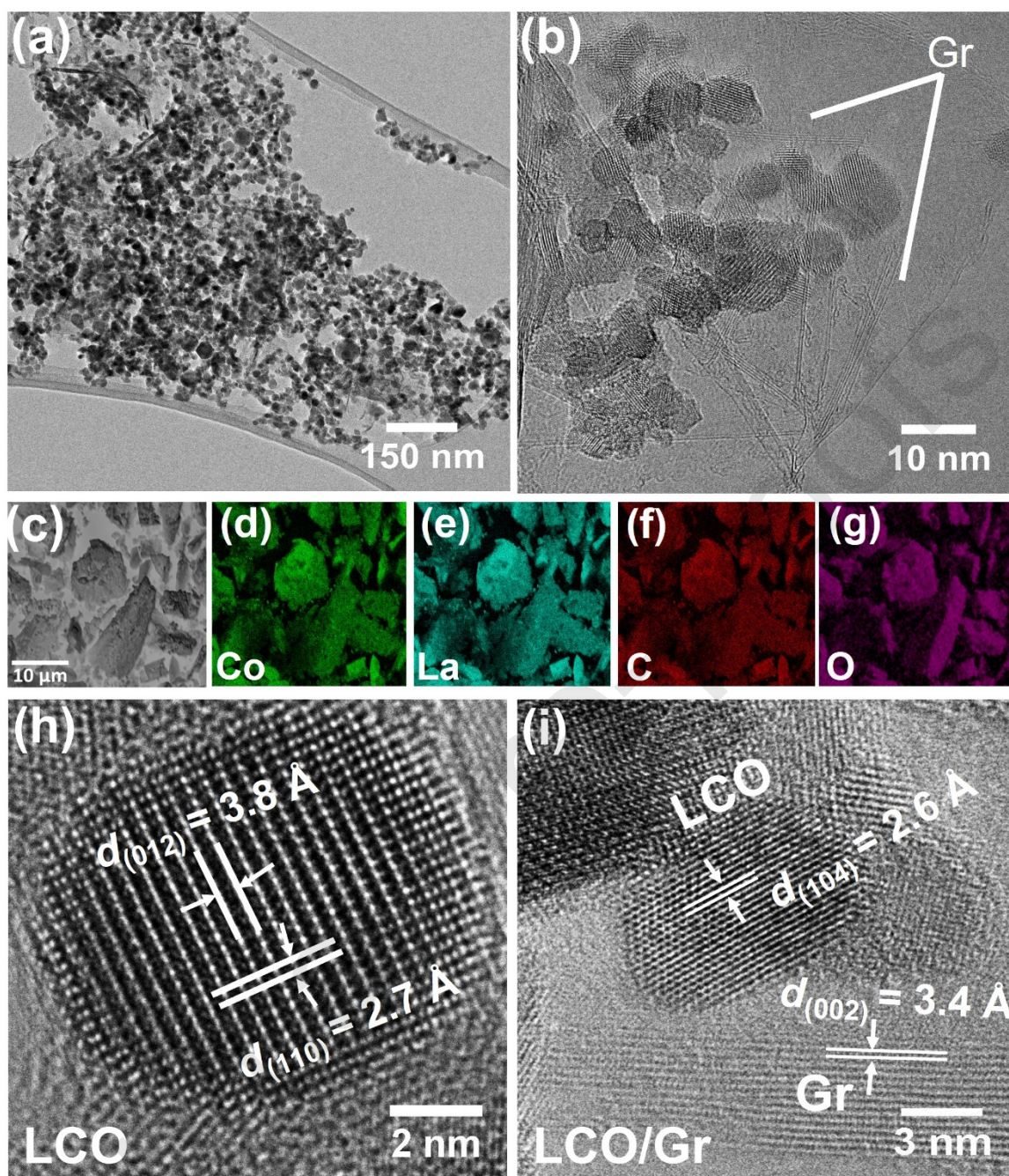
Figure 2. a) Low-magnification, b) high-magnification TEM image, c–g) SEM image of LCO/Gr composites and the corresponding elemental mapping of cobalt, lanthanum, carbon, and oxygen, and h–i) HRTEM image of LCO and LCO/Gr particles.

The findings regarding LCO particle size and formation of few-layer graphene are further supported by the results of nitrogen sorption. The mean particle diameter can be calculated from the results with the following formula:

331
$$SSA = \frac{6}{\rho d_p}$$
(Equation 3)

332 where SSA is the specific surface area (m^2/g), d_p stands for the particle diameter (nm), and ρ is the

333 density of the analyzed materials system (g/cm^3). Assuming spherical and non-aggregated particles,

334 average particle sizes of 8.8 nm were derived from the measured BET surface areas of 94 m^2/g, using a

335 LCO density of 7.25 g/cm^3. The average layer number of graphene can be estimated from the SSA of

336 single-layer graphene (2630 m^2/g) versus the measured SSA of graphene. The SSA of graphene was

337 measured as 300 m^2/g and suggests the formation of few-layer graphene with a mean number of

338 nine graphene sheets stacked on top of each other. As expected, the SSA of the LCO/Gr composite was

339 in between and was determined to be 154 m^2/g. Moreover, the pore-size distribution curve of LCO/Gr

340 composite determined by the Washburn equation showed that the pore-size distribution is broad with 65

341 % of the volume accounting for pores in the 2–3 nm range and 35 % are in the 6–12 nm range (see

342 supplementary material, Figure S4). The mesoporous nature of LCO/Gr with high surface area suggests

343 the presence of abundant active sites, which can activate PMS rapidly due to low mass transport

344 resistance [62].

345 To confirm the surface interaction between LCO nanoparticles and graphene, XPS and FTIR

346 spectroscopy was further studied. The surface chemical composition of LCO and LCO/Gr materials was

347 investigated by XPS analysis (Figure 3a–b and Figure S5). Figure S5a shows the full surface XPS

348 spectra of all samples. The four characteristic peak areas located at binding energies around 285, 530,

349 779, and 835 eV belong to C1s, O1s, Co2p, and La3d, respectively. In the surface La3d high-resolution

350 XPS spectra (see supplementary material, Figure S3d), the spectrum was fitted by peaks at 834 eV and

351 851.5 eV for La3d$_{5/2}$ and La3d$_{3/2}$, respectively, and their corresponding satellite peaks around 837.9 eV

352 and 855.1 eV, which is assigned to La^{3+} ions in perovskite structures [63]. Besides, compared to LCO,

353 the La3d peaks of the LaCoO$_3$/graphene was slightly shifted to a higher binding energy, which can be

354 attributed to the interaction between LaCoO$_3$ and graphene [64]. The surface Co2p XPS spectrum of

355 LCO material was fitted by peaks at 779.7 and 794.5 eV. These are assigned to the Co2p$_{3/2}$ and Co2p$_{1/2}$

356 spin-orbital peaks of LaCoO$_3$ [65]. The energy difference of the doublet is about 15.2–15.3 eV, which

357 is characteristic for the mixed oxide LaCoO$_3$ structure [66]. Besides, small Co2p$_{3/2}$ satellite peaks

358 positioned between 785–790 eV indicate the presence of a mixed oxidation state of Co^{3+} and Co^{2+}

359 surface ions. Upon mixing LCO and graphene (LCO+Gr), we could not observe any significant change

360 in the intensity of the satellite peak and the peak position of $Co2p_{3/2}$ and $Co2p_{1/2}$. However, compared to

361 LCO+Gr, the surface Co2p XPS spectrum of the LCO/Gr material exhibits peaks at 780.5 eV and 796.4

362 eV corresponding to the $Co2p_{3/2}$ and $Co2p_{1/2}$ states [67]. The increased intensity of the satellite peak

363 around 785 eV along with the shifted peak position of $Co2p_{3/2}$ and $Co2p_{1/2}$ indicates that a part of the

364 Co^{3+} ions was converted to Co^{2+} and formed oxygen vacancies (O_{vac}). In order to evaluate the surface

365 O_{vac} in both LCO and LOC/Gr samples, surface O1s spectra were deconvoluted into three major peaks

366 centered at 528.7, 529.5, and 531.6 eV. This corresponds to surface lattice oxygen (O_L), adsorbed

367 oxygen species on the surface vacancy (O_S), and surface hydroxyl groups (OH), respectively (Figure

368 3b) [68]. The relative concentration of surface O_{vac} in the LCO/Gr sample was determined to be 23 %,

369 which is higher compared to LCO nanoparticles (15 %) and LCO+Gr (14 %) and confirms the reduced

370 oxidation of cobalt ions in the LCO/Gr sample, further manifesting the formation of O_{vac}. Interestingly,

371 the new peak centered at 530.4 eV in O1s spectra of LCO/Gr sample confirms the formation of surface

372 Co–O–C bonds (Figure 3b, highlighted with an arrow). This peak results from the strong surface

373 interaction between LCO and graphene [69]. Details are given in the supplementary material (Figure

374 S5). In addition, EPR measurements were carried out to examine unpaired electrons in LCO, graphene,

375 LCO+Gr, and LCO/Gr (Figure 3c). The broad EPR signal observed for LCO is assigned to the

376 ferromagnetic (FM) clustering of the cobalt ions [70]. For the graphene sample, the narrow signal

377 observed at g ≈ 2.005 can be tentatively assigned to the presence of conduction electrons and/or localized

378 sigma "dangling bond" spins associated with defects. In case of LCO+Gr sample, the broad signal

379 assigned to clustering of cobalt ions is decreased along with the presence of a small narrow signal

380 appearing from the graphene sample. In contrast, the intensity of the narrow signal was increased for

381 LCO/Gr sample. This confirmed reduced oxidation of cobalt ions in the LCO/Gr sample and thus further

382 manifests the formation of O_{vac}.
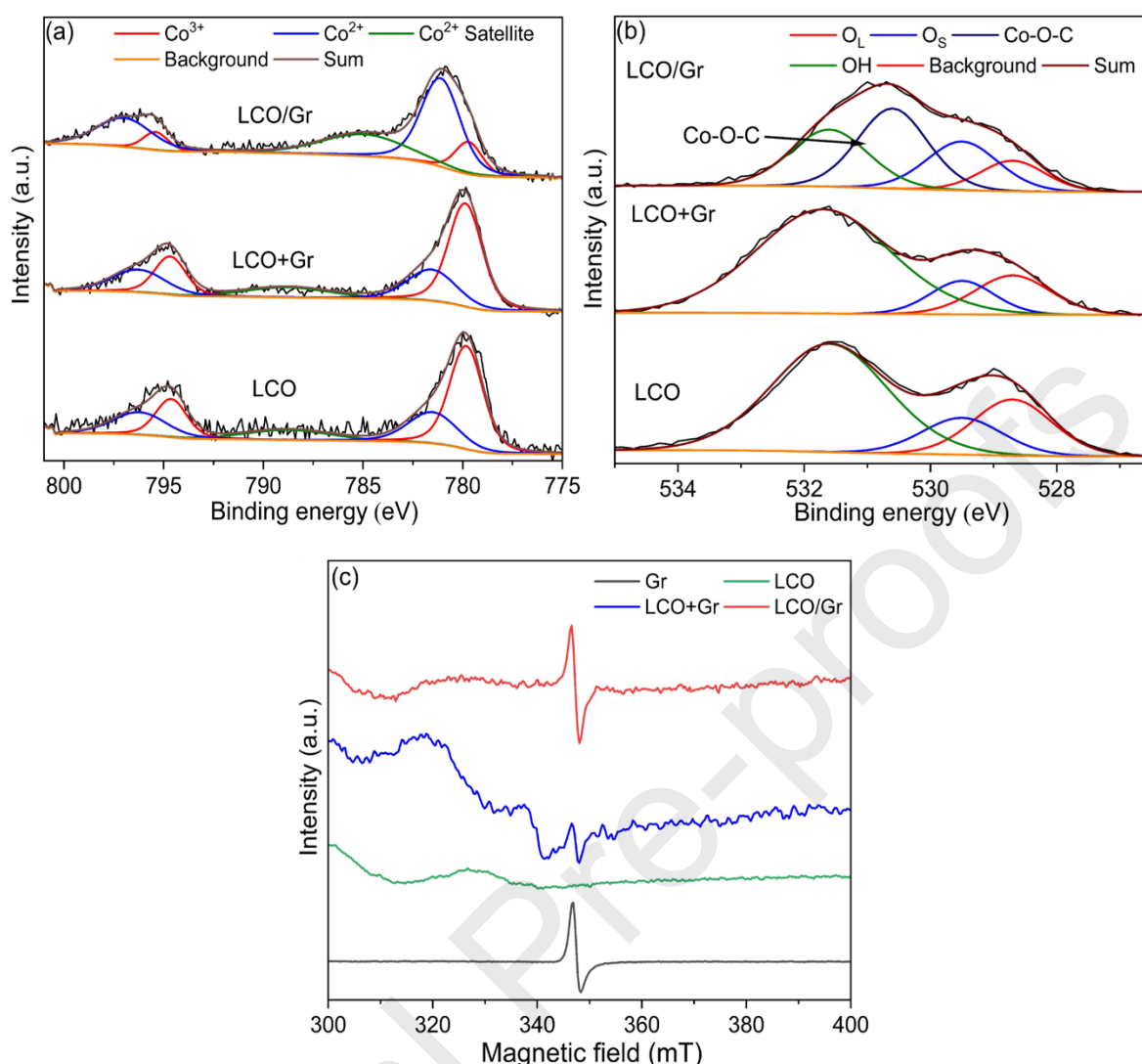
Figure 3. a) XPS curve fit of Co2p and b) O1s of the LCO, LCO+Gr, and LCO/Gr powder and c) EPR spectra of graphene, LCO, LCO+Gr, and LCO/Gr.

Furthermore, FTIR spectroscopy was carried out to confirm the formation of LCO/Gr nanocomposite (See supplementary material Figure S6). In the FTIR spectrum of LCO, the peaks at ~550 and 590 cm^{-1} are assigned to characteristic Co–O stretching vibration and O–Co–O deformation modes of $LaCoO_3$, respectively [71], whereas the characteristic peaks at 845 and 1540 cm^{-1}, and 3200–3600 cm^{-1} are attributed to symmetric and asymmetric COO^- vibration and O–H stretching vibration [72,73]. However, after the introduction of graphene, the peak intensities of O–H and COO^- groups decreased significantly, suggesting that the O–H and COO^- groups are substituted to form a Co–O–C bond between LCO and graphene nanoparticles [74]. This robust interaction between LCO and graphene nanoparticles is assumed to prevent cobalt leaching and mediates fast electron transport through the

18

graphene matrix to the LCO nanoparticles, enhancing their catalytic performance [42]. Besides, new absorption peaks in the 1380–1470 cm^{-1} range and at 1640 cm^{-1} are ascribed to aromatic carbon ring vibrations [75] and C=C stretching vibration [76], respectively, confirming the presence of graphene in LCO/Gr. Noteworthy, this result is consistent with TEM, XRD, Raman, and XPS analyses, altogether proving a strong interaction between LCO and graphene and thus the successful formation of a stable LCO/Gr composite.

3.3 Electrochemical characterization of LCO/Gr nanocomposites

The interfacial and composite conductivity of the catalyst can affect its catalytic performance. Thus, electrochemical impedance spectroscopy was performed to evaluate the conductivity of the pure LCO catalysts (pressed pellets) and the LCO/Gr nanocomposite. The Argand diagram of LCO (Fig S7a) shows the typical characteristics of a polycrystalline oxide semiconductor and an equivalent circuit for the grain boundary and bulk conductivity consisting of two R/CPE elements could be fitted to the measured data. The observed conductivity is surprisingly high for a nanocrystalline semiconductor material, whose conductivity is dominated by grain boundary resistances.

The electrical behavior of the composite material (Fig S7b) is characterized by the very high conductivity of the graphene. All parasitic resistances of our 2-point experimental setup sum up to about 1.2 Ohm, so that essentially Ohmic behavior is observed. Towards higher frequencies (from about 1 kHz) inductive effects appear visibly, which can be fitted by a R/CPE. Compared to the known capacitive behavior, however, the phase angle of this CPE is shifted by about 180° to a capacitor, so that it acts as an inductor. Due to the combination of highly conductive graphene and electrically well-conducting LCO nanoparticles, a very good electrical contact of LCO nanoparticles and graphene can be assumed here, which we believe greatly promotes the catalytic performance of the LCO/Gr material.

3.4 Stability of nanoparticle dispersions

High dispersion stability of the generated catalysts is a key factor to achieve good catalytic activity during PMS activation. Hence, identifying appropriate parameters that distinguish surface

19

421   characteristics before and after graphene introduction is important. Hansen solubility parameters (HSP)

422   represent surface characteristics and were determined here using analytical centrifuge (AC) experiments

423   [55]. From the AC software (SEPView), we obtain optical transmission profiles (fingerprints) that can

424   be employed to calculate so-called stability trajectories (see supplementary material, Figure S8-9). These

425   enable to assess the interaction of the particle surface with the continuous phase and thus a categorization

426   of probe liquids into good and poor according to the nanoparticle dispersion stability (see supplementary

427   material, Table S3-S4). As shown in Figure 4, the dispersion stability of LCO/Gr was analyzed in five

428   probe liquids (water, dimethylformamide, isopropanol, acetonitrile, and N-methyl-2-pyrrolidon). In case

429   of LCO, the nanoparticles were well-dispersible in only two probe liquids (acetonitrile and N-methyl-

430   2-pyrrolidon). Finally derived HSP values are summarized in the Table 1. The strong difference between

431   LCO and LCO/Gr further corroborates the findings of the previous chapters regarding the successful

432   synthesis of stable LCO/Gr composites.
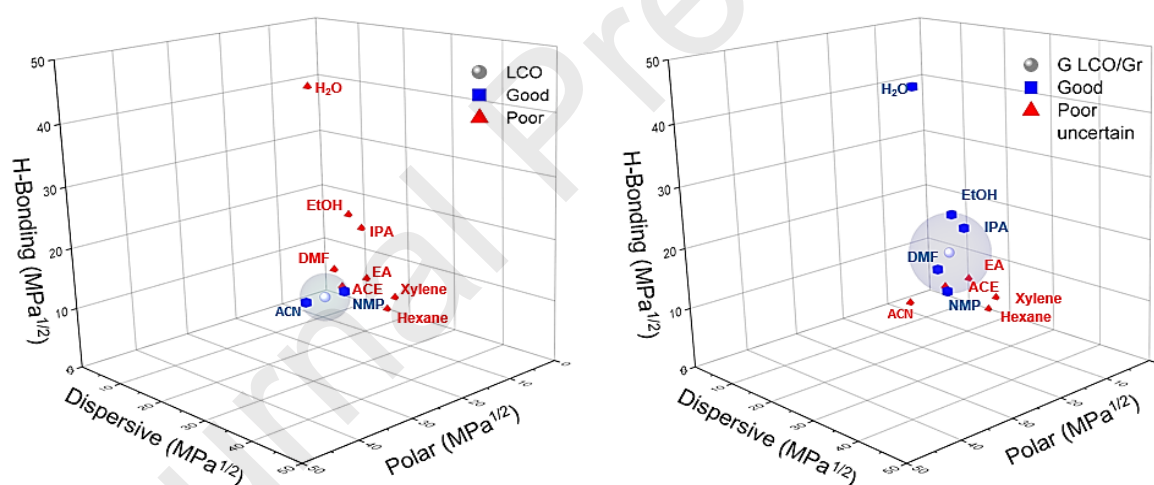
433

434   Figure 4. HSP sphere of LCO and LCO/Gr derived from HSPiP software and derived Hansen coordinates.

20

435   Table 1: HSP parameters of LCO and the range of HSP for LCO/Gr samples

Materials	LCO	LCO/Gr
Dispersive interactions δ_D (MPa$^{1/2}$)	16.7	15.3 – 20.5
Dispersive interactions δ_P (MPa$^{1/2}$)	15.2	8.4 – 15.4
Dispersive interactions δ_H (MPa$^{1/2}$)	6.7	11.8 – 14.9
Sphere radius (MPa$^{1/2}$)	4	6.8 – 15.3
Total combinations possible	-	1024
Combinations chosen for HSP	-	7 out of 8
Outliers	-	1

436

437   It needs to be mentioned that for deriving HSP, water was not considered due to its hydrogen bonding

438   capabilities ($\delta_H = 42$ MPa$^{1/2}$) and hence its large distance compared to other solvents [77]. However,

439   water is one of the most stable solvents for LCO/Gr, which is important for PMS activation. It is

440   noteworthy to mention that the catalytic reaction was conducted in aqueous medium, suggesting that

441   LCO/Gr might exhibit improved PMS activation compared to LCO which showed a poor dispersibility

442   in water. This leads to agglomeration and sediments, and therefore additionally lowers the catalytic

443   activity. Thus, dispersion studies in water were performed separately employing transmittograms (see

444   supplementary materials, Figure S10). The LCO/Gr nanoparticles that are dispersed in tap water show

445   the quickest sedimentation due to the presence of inorganic anions that interact with the nanoparticles

446   surface and lead to poor dispersion. In contrast, the LCO/Gr nanoparticles dispersed in deionized water

447   have the best dispersion stability, and even after 330 minutes, the full particles have not settled.

448   However, when LCO/Gr particles were mixed with PMS, the dispersion stability of the LCO/Gr

449   decreased significantly. This can be mainly attributed to a drop from pH 7 to 5 within a few minutes

450   after the addition of PMS (see supplementary material, Figure S19).

3.5 Catalytic performance and stability of catalysts

BPA, an endocrine-disrupting compound, is intensely used for the production of polycarbonate plastics and epoxy resins in the internal coatings of food packaging [78]. As a result of its widespread use, BPA is ubiquitously detected in food, drinking water, aquatic animals, and humans, and it decomposes only slowly under natural conditions [79]. Therefore, the catalytic performance of LCO/Gr was evaluated with regard to the degradation of BPA. 0.1 g/l LCO/Gr and a PMS concentration of 0.5 mmol/l was selected for subsequent experiments. Details are given in the supplementary material (Section 2, Figure S11-12).

The catalytic performance of LCO, graphene, and LCO/Gr nanoparticles was studied at pH 7 to understand the synergetic effect between LCO and graphene nanoparticles (Figure 5a). In the case of either LCO (0.1 g/l) or graphene (0.1 g/l) with PMS, the removal efficiency of BPA achieved 75 % and 30 % within 30 min, respectively. Interestingly, the BPA degradation efficiency of the LCO+Gr+PMS (0.068 g/l LCO + 0.032 g/l graphene) system reached only 80 % within 30 min. In contrast, the LCO/Gr+PMS (0.1 g/l) system showed complete BPA degradation after about 10 min, indicating that the enhanced catalytic performance of LCO/Gr is based on a robust interaction between LCO and graphene and the presence of oxygen vacancies, as proven by Raman, XPS, and EPR studies. Based on Equation 2, k_{app} values of the BPA degradation were calculated as 0.17 and 0.52 min^{-1} for LCO and LCO/Gr samples, respectively, confirming that the catalytic performance of the LCO/Gr catalyst is significantly higher than that of pure LCO material. We attribute the catalytic enhancement of LCO/Gr to the following features:

(i) The higher specific surface area of the LCO/Gr composite provides a better accessibility of active sites than pure LCO since the composite supports BPA molecules adsorption through strong π–π and hydrogen-bond interaction, leading to faster degradation of BPA.

(ii) The presence of unpaired π electrons in the LCO/Gr structure facilitates fast electron transport from LCO to PMS molecules through graphene nanosheets, supported by robust Co–O–C interactions that prevent cobalt leaching from LCO/Gr nanoparticles and therefore improve the catalytic performance of LCO/Gr.

22

478
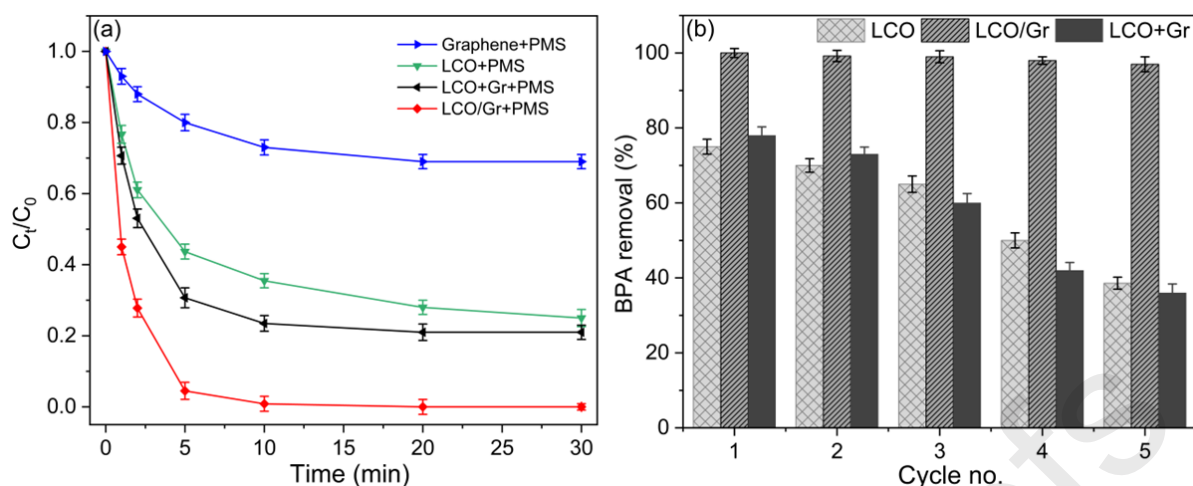
Figure 5. a) BPA degradation with various catalysts in different reaction systems and b) stability tests of LCO/Gr+PMS system. Reaction conditions: BPA = 40 mg/l; PMS = 0.5 mmol/l; Catalyst = 0.1 g/l; pH = 7.

The residual PMS concentration was varied during PMS activation in different systems (see supplementary material, Figure S13). The concentration of residual PMS in the LCO+PMS and LCO+Gr+PMS system was about 0.27 and 0.23 mmol/l, which attributed to about 54 and 46 % of the initial PMS concentration, respectively. However, in the LCO/Gr+PMS system, the residual PMS concentration declined to about 0.08 mmol/l (16 %). This result suggests that the LCO/Gr+PMS system consumes more PMS which we attribute to the fast electron transport from PMS molecules to the LCO through graphene nanosheets. Therefore, faster BPA degradation is achieved.

The reusability of catalysts is important to determine the catalyst stability for practical applications in water treatment. To confirm the durability of the catalyst in the LCO/Gr+PMS system, five cycling experiments were conducted under identical conditions. As displayed in Figure 5b, the reused LCO/Gr catalyst presented higher catalytic activity and stability compared to LCO and LCO+Gr in all five reaction runs. The insignificant decrease in BPA removal with LCO/Gr+PMS is due to the mass loss of catalyst after washing during the recycling process. In addition, the mineralization extent of BPA removal was measured for all catalytic tests by TOC measurements after 30 min. The TOC removal of BPA was around 35 and 62 % for LCO and LCO/Gr catalysts, respectively, while the TOC removal of BPA for LCO/Gr+PMS remains unabatedly high after five recycling operations (see supplementary

497   material, Figure S14). This indicates that the stable LCO/Gr+PMS system exhibits excellent catalytic

498   performance through the multi-cycle process.

499   As an important catalyst characteristic, leaching of cobalt ions was investigated by AAS analysis during

500   PMS activation. Despite the fact that both LCO+Gr+PMS and LCO+PMS exhibited good catalytic

501   activity, the cobalt leaching amount (2.9 mg/l for LCO+Gr and 3.5 mg/l for LCO) is much higher than

502   that with the LCO/Gr+PMS system (0.004 mg/l), which is clearly below the threshold limit value

503   (0.05 mg/l) set by the World Health Organization (WHO) [80]. To investigate whether the leached

504   cobalt shows some catalytic activity, the BPA removal efficiency using the Co^{2+}+PMS system was

505   studied under the same conditions (see supplementary material, Figure S15). The BPA removal of the

506   homogeneous Co^{2+}+PMS system was less than 4 %, suggesting that the high catalytic performance

507   mainly benefitted from the heterogeneous LCO/Gr+PMS system. The unchanged chemical structure of

508   the LCO/GR catalyst after five runs also supports its high stability (see supplementary material, Figure

509   S16). There is no change in the XRD diffraction pattern of the multiply-used catalyst as compared to

510   pristine LCO/Gr. These results indicate that the LCO/Gr system is a much more eco-friendly, efficient,

511   and effective catalyst for practical water treatment applications compared to previously reported

512   heterogeneous carbon-supported catalysts as only a vanishingly small proportion of cobalt is lost with

513   this catalyst material (Table 2).

514

Table 2: Comparison of the BPA removal by LCO/Gr in this work with those of other related carbon-supported catalysts in the literature.

Catalyst	Dosage (mg/l)	BPA conc. (mg/l)	PMS conc (mmol/l)	BPA removal (%)	Time (min)	Metal leaching (mg/l)	References
Fe3C@NCNTs/ Gr	100	20	0.65	98	30	(Fe)≈ 0.36	[81]
Co$_3$O$_4$/MXene	100	20	1	99	20	(Co) ≈ 0.36	[82]
CoS/Gr	100	20	0.32	92	8	(Co) ≈ 0.52	[83]
Fe$_3$Co$_7$/Gr	100	20	0.65	98	30	(Co) ≈ 3.30	[84]
Co$_3$O$_4$/MOFs	100	20	1.6	95	10	(Co) ≈ 0.35	[85]
LaFeO$_3$/GO	500	20	2	100	60	(Fe) ≈ 0.24 (La) ≈ 0.88	[86]
Co$_3$O$_4$/CC	100	10	0.32	99	10	(Co) ≈ 0.25	[87]
LCO/Gr	100	40	0.32	100	10	(Co) ≈ 0.004	This work

3.6 Reactive species identification

To understand the catalytic mechanism of the LCO/Gr+PMS system, EPR spectra of solutions and XPS spectra of LCO/Gr before and after catalytic experiments were recorded and analyzed. The contribution of different reactive radicals such as $SO_4^{\cdot-}$, $^{\cdot}OH$, $O_2^{\cdot-}$, and $^1O_2$ for BPA degradation was investigated by adding commonly used radical scavengers like ethanol (EtOH), tert-butanol (TBA), p-benzoquinone (BQ), and β-carotene (Crt). Here, EtOH was employed to scavenge both $SO_4^{\cdot-}$ and $^{\cdot}OH$, TBA was used to quench $^{\cdot}OH$ [88], whereas Crt and BQ were chosen as scavengers of $^1O_2$ and $O_2^{\cdot-}$, respectively [89].

As depicted in Figure 6a, the removal rate of BPA was decreased from 100 to 87 % when using 0.1 mol/l EtOH and more inhibition (79 %) was observed with the addition of high concentration of 0.5 mol/l EtOH. In contrast, no significant change in BPA removal was observed with the addition of 0.1 and 0.5 mol/l TBA. This suggests a minor contribution of $SO_4^{\cdot-}$ and $^{\cdot}OH$ to BPA degradation. Moreover, the

528 removal efficiency declined to 40 % when adding 5 mmol/l BQ. The addition of a small dose of Crt (0.5

529 mmol/l) led to a BPA removal efficiency of only 26 %, indicating that $^1O_2$ and $O_2^{\bullet-}$ are the primary

530 reactive species in the LCO/Gr+PMS system.

531 The pseudo-first-order constants with the addition of TBA and EtOH were calculated to determine the

532 contribution of different reactive species in the LCO/Gr+PMS system. The contributions of $^{\bullet}OH$ and

533 $SO_4^{\bullet-}$ radicals were calculated using the following equations (4-5) [90]:

$$\lambda_{(^{\bullet}OH)} = (k_0 - k_1)/k_0 \qquad \text{(Equation 4)}$$

$$\lambda_{(SO_4^{\bullet-})} = (k_1 - k_2)/k_0 \qquad \text{(Equation 5)}$$

536 where k_0 is the rate constant of BPA degradation in LCO/Gr+PMS system without scavenger, k_1 and k_2

537 are the rates constant for degradation of BPA by $^{\bullet}OH$ and $SO_4^{\bullet-}$.

538 Since $^1O_2$ might be generated from the oxidation of $O_2^{\bullet-}$, their common contributions ($\lambda (O_2^{\bullet-}/^1O_2)$)

539 were estimated according to the following equation 6 [91]:

$$\lambda_{O_2^{\bullet-}/^1O_2} = \lambda_{(overall)} - (\lambda_{(SO_4^{\bullet-})} + \lambda_{(^{\bullet}OH)}) \qquad \text{(Equation 6)}$$

541 The values of k_0, k_1, and k_2 were calculated as 0.52, 0.45, and 0.28 min^{-1}, respectively, according to

542 equation 2. As a result, the relative contributions of $^{\bullet}OH$, $SO_4^{\bullet-}$, and $^1O_2/O_2^{\bullet-}$ in the LCO/Gr+PMS

543 systems were determined to 13.4, 32.6, and 54 %, respectively.

544 Furthermore, EPR tests using DMPO and TEMP as radical spin-trapping agents for $SO_4^{\bullet-}$ and $^{\bullet}OH$, and

545 $^1O_2$, respectively, were carried out to confirm the formation of reactive radicals from PMS activation.

546 As shown in Figure 6b, when LCO+PMS were added, characteristic signals for DMPO-$^{\bullet}OH$ adducts

547 (with hyperfine splitting constants of $\alpha_H = \alpha_N = 14.8$ G) and DMPO-$SO_4^{\bullet-}$ adducts ($\alpha_N = 13.2$ G, $\alpha_N =$

548 9.6 G, $\alpha_H = 1.48$ G, $\alpha_H = 0.78$ G) were observed, demonstrating the generation of both $^{\bullet}OH$ and $SO_4^{\bullet-}$

549 radicals by the LCO+PMS system. Similar results are obtained in the LCO+Gr+PMS system with

550 reduced $^{\bullet}OH$ and $SO_4^{\bullet-}$ signals, due to a decrease in the LCO dosage (0.07 g/l LCO + 0.03 g/l graphene)

551 compared to the LCO system (0.1 g/l). This suggests that there is no interaction between graphene and

552 LCO nanoparticles. However, in case of LCO/Gr+PMS, the appearance of seven-line EPR adducts

26

assigned to 5,5-dimethyl-1-pyrrolidone-2-oxyl (DMPOX) could be indexed to the direct oxidation of DMPO with nonradical species $^1O_2$ [92] (Figure 6b). Additionally, the characteristic triplet signal of the TEMP-$^1O_2$ adduct (α_N = 1.72 mT) was observed when TEMP was added, confirming the presence of $^1O_2$ in the LCO/Gr+PMS system (Figure 6c). The peak intensity of $^1O_2$ in LCO/Gr+PMS system was significantly higher than that of the LCO+PMS and LCO+Gr+PMS system, suggesting the boosted generation of $^1O_2$ which might be attributed to oxygen vacancies. These results are also consistent with the radical scavenging experiments. Hence, it can be concluded that the nonradical pathway ($^1O_2$) plays a dominant role in the BPA degradation while the radical pathway ($SO_4^{\cdot-}$ and $^\cdot OH$) contributes significantly less.
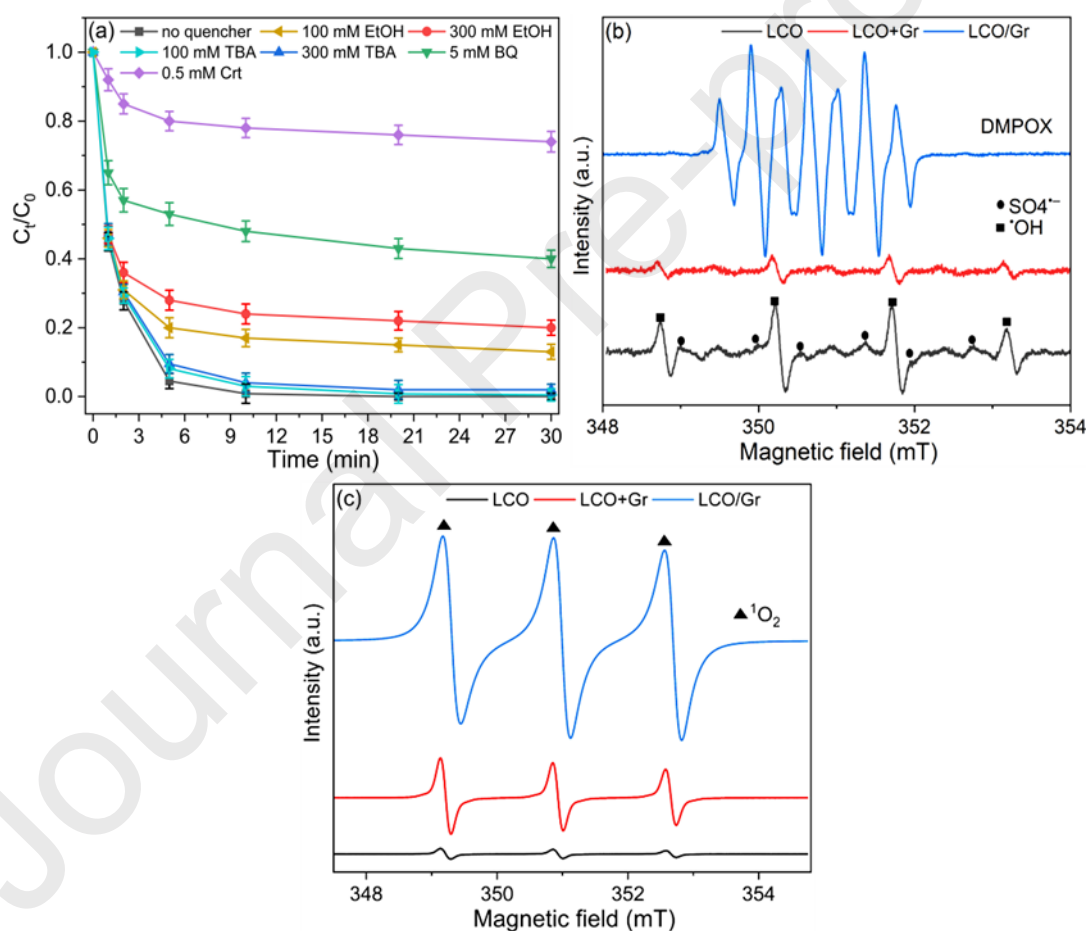
Figure 6. a) Effect of different radical scavengers on the BPA degradation process with LCO/Gr+PMS. EPR spectra using b) DMPO, and c) TEMP as the trapping agent for solutions with PMS, LCO/Gr and LCO/Gr+PMS, respectively. Reaction conditions: BPA = 40 mg/l, PMS = 0.5 mmol/l, Catalyst = 0.1 g/l, DMPO = 50 mmol/l, TEMP = 20 mmol/l.

3.7 Surface active site identification and possible mechanisms

To investigate the catalytic active sites of LCO/Gr, the activity of LCO/Gr was compared to that of gas-phase synthesized Co_3O_4, La_2O_3, $LaCoO_3$, and graphene (see supplementary material, Figure S17). The removal efficiency of BPA achieved less than 30 % with La_2O_3+PMS and graphene+PMS, which indicated that the La and C atoms of LCO/Gr were not the main active sites for BPA removal. In case of Co_3O_4 and $LaCoO_3$, the BPA degradation efficiency reached 45 and 75 %, respectively, suggesting that the Co atom in the LCO/Gr catalyst structure can serve as the active center for BPA degradation. To identify the impact of Co in the PMS activation, XPS spectra of LCO/Gr before and after the catalytic reactions were studied. From fitting the spectra shown in Figure 7 it can be seen that the proportions of Co^{2+} and Co^{3+} for the fresh catalyst were determined to be 85 and 15 %, while after the catalytic reaction the Co^{3+} content increased to 22 %. This indicates that the conversion process in the catalyst occurs at the LCO/Gr surface and Co^{2+} may participate in the activation of PMS. It is noteworthy that the addition of citric acid with cobalt-based catalysts during PMS activation can inhibit the degradation process due to formation of cobalt carboxyl complexes [93]. The addition of 2 mmol/l citric acid decreased the removal efficiency of BPA from 100 to 80 %, and the strong inhibition effect was observed with the increase of citric acid concentration (see supplementary material, Figure S18), further indicating that Co sites need to be considered as the active sites for PMS activation. Additionally, It has been reported that O_{vac} can promote the bonding and electron transfer of PMS on the catalyst surface [94]. To ascertain the role of O_{vac} on the non-radical mechanism during PMS activation, the change of oxygen content before and after the reaction was analyzed (Figure 7b). From the O1s spectra, it could be deduced that the percentage of surface oxygen (O_S) decreased from 23 to 14 % after the catalytic reaction, suggesting that O_{vac} played a dominant role in BPA degradation and was involved in generation of $^1O_2$. This finding is supported by analyzing the EPR spectra of fresh and used LCO/Gr catalyst after five reaction runs (Figure 7c). Compared with fresh LCO/Gr, the EPR signal of the used LCO/Gr was reduced, revealing that O_{vac} participated in PMS activation.
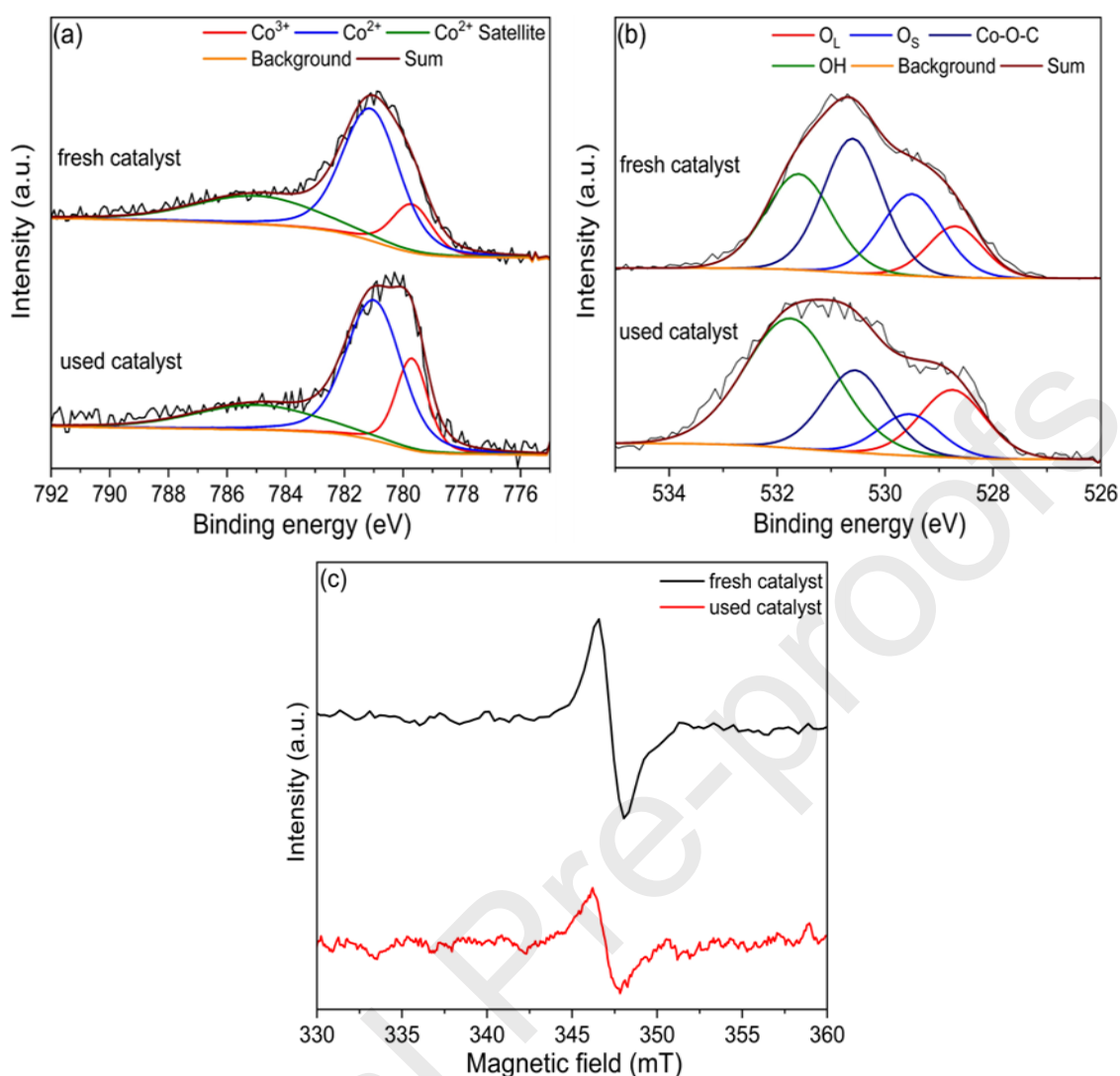
592

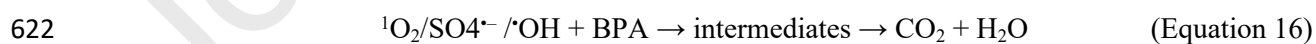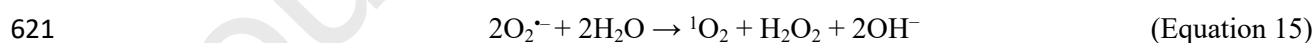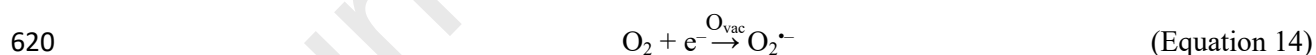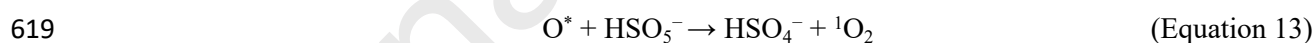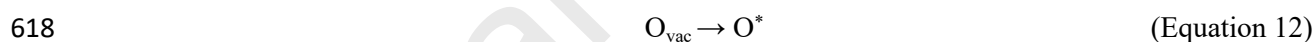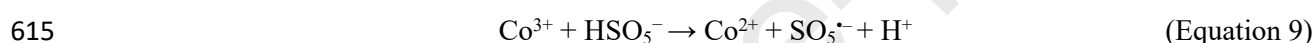593   Figure 7. XPS spectra of (a) Co2p and (b) O1s for fresh and used LCO/Gr nanopowder, and c) EPR spectra of

594   fresh and used LCO/Gr.

595   Based on the above results, a catalytic mechanism for BPA degradation by the LCO/Gr+PMS system is

596   suggested including two reaction pathways: A radical ($SO_4^{\bullet-}$ and $^{\bullet}OH$) and a non-radical process ($^1O_2$).

597   For the radical pathway, $SO_4^{\bullet-}$ is generated through a reaction of PMS with the surface Co^{2+} of the

598   LCO/Gr material (Equation 7) and consequently $^{\bullet}OH$ is produced from the reaction of $SO_4^{\bullet-}$ with the

599   hydroxide ion (Equation 8) [56]. The produced Co^{3+} will react with PMS molecules and convert to Co^{2+},

600   since the standard potential value of the Co^{2+}/Co^{3+} redox pair (1.8 V) is higher than that of $HSO_5^-/SO_5^{\bullet-}$

601   (1.1 V) (Equation 9). Thus, the high catalytic performance through the multiple-cycle process can be

602   achieved by the redox reaction of Co^{3+}/Co^{2+}. Moreover, as has been shown in Figure 7b, a hydroxylation

603   of LCO/Gr occurs, which is attributed to the binding of water molecules to the catalyst surface during

29

604   PMS activation. Subsequently, these hydroxyl groups will combine with PMS to generate $SO_4^{\bullet-}$

605   (Equation 10-11). The non-radical pathway (creation of $^1O_2$) is mainly attributed to adsorbed oxygen of

606   metal oxide catalysts [95] and the direct oxidation or recombination of $O_2^{\bullet-}$. Therefore, the generation

607   of $^1O_2$ can be attributed to the reaction of adsorbed oxygen species onto the surface vacancy, in which

608   O_{vac} is converted to active oxygen (O^*) leading to the formation of $^1O_2$ (Equation 12-13) [96]. Moreover,

609   the quenching test results confirmed that $O_2^{\bullet-}$ played a role in BPA degradation as explained before.

610   Thus, another possibility to generate $^1O_2$ is the direct oxidation of $O_2^{\bullet-}$ that is produced from the reaction

611   of O_2 via O_{vac} (Equation 14-15). Finally, BPA can be attacked by the generated reactive oxygen species,

612   degrading into small molecular intermediates, and then converting into CO_2 and H_2O (Equation 16).

613
$$Co^{2+} + HSO_5^- \rightarrow Co^{3+} + SO_4^{\bullet-} + OH^- \qquad \text{(Equation 7)}$$

614
$$SO_4^{\bullet-} + OH^- \rightarrow {}^{\bullet}OH + SO_4^{2-} \qquad \text{(Equation 8)}$$

615
$$Co^{3+} + HSO_5^- \rightarrow Co^{2+} + SO_5^{\bullet-} + H^+ \qquad \text{(Equation 9)}$$

616
$$Co^{2+}/\,Co^{3+}\!-OH^- + HSO_5^- \rightarrow Co^{2+}/\,Co^{3+}\!-(HO)OSO_3^- + OH^- \qquad \text{(Equation 10)}$$

617
$$Co^{2+}/\,Co^{3+}\!-(HO)OSO_3^- \rightarrow Co^{2+}/\,Co^{3+}\!-OH + SO_4^{\bullet-} \qquad \text{(Equation 11)}$$

618
$$O_{vac} \rightarrow O^* \qquad \text{(Equation 12)}$$

619
$$O^* + HSO_5^- \rightarrow HSO_4^- + {}^1O_2 \qquad \text{(Equation 13)}$$

620
$$O_2 + e^- \xrightarrow{O_{vac}} O_2^{\bullet-} \qquad \text{(Equation 14)}$$

621
$$2O_2^{\bullet-} + 2H_2O \rightarrow {}^1O_2 + H_2O_2 + 2OH^- \qquad \text{(Equation 15)}$$

622
$${}^1O_2/SO4^{\bullet-}/{}^{\bullet}OH + BPA \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O \qquad \text{(Equation 16)}$$
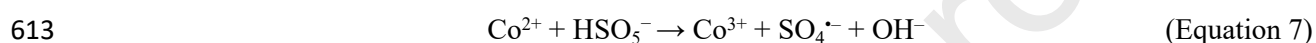
3.8 Effect of reaction conditions on BPA degredation

3.8.1 Effect of initial pH

Since changing the pH will affect the surface functional groups of LCO/Gr material and PMS activation, changing the working pH range is expected to play a crucial role in the catalytic stability of the LCO/Gr material. Thus, the effect of pH on BPA degradation was analyzed ranging from pH = 3.0 to 11.0. Figure 8a depicts the influence of the initial pH on BPA removal. It is obvious that the BPA removal efficiency enhanced apparently within 10 min over a pH of 3 to 9 and is decreasing dramatically when the initial pH was adjusted to 11. Accordingly, the pseudo-first order rate constant (k_{app}) of BPA degradation rises from 0.153 to 0.594 min^{-1} when going from pH = 3 to 9 (see inset Figure 8a). However, when the initial pH of the solution was adjusted to 11, the k_{app} dropped to 0.075 min^{-1}, which is about eight times lower than that of pH 9. To understand this phenomenon, the pH change with reaction time under different initial pH values during the PMS activation process was studied (see supplementary material, Figure S19). For initial pH values between 3 and 9, the pH drops sharply within a few minutes after the addition of PMS and decreases only slightly thereafter. For instance, when adjusting the pH to 9, it dropped to 7.5 within 5 min and reached 6.8 after 30 min. In contrast, the pH of the solution with an initial pH of 11 maintained almost stable. This pH is higher than the pH_{pzc} of LCO/Gr nanoparticles (see supplementary material, Figure S20). Since the pK_{a1} of PMS is 0 and pK_{a2} is 9.4, PMS is present as HSO_5^- under the investigated pH range of 0–9.4. Accordingly, for a pH of 11, HSO_5^- dissociates into SO_5^{2-}, which diminishes the LCO/Gr catalytic efficiency due to the weak oxidative potential of SO_5^{2-} [63]. Moreover, a high pH can result in the formation of C–OH, La(OH)$_3$, and Co(OH)$_2$ (see supplementary material, Figure S21), causing the generation of $^\bullet OH$ from the reaction of $SO_4^{\bullet-}$ with the hydroxide ion (Equation 5), which also can decrease the catalytic activity of LCO/Gr [97].

3.8.2 Effect of temperature

The effect of reaction temperature on BPA removal with the LCO/Gr+PMS system was studied at an initial pH of 7. As expected and shown in Figure 8b, the BPA degradation efficiency was enhanced with the increasing reaction temperature. As the reaction temperature increased from 25 to 55 °C, the k_{app}

649 (1.05 min⁻¹) is almost two times higher than at 25 °C (0.52 min⁻¹). We attribute this result to the fast

650 generation of reactive species by thermolytic rupture of O–O bond of PMS. The respective activation

651 energy (E_a) was determined from the Arrhenius equation:

652
$$\ln k_{\mathrm{app}} = \ln A - \frac{E_{\mathrm{a}}}{R\,T} \qquad \text{(Equation 17)}$$

653 Where A is the pre-exponential factor, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), and T is the

654 solution temperature. The activation energy E_{a} of the LCO/Gr+PMS system was derived as 14 kJ/mol

655 based on plotting $\ln k_{\mathrm{app}}$ against $1/T$ (see inset, Figure 8b), which is much lower than the values reported

656 for Co_3O_4/graphene (26.5 kJ/mol) [98] and $MnFe_2O_4$/graphene (25.7 kJ/mol) [99]. These findings imply

657 that the reaction energy barrier for PMS activation is decreased in our LCO/Gr system indicating a

658 higher catalytic activity and performance.

659

660 ### 3.8.3   Effect of co-existing ions and NOM

661 Various inorganic anions are ubiquitous in real aquatic environments, which might affect the PMS

662 activation in wastewater treatment as well [19]. Therefore, the effect of various anions relevant in

663 aqueous systems (such as Cl^-, NO_3^- $H_2PO_4^-$, HCO_3^-, etc.) on the BPA removal with LCO/Gr

664 nanoparticles was analyzed (Figure 8c and supplementary material Figure S22). The comparison of the

665 respective results shows that the NO_3^- anion had negligible adverse effects on BPA degradation, while

666 the Cl^- anions had a positive influence on BPA degradation. The positive effect of Cl^- ions on BPA

667 degradation may be attributed to the generation of active chlorine species (e.g. HOCl) which enhance

668 BPA degradation [100] (Equation 18). Thus, to understand the impact of Cl^- on BPA degradation, the

669 BPA removal was analyzed in the presence of only PMS (see supplementary material, Figure S23a).

670 The BPA removal efficiency was dramatically enhanced with 6 mg/ml Cl^-, suggesting that HOCl was

671 generated as a result of the reaction between PMS and Cl^-. Besides, we evaluated the adsorption of BPA

672 by LCO/Gr with the different Cl^- concentrations (see supplementary material, Figure S23b). As before,

673 20–23 % of BPA was adsorbed by LCO/Gr at different Cl^- concentrations, indicating that the influence

674   of Cl⁻ on BPA adsorption was insignificant. Thus, we propose that the accelerated BPA degradation is

675   based on the generation of HOCl along with $^1O_2$ in the LCO/Gr+PMS+Cl⁻ system.

676   $$Cl^- + HSO_5^- \rightarrow HOCl + SO_4^{2-}$$ (Equation 18)
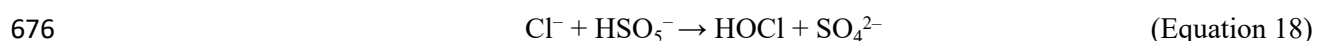
677   In contrast to Cl⁻ and NO_3^-, $H_2PO_4^-$ exhibits an inhibitory effect on BPA degradation efficiency because

678   it can chelate with Co and form the Co-phosphate complex (see supplementary material, Figure S24),

679   which in turn inhibits the PMS activation. Similarly, the removal efficiency of BPA was decreased with

680   the addition of HCO_3^- due to the scavenging effect of $O_2^{\cdot-}$, $SO_4^{\cdot-}$, and ·OH by HCO_3^- in the system,

681   resulting in a decreased performance of the catalyst [101].

682   NOM is a constituent of all natural waters and soils and can consume a large number of reactive oxygen

683   species such as $SO_4^{\cdot-}$ and ·OH and block the active site on the catalyst surface during PMS activation

684   [89], resulting in the decreased removal efficiency towards organic contaminants. As depicted in Figure

685   8d, the removal rate of BPA was slightly inhibited with the presence of 10 and 25 mg/l NOM. The

686   decrease might be related to the adsorption of NOM on the surface of the catalyst which could reduce

687   the complexation of PMS to generate reactive oxygen species and is consistent with previous reports

688   showing NOM to have a negligible impact on the performance of nonradical-based systems [102,103].

689   To evaluate the applicability of the LCO/Gr + PMS system in real aquatic environments, additional BPA

690   removal experiments were conducted in tap and drinking water. The characteristics of tap and drinking

691   water samples are depicted in Table S5. As shown in Figure 8e, the BPA removal efficiency was

692   insignificantly decreased in the drinking water sample while the BPA degradation efficiency was

693   slightly changed to 90 % in the tap water sample. The results indicate that the inorganic anions in the

694   water have only negligible adverse effects on BPA degradation.

695   **3.8.4   Effect of different pharmaceutical drugs**

696   Moreover, the catalytic performance of the LCO/Gr+PMS system has been tested for different kinds of

697   drugs which is important for wastewater treatment applications. Hence, the catalytic activity of LCO/Gr

698   was evaluated with diclofenac (DCF), metoprolol (MTP), and carbamazepine (CBZ). As shown in

699   Figure 8f, the degradation of DCF, MTP, and CBZ reaches 100 % after 2 min, implying the

33

700 exceptionally high catalytic performance of the LCO/Gr+PMS system. The TOC removal of DCF, MTP,

701 and CBZ after 30 min was surprisingly high (57, 55, and 61 %, respectively, see supplementary material

702 Figure S25), proving that the LCO/Gr material is a promising catalyst for use in real wastewater

703 treatment systems.
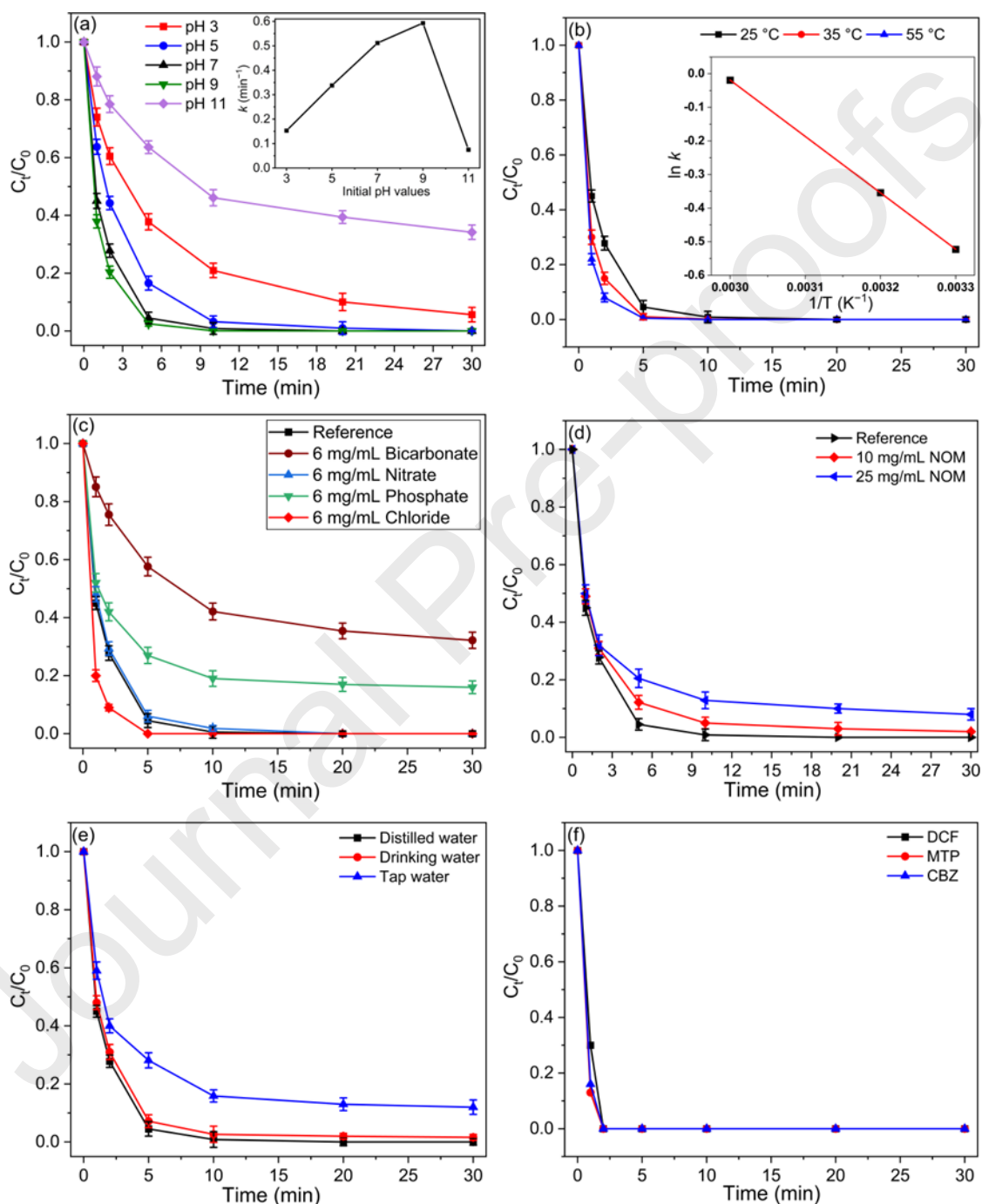
705 Figure 8. Effects of (a) initial pH values, (b) temperature, (c) inorganic anions, (d) NOM, and (e) water matrices

706 BPA degradation by $La_2CoO_{4+\delta}$/PMS, and (f) the catalytic activity of LCO/Gr+PMS system on the removal of

707 various drugs. Reaction conditions: Drug/BPA = 40 mg/l; PMS = 0.5 mmol/l; Catalyst = 0.1 g/l; pH = 7.

34

3.9 Possible degradation pathways

The degradation pathway of BPA via the LCO/Gr+/PMS system was investigated and identified by LC-MS (see supplementary material, Figure S26). According to the mass spectrometric results, seven intermediates were detected for the BPA degradation using the LCO\Gr+PMS system (see supplementary material, table S6). First, BPA is mainly attacked by $^1O_2$ to produce phenol and p-isopropyl phenol due to a β-scission of isopropyl between two phenyl groups in BPA [104]. Afterwards, the reaction products are further oxidized to form hydroquinone and 1-(4-methyl phenyl) ethenone, followed by a subsequent oxidative ring-opening leading to the formation of small-molecule intermediates including penta-1,4-dien-3-one, succinic acid, 1,5-hexadiene-3-ol, and 2-hydroxypropanoic acid. Finally, the small-molecule intermediates are further oxidized and mineralized into CO_2 and H_2O.

4 Conclusions

In summary, we have demonstrated a robust and scalable method to synthesize LCO/Gr nanocomposites that have been employed as novel catalysts to activate PMS for different pollutants degradation. The developed approach consisting of a spray-flame synthesis method followed by the self-assembling technique has practical advantages such as scalability, reproducibility, easy control of the LCO size, and the subsequent decoration of the graphene nanosheets, eco-friendliness, and cost-effectivity.

The enhanced catalytic activity of the LCO/Gr composite compared to LCO nanoparticles is based on several, especially nano-specific features: First, we observed a synergistic and robust interaction between LCO and graphene, supported by stable Co–O–C interactions, leading to an outstanding BPA degradation efficiency (>99 %) and excellent stability with less cobalt leaching (0.004 mg/l) in the presence of PMS. Secondly, the high surface area of graphene (300 m^2/g) and the presence of unpaired π electrons in the LCO/Gr structure facilitates a better accessibility of active sites, which is supported by a fast electron transport from LCO to PMS molecules through graphene nanosheets. Thirdly, LCO/Gr has an excellent catalytic activity through the multiple-cycle process (>95 %) and can be utilized over a wide pH range (pH 3-11). Fourthly, the LCO/Gr catalytic system exhibits a very effective removal of

different drugs such as diclofenac (>99 %), metoprolol (>99 %), and carbamazepine (>99 %), which are widely detected in municipal and industrial wastewater. Finally, the catalytic efficiency of LCO/Gr is insignificantly reduced in drinking water and tap water samples and showed high resistance to co-existing ions and NOM, proving that the LCO/Gr material is a promising catalyst for subsequent use in real wastewater treatment systems.

5 References

[1]   A. Küster, N. Adler, Pharmaceuticals in the environment: scientific evidence of risks and its regulation, Philos. Trans. R. Soc. Lond. B. Biol. Sci. 369 (2014) 20130587. https://doi.org/10.1098/rstb.2013.0587.

[2]   W. Guo, B. Pan, S. Sakkiah, G. Yavas, W. Ge, W. Zou, W. Tong, H. Hong, Persistent Organic Pollutants in Food: Contamination Sources, Health Effects and Detection Methods, Int. J. Environ. Res. Public Health. 16 (2019) 4361. https://doi.org/10.3390/ijerph16224361.

[3]   J. Wang, S. Wang, Reactive species in advanced oxidation processes: Formation, identification and reaction mechanism, Chem. Eng. J. 401 (2020) 126158.

36

759　　　　　https://doi.org/https://doi.org/10.1016/j.cej.2020.126158.

760　　[4]　　A. Fischbacher, C. von Sonntag, T.C. Schmidt, Hydroxyl radical yields in the Fenton process

761　　　　　under various pH, ligand concentrations and hydrogen peroxide/Fe(II) ratios, Chemosphere.

762　　　　　182 (2017) 738–744. https://doi.org/https://doi.org/10.1016/j.chemosphere.2017.05.039.

763　　[5]　　M. Zhang, H. Dong, L. Zhao, D. Wang, D. Meng, A review on Fenton process for organic

764　　　　　wastewater treatment based on optimization perspective, Sci. Total Environ. 670 (2019) 110–

765　　　　　121. https://doi.org/https://doi.org/10.1016/j.scitotenv.2019.03.180.

766　　[6]　　Q. Yang, Y. Ma, F. Chen, F. Yao, J. Sun, S. Wang, K. Yi, L. Hou, X. Li, D. Wang, Recent

767　　　　　advances in photo-activated sulfate radical-advanced oxidation process (SR-AOP) for

768　　　　　refractory organic pollutants removal in water, Chem. Eng. J. 378 (2019) 122149.

769　　　　　https://doi.org/https://doi.org/10.1016/j.cej.2019.122149.

770　　[7]　　Y. Liu, Y. Wang, Q. Wang, J. Pan, J. Zhang, Simultaneous removal of NO and SO2 using

771　　　　　vacuum ultraviolet light (VUV)/heat/peroxymonosulfate (PMS), Chemosphere. 190 (2018)

772　　　　　431–441. https://doi.org/https://doi.org/10.1016/j.chemosphere.2017.10.020.

773　　[8]　　R. Xie, J. Ji, K. Guo, D. Lei, Q. Fan, D.Y.C. Leung, H. Huang, Wet scrubber coupled with

774　　　　　UV/PMS process for efficient removal of gaseous VOCs: Roles of sulfate and hydroxyl

775　　　　　radicals, Chem. Eng. J. 356 (2019) 632–640.

776　　　　　https://doi.org/https://doi.org/10.1016/j.cej.2018.09.025.

777　　[9]　　Z.-H. Diao, Z.-Y. Lin, X.-Z. Chen, L. Yan, F.-X. Dong, W. Qian, L.-J. Kong, J.-J. Du, W. Chu,

778　　　　　Ultrasound-assisted heterogeneous activation of peroxymonosulphate by natural pyrite for 2,4-

779　　　　　diclorophenol degradation in water: Synergistic effects, pathway and mechanism, Chem. Eng.

780　　　　　J. (2019) 123771. https://doi.org/https://doi.org/10.1016/j.cej.2019.123771.

781　　[10]　　H. Song, L. Yan, Y. Wang, J. Jiang, J. Ma, C. Li, G. Wang, J. Gu, P. Liu, Electrochemically

782　　　　　activated PMS and PDS: Radical oxidation versus nonradical oxidation, Chem. Eng. J. (2019)

783　　　　　123560. https://doi.org/https://doi.org/10.1016/j.cej.2019.123560.

784　　[11]　　B. Bouzayani, E. Rosales, M. Pazos, S.C. Elaoud, M.A. Sanromán, Homogeneous and

37

785   heterogeneous peroxymonosulfate activation by transition metals for the degradation of

786   industrial leather dye, J. Clean. Prod. 228 (2019) 222–230.

787   https://doi.org/https://doi.org/10.1016/j.jclepro.2019.04.217.

788   [12]   Z. Li, M. Wang, C. Jin, J. Kang, J. Liu, H. Yang, Y. Zhang, Q. Pu, Y. Zhao, M. You, Z. Wu,

789   Synthesis of novel Co3O4 hierarchical porous nanosheets via corn stem and MOF-Co

790   templates for efficient oxytetracycline degradation by peroxymonosulfate activation, Chem.

791   Eng. J. 392 (2020) 123789. https://doi.org/https://doi.org/10.1016/j.cej.2019.123789.

792   [13]   S. Chen, J. Deng, C. Ye, C. Xu, L. Huai, J. Li, X. Li, Simultaneous removal of para-arsanilic

793   acid and the released inorganic arsenic species by CuFe2O4 activated peroxymonosulfate

794   process, Sci. Total Environ. 742 (2020) 140587.

795   https://doi.org/https://doi.org/10.1016/j.scitotenv.2020.140587.

796   [14]   S. Ben Hammouda, F. Zhao, Z. Safaei, V. Srivastava, D. Lakshmi Ramasamy, S. Iftekhar, S.

797   kalliola, M. Sillanpää, Degradation and mineralization of phenol in aqueous medium by

798   heterogeneous monopersulfate activation on nanostructured cobalt based-perovskite catalysts

799   ACoO3 (A=La, Ba, Sr and Ce): Characterization, kinetics and mechanism study, Appl. Catal.

800   B Environ. 215 (2017) 60–73. https://doi.org/https://doi.org/10.1016/j.apcatb.2017.05.051.

801   [15]   J. Cao, L. Lai, B. Lai, G. Yao, X. Chen, L. Song, Degradation of tetracycline by

802   peroxymonosulfate activated with zero-valent iron: Performance, intermediates, toxicity and

803   mechanism, Chem. Eng. J. 364 (2019) 45–56.

804   https://doi.org/https://doi.org/10.1016/j.cej.2019.01.113.

805   [16]   S. Wang, J. Wang, Kinetics of PMS activation by graphene oxide and biochar, Chemosphere.

806   239 (2020) 124812. https://doi.org/https://doi.org/10.1016/j.chemosphere.2019.124812.

807   [17]   C. Cheng, S. Gao, J. Zhu, G. Wang, L. Wang, X. Xia, Enhanced performance of LaFeO3

808   perovskite for peroxymonosulfate activation through strontium doping towards 2,4-D

809   degradation, Chem. Eng. J. 384 (2020) 123377.

810   https://doi.org/https://doi.org/10.1016/j.cej.2019.123377.

811   [18]   Y. Wang, Z. Chi, C. Chen, C. Su, D. Liu, Y. Liu, X. Duan, S. Wang, Facet- and defect-

812   dependent activity of perovskites in catalytic evolution of sulfate radicals, Appl. Catal. B

813   Environ. 272 (2020) 118972. https://doi.org/https://doi.org/10.1016/j.apcatb.2020.118972.

814   [19]   M. Hammad, B. Alkan, A. k. Al-kamal, M. Yusuf Ali, C. Kim, H. T. A. Wiedemann, D.

815   Klippert, T.C. Schmidt, C. W. M. Kay, H. Wiggers, Enhanced heterogeneous activation of

816   peroxymonosulfate by Ruddlesden-Popper-type $La_2CoO_{4+\delta}$ nanoparticles for bisphenol A

817   degradation, Chem. Eng. J. (2021) 131447.

818   https://doi.org/https://doi.org/10.1016/j.cej.2021.131447.

819   [20]   X. Duan, C. Su, J. Miao, Y. Zhong, Z. Shao, S. Wang, H. Sun, Insights into perovskite-

820   catalyzed peroxymonosulfate activation: Maneuverable cobalt sites for promoted evolution of

821   sulfate radicals, Appl. Catal. B Environ. 220 (2018) 626–634.

822   https://doi.org/https://doi.org/10.1016/j.apcatb.2017.08.088.

823   [21]   B. Alkan, S. Cychy, S. Varhade, M. Muhler, C. Schulz, W. Schuhmann, H. Wiggers, C.

824   Andronescu, Spray-Flame-Synthesized $LaCo_{1-x}Fe_xO_3$ Perovskite Nanoparticles as

825   Electrocatalysts for Water and Ethanol Oxidation, ChemElectroChem. 6 (2019) 4266–4274.

826   https://doi.org/10.1002/celc.201900168.

827   [22]   J. Büker, B. Alkan, Q. Fu, W. Xia, J. Schulwitz, D. Waffel, T. Falk, C. Schulz, H. Wiggers, M.

828   Muhler, B. Peng, Selective cyclohexene oxidation with O2, H2O2 and tert-butyl hydroperoxide

829   over spray-flame synthesized $LaCo_{1-x}Fe_xO_3$ nanoparticles, Catal. Sci. Technol. 10 (2020)

830   5196–5206. https://doi.org/10.1039/D0CY00906G.

831   [23]   H. Chen, W. Cui, D. Li, Q. Tian, J. He, Q. Liu, X. Chen, M. Cui, X. Qiao, Z. Zhang, J. Tang,

832   Z. Fei, Selectively Etching Lanthanum to Engineer Surface Cobalt-Enriched $LaCoO_3$

833   Perovskite Catalysts for Toluene Combustion, Ind. Eng. Chem. Res. 59 (2020) 10804–10812.

834   https://doi.org/10.1021/acs.iecr.0c01182.

835   [24]   Y. Yamada, K. Yano, D. Hong, S. Fukuzumi, $LaCoO_3$ acting as an efficient and robust catalyst

836   for photocatalytic water oxidation with persulfate, Phys. Chem. Chem. Phys. 14 (2012) 5753–

837   5760. https://doi.org/10.1039/C2CP00022A.

838   [25]   P. Liang, D. Meng, Y. Liang, Z. Wang, C. Zhang, S. Wang, Z. Zhang, Cation deficiency tuned

839   LaCoO3−δ perovskite for peroxymonosulfate activation towards bisphenol A degradation,

840   Chem. Eng. J. 409 (2021) 128196. https://doi.org/https://doi.org/10.1016/j.cej.2020.128196.

841   [26]   X. Huang, G. Zhao, G. Wang, J.T.S. Irvine, Synthesis and applications of nanoporous

842   perovskite metal oxides, Chem. Sci. 9 (2018) 3623–3637.

843   https://doi.org/10.1039/C7SC03920D.

844   [27]   S. Royer, D. Duprez, F. Can, X. Courtois, C. Batiot-Dupeyrat, S. Laassiri, H. Alamdari,

845   Perovskites as Substitutes of Noble Metals for Heterogeneous Catalysis: Dream or Reality,

846   Chem. Rev. 114 (2014) 10292–10368. https://doi.org/10.1021/cr500032a.

847   [28]   P. Granger, V.I. Parvulescu, S. Kaliaguine, W. Prellier, Perovskites and Related Mixed Oxides,

848   Wiley-VCH Verlag GmbH \& Co. KGaA, 2016. https://hal-normandie-univ.archives-

849   ouvertes.fr/hal-02185521.

850   [29]   N.T. Thuy, D. Le Minh, Size Effect on the Structural and Magnetic Properties of Nanosized

851   Perovskite <svg style="vertical-align:-4.67647pt;width:70.75px;" id="M1" height="21.1"

852   version="1.1" viewBox="0 0 70.75 21.1" width="70.75"

853   xmlns="http://www.w3.org/2000/svg"><g transform=, Adv. Mater. Sci. Eng. 2012 (2012)

854   380306. https://doi.org/10.1155/2012/380306.

855   [30]   B. Alkan, D. Medina, J. Landers, M. Heidelmann, U. Hagemann, S. Salamon, C. Andronescu,

856   H. Wende, C. Schulz, W. Schuhmann, H. Wiggers, Spray-Flame-Prepared LaCo1–xFexO3

857   Perovskite Nanoparticles as Active OER Catalysts: Influence of Fe Content and Low-

858   Temperature Heating, ChemElectroChem. 7 (2020) 2564–2574.

859   https://doi.org/https://doi.org/10.1002/celc.201902051.

860   [31]   S. Angel, J.D. Tapia, J. Gallego, U. Hagemann, H. Wiggers, Spray-Flame Synthesis of

861   LaMnO3+δ Nanoparticles for Selective CO Oxidation (SELOX), Energy & Fuels. 35 (2021)

862   4367–4376. https://doi.org/10.1021/acs.energyfuels.0c03659.

863 [32] C. Schulz, T. Dreier, M. Fikri, H. Wiggers, Gas-phase synthesis of functional nanomaterials:

864 Challenges to kinetics, diagnostics, and process development, Proc. Combust. Inst. 37 (2019)

865 83–108. https://doi.org/https://doi.org/10.1016/j.proci.2018.06.231.

866 [33] M. Abdul Nasir Khan, P. Kwame Klu, C. Wang, W. Zhang, R. Luo, M. Zhang, J. Qi, X. Sun,

867 L. Wang, J. Li, Metal-organic framework-derived hollow Co3O4/carbon as efficient catalyst

868 for peroxymonosulfate activation, Chem. Eng. J. 363 (2019) 234–246.

869 https://doi.org/https://doi.org/10.1016/j.cej.2019.01.129.

870 [34] C. Liu, L. Liu, X. Tian, Y. Wang, R. Li, Y. Zhang, Z. Song, B. Xu, W. Chu, F. Qi, A. Ikhlaq,

871 Coupling metal–organic frameworks and g-C3N4 to derive Fe@N-doped graphene-like carbon

872 for peroxymonosulfate activation: Upgrading framework stability and performance, Appl.

873 Catal. B Environ. 255 (2019) 117763.

874 https://doi.org/https://doi.org/10.1016/j.apcatb.2019.117763.

875 [35] W. Han, D. Li, M. Zhang, H. Ximin, X. Duan, S. Liu, S. Wang, Photocatalytic activation of

876 peroxymonosulfate by surface-tailored carbon quantum dots, J. Hazard. Mater. 395 (2020)

877 122695. https://doi.org/https://doi.org/10.1016/j.jhazmat.2020.122695.

878 [36] W. Lin, X. Xie, X. Wang, Y. Wang, D. Segets, J. Sun, Efficient adsorption and sustainable

879 degradation of gaseous acetaldehyde and o-xylene using rGO-TiO2 photocatalyst, Chem. Eng.

880 J. 349 (2018) 708–718. https://doi.org/https://doi.org/10.1016/j.cej.2018.05.107.

881 [37] N. Baig, Ihsanullah, M. Sajid, T.A. Saleh, Graphene-based adsorbents for the removal of toxic

882 organic pollutants: A review, J. Environ. Manage. 244 (2019) 370–382.

883 https://doi.org/https://doi.org/10.1016/j.jenvman.2019.05.047.

884 [38] J. Xu, L. Wang, Y. Zhu, Decontamination of Bisphenol A from Aqueous Solution by Graphene

885 Adsorption, Langmuir. 28 (2012) 8418–8425. https://doi.org/10.1021/la301476p.

886 [39] Q. Xiang, J. Yu, M. Jaroniec, Graphene-based semiconductor photocatalysts, Chem. Soc. Rev.

887 41 (2012) 782–796. https://doi.org/10.1039/C1CS15172J.

888 [40] N. Zhang, M.-Q. Yang, S. Liu, Y. Sun, Y.-J. Xu, Waltzing with the Versatile Platform of

41

889   Graphene to Synthesize Composite Photocatalysts, Chem. Rev. 115 (2015) 10307–10377.

890   https://doi.org/10.1021/acs.chemrev.5b00267.

891 [41] A. V Karim, A. Selvaraj, Graphene composites in photocatalytic oxidation of aqueous organic

892   contaminants – A state of art, Process Saf. Environ. Prot. 146 (2021) 136–160.

893   https://doi.org/https://doi.org/10.1016/j.psep.2020.08.042.

894 [42] M. Hammad, P. Fortugno, S. Hardt, C. Kim, S. Salamon, T.C. Schmidt, H. Wende, C. Schulz,

895   H. Wiggers, Large-scale synthesis of iron oxide/graphene hybrid materials as highly efficient

896   photo-Fenton catalyst for water remediation, Environ. Technol. Innov. (2020) 101239.

897   https://doi.org/https://doi.org/10.1016/j.eti.2020.101239.

898 [43] U.K. Sur, Graphene: A Rising Star on the Horizon of Materials Science, Int. J. Electrochem.

899   2012 (2012) 237689. https://doi.org/10.1155/2012/237689.

900 [44] C. Wang, P. Shi, X. Cai, Q. Xu, X. Zhou, X. Zhou, D. Yang, J. Fan, Y. Min, H. Ge, W. Yao,

901   Synergistic Effect of Co3O4 Nanoparticles and Graphene as Catalysts for Peroxymonosulfate-

902   Based Orange II Degradation with High Oxidant Utilization Efficiency, J. Phys. Chem. C. 120

903   (2016) 336–344. https://doi.org/10.1021/acs.jpcc.5b10032.

904 [45] V. Murugadoss, P. Panneerselvam, C. Yan, Z. Guo, S. Angaiah, A simple one-step

905   hydrothermal synthesis of cobaltnickel selenide/graphene nanohybrid as an advanced platinum

906   free counter electrode for dye sensitized solar cell, Electrochim. Acta. 312 (2019) 157–167.

907   https://doi.org/https://doi.org/10.1016/j.electacta.2019.04.142.

908 [46] F. Yang, J. Mao, S. Li, J. Yin, J. Zhou, W. Liu, Cobalt–graphene nanomaterial as an efficient

909   catalyst for selective hydrogenation of 5-hydroxymethylfurfural into 2,5-dimethylfuran, Catal.

910   Sci. Technol. 9 (2019) 1329–1333. https://doi.org/10.1039/C9CY00330D.

911 [47] M. Khan, M.N. Tahir, S.F. Adil, H.U. Khan, M.R.H. Siddiqui, A.A. Al-warthan, W. Tremel,

912   Graphene based metal and metal oxide nanocomposites: synthesis, properties and their

913   applications, J. Mater. Chem. A. 3 (2015) 18753–18808. https://doi.org/10.1039/C5TA02240A.

914 [48] J. Liu, J. Tang, J.J. Gooding, Strategies for chemical modification of graphene and applications

915   of chemically modified graphene, J. Mater. Chem. 22 (2012) 12435–12452.

916   https://doi.org/10.1039/C2JM31218B.

917   [49] Y. Chen, X. Bai, Y. Ji, T. Shen, Reduced graphene oxide-supported hollow Co3O4@N-doped

918   porous carbon as peroxymonosulfate activator for sulfamethoxazole degradation, Chem. Eng. J.

919   430 (2022) 132951. https://doi.org/https://doi.org/10.1016/j.cej.2021.132951.

920   [50] J. Ye, D. Yang, J. Dai, C. Li, Y. Yan, Confinement of ultrafine Co3O4 nanoparticles in

921   nitrogen-doped graphene-supported macroscopic microspheres for ultrafast catalytic oxidation:

922   Role of oxygen vacancy and ultrasmall size effect, Sep. Purif. Technol. 281 (2022) 119963.

923   https://doi.org/https://doi.org/10.1016/j.seppur.2021.119963.

924   [51] Y. Yao, Y. Hu, H. Hu, L. Chen, M. Yu, M. Gao, S. Wang, Metal-free catalysts of graphitic

925   carbon nitride–covalent organic frameworks for efficient pollutant destruction in water, J.

926   Colloid Interface Sci. 554 (2019) 376–387.

927   https://doi.org/https://doi.org/10.1016/j.jcis.2019.07.002.

928   [52] S. Hardt, I. Wlokas, C. Schulz, H. Wiggers, Impact of ambient pressure on titania nanoparticle

929   formation during spray-flame synthesis, J. Nanosci. Nanotechnol. 15 (2015) 9449–9456.

930   https://doi.org/10.1166/jnn.2015.10607.

931   [53] F. Schneider, S. Suleiman, J. Menser, E. Borukhovich, I. Wlokas, A. Kempf, H. Wiggers, C.

932   Schulz, SpraySyn—A standardized burner configuration for nanoparticle synthesis in spray

933   flames, Rev. Sci. Instrum. 90 (2019) 85108. https://doi.org/10.1063/1.5090232.

934   [54] A. Münzer, L. Xiao, Y.H. Sehlleier, C. Schulz, H. Wiggers, All gas-phase synthesis of

935   graphene: Characterization and its utilization for silicon-based lithium-ion batteries,

936   Electrochim. Acta. 272 (2018) 52–59.

937   https://doi.org/https://doi.org/10.1016/j.electacta.2018.03.137.

938   [55] S. Bapat, D. Segets, Sedimentation Dynamics of Colloidal Formulations through Direct

939   Visualization: Implications for Fuel Cell Catalyst Inks, ACS Appl. Nano Mater. 3 (2020)

940   7384–7391. https://doi.org/10.1021/acsanm.0c01467.

941 [56] C. Liang, C.-F. Huang, N. Mohanty, R.M. Kurakalva, A rapid spectrophotometric

942   determination of persulfate anion in ISCO, Chemosphere. 73 (2008) 1540–1543.

943   https://doi.org/https://doi.org/10.1016/j.chemosphere.2008.08.043.

944 [57] L. Tepech-Carrillo, A. Escobedo-Morales, A. Pérez-Centeno, E. Chigo-Anota, J.F. Sánchez-

945   Ramírez, E. López-Apreza, J. Gutiérrez-Gutiérrez, Preparation of Nanosized $LaCoO_3$ through

946   Calcination of a Hydrothermally Synthesized Precursor, J. Nanomater. 2016 (2016) 6917950.

947   https://doi.org/10.1155/2016/6917950.

948 [58] M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, L.G. Cançado, A. Jorio, R. Saito, Studying

949   disorder in graphite-based systems by Raman spectroscopy, Phys. Chem. Chem. Phys. 9 (2007)

950   1276–1290. https://doi.org/10.1039/B613962K.

951 [59] T. Ishimoto, Y. Ito, T. Tada, R. Oike, T. Nakamura, K. Amezawa, M. Koyama, Theoretical

952   study on temperature effect of electronic structure and spin state in LaCoO3 by using density

953   functional theory, Solid State Ionics. 285 (2016) 195–201.

954   https://doi.org/https://doi.org/10.1016/j.ssi.2015.08.017.

955 [60] F. Cheng, T. Zhang, Y. Zhang, J. Du, X. Han, J. Chen, Enhancing Electrocatalytic Oxygen

956   Reduction on MnO2 with Vacancies, Angew. Chemie Int. Ed. 52 (2013) 2474–2477.

957   https://doi.org/https://doi.org/10.1002/anie.201208582.

958 [61] J. Hu, X. Zeng, G. Wang, B. Qian, Y. Liu, X. Hu, B. He, L. Zhang, X. Zhang, Modulating

959   mesoporous Co3O4 hollow nanospheres with oxygen vacancies for highly efficient

960   peroxymonosulfate activation, Chem. Eng. J. 400 (2020) 125869.

961   https://doi.org/https://doi.org/10.1016/j.cej.2020.125869.

962 [62] C. Santhosh, A. Malathi, E. Daneshvar, P. Kollu, A. Bhatnagar, Photocatalytic degradation of

963   toxic aquatic pollutants by novel magnetic 3D-TiO2@HPGA nanocomposite, Sci. Rep. 8

964   (2018) 15531. https://doi.org/10.1038/s41598-018-33818-9.

965 [63] P.H.T. Ngamou, K. Kohse-Höinghaus, N. Bahlawane, CO and ethanol oxidation over LaCoO3

966   planar model catalysts: Effect of the thickness, Catal. Commun. 12 (2011) 1344–1350.

967   https://doi.org/https://doi.org/10.1016/j.catcom.2011.04.029.

968   [64]   C. Lv, H. Chen, M. Hu, T. Ai, H. Fu, Nano-oxides washcoat for enhanced catalytic oxidation

969   activity toward the perovskite-based monolithic catalyst, Environ. Sci. Pollut. Res. 28 (2021)

970   37142–37157. https://doi.org/10.1007/s11356-021-13354-2.

971   [65]   L. Armelao, M. Bettinelli, G. Bottaro, D. Barreca, E. Tondello, LaCoO3 Nanopowders by XPS,

972   Surf. Sci. Spectra. 8 (2001) 24–31. https://doi.org/10.1116/11.20010701.

973   [66]   M. Guiotto, M. Pacella, G. Perin, A. Iovino, N. Michelon, M.M. Natile, A. Glisenti, P. Canu,

974   Washcoating vs. direct synthesis of LaCoO3 on monoliths for environmental applications,

975   Appl. Catal. A Gen. 499 (2015) 146–157.

976   https://doi.org/https://doi.org/10.1016/j.apcata.2015.04.013.

977   [67]   Y. Li, L. Liu, Z. Wang, L. Zhou, Y. Lan, C. Chen, Simultaneous oxidation of 4-

978   aminophenylarsonic acid and adsorption of the produced inorganic arsenic by a combination of

979   Co3O4-La2CO5@RSBC with peroxymonosulfate, Chem. Eng. J. 413 (2021) 127417.

980   https://doi.org/https://doi.org/10.1016/j.cej.2020.127417.

981   [68]   S. Dong, Q. Ji, Y. Wang, H. Liu, J. Qu, Enhanced phosphate removal using zirconium

982   hydroxide encapsulated in quaternized cellulose, J. Environ. Sci. 89 (2020) 102–112.

983   https://doi.org/https://doi.org/10.1016/j.jes.2019.10.005.

984   [69]   S. Yang, Y. Liu, Y. Hao, X. Yang, W.A. Goddard III, X.L. Zhang, B. Cao, Oxygen-Vacancy

985   Abundant Ultrafine Co3O4/Graphene Composites for High-Rate Supercapacitor Electrodes,

986   Adv. Sci. 5 (2018) 1700659. https://doi.org/10.1002/advs.201700659.

987   [70]   T.L. Phan, L. V Bau, N. V Khiem, N.X. Phuc, S.C. Yu, ESR study of Sr-doped LaCoO3

988   cobaltites, Phys. Status Solidi. 242 (2005) 1522–1527.

989   https://doi.org/https://doi.org/10.1002/pssb.200440033.

990   [71]   C. Sanchez, B. Lebeau, F. Chaput, J.-P. Boilot, Optical Properties of Functional Hybrid

991   Organic–Inorganic Nanocomposites, Adv. Mater. 15 (2003) 1969–1994.

992   https://doi.org/10.1002/adma.200300389.

993   [72]   A.M. Salih, M. Bin Ahmad, N.A. Ibrahim, K.Z.H.M. Dahlan, R. Tajau, M.H. Mahmood,

994   W.M.Z.W. Yunus, Synthesis of Radiation Curable Palm Oil-Based Epoxy Acrylate: NMR and

995   FTIR Spectroscopic Investigations., Molecules. 20 (2015) 14191–14211.

996   https://doi.org/10.3390/molecules200814191.

997   [73]   C. Berthomieu, R. Hienerwadel, Fourier transform infrared (FTIR) spectroscopy, Photosynth.

998   Res. 101 (2009) 157–170. https://doi.org/10.1007/s11120-009-9439-x.

999   [74]   G. Zhou, D.-W. Wang, L.-C. Yin, N. Li, F. Li, H.-M. Cheng, Oxygen Bridges between NiO

1000   Nanosheets and Graphene for Improvement of Lithium Storage, ACS Nano. 6 (2012) 3214–

1001   3223. https://doi.org/10.1021/nn300098m.

1002   [75]   B. Apicella, M. Alfè, R. Barbella, A. Tregrossi, A. Ciajolo, Aromatic structures of

1003   carbonaceous materials and soot inferred by spectroscopic analysis, Carbon N. Y. 42 (2004)

1004   1583–1589. https://doi.org/https://doi.org/10.1016/j.carbon.2004.02.010.

1005   [76]   V. Ţucureanu, A. Matei, A.M. Avram, FTIR Spectroscopy for Carbon Family Study, Crit. Rev.

1006   Anal. Chem. 46 (2016) 502–520. https://doi.org/10.1080/10408347.2016.1157013.

1007   [77]   S. Abbott, C.M. Hansen, H. Yamamoto, Hansen solubility parameters in practice complete

1008   with eBook , software and data, 2013.

1009   [78]   T. Vasiljevic, T. Harner, Bisphenol A and its analogues in outdoor and indoor air: Properties,

1010   sources and global levels, Sci. Total Environ. 789 (2021) 148013.

1011   https://doi.org/https://doi.org/10.1016/j.scitotenv.2021.148013.

1012   [79]   S. Sharma, S. Basu, N.P. Shetti, M.N. Nadagouda, T.M. Aminabhavi, Microplastics in the

1013   environment: Occurrence, perils, and eradication, Chem. Eng. J. 408 (2021) 127317.

1014   https://doi.org/https://doi.org/10.1016/j.cej.2020.127317.

1015   [80]   F. Shoushtarian, M. Negahban-Azar, Worldwide Regulations and Guidelines for Agricultural

1016   Water Reuse: A Critical Review, Water. 12 (2020). https://doi.org/10.3390/w12040971.

1017   [81]   W. Ma, N. Wang, Y. Du, T. Tong, L. Zhang, K.-Y. Andrew Lin, X. Han, One-step synthesis of

1018   novel Fe3C@nitrogen-doped carbon nanotubes/graphene nanosheets for catalytic degradation

1019   of Bisphenol A in the presence of peroxymonosulfate, Chem. Eng. J. 356 (2019) 1022–1031.

1020   https://doi.org/https://doi.org/10.1016/j.cej.2018.09.093.

1021   [82]   Y. Liu, R. Luo, Y. Li, J. Qi, C. Wang, J. Li, X. Sun, L. Wang, Sandwich-like Co3O4/MXene

1022   composite with enhanced catalytic performance for Bisphenol A degradation, Chem. Eng. J.

1023   347 (2018) 731–740. https://doi.org/https://doi.org/10.1016/j.cej.2018.04.155.

1024   [83]   C. Zhu, F. Liu, C. Ling, H. Jiang, H. Wu, A. Li, Growth of graphene-supported hollow cobalt

1025   sulfide nanocrystals via MOF-templated ligand exchange as surface-bound radical sinks for

1026   highly efficient bisphenol A degradation, Appl. Catal. B Environ. 242 (2019) 238–248.

1027   https://doi.org/https://doi.org/10.1016/j.apcatb.2018.09.088.

1028   [84]   X. Li, A.I. Rykov, B. Zhang, Y. Zhang, J. Wang, Graphene encapsulated FexCoy nanocages

1029   derived from metal–organic frameworks as efficient activators for peroxymonosulfate, Catal.

1030   Sci. Technol. 6 (2016) 7486–7494. https://doi.org/10.1039/C6CY01479H.

1031   [85]   C. Wang, H. Wang, R. Luo, C. Liu, J. Li, X. Sun, J. Shen, W. Han, L. Wang, Metal-organic

1032   framework one-dimensional fibers as efficient catalysts for activating peroxymonosulfate,

1033   Chem. Eng. J. 330 (2017) 262–271. https://doi.org/https://doi.org/10.1016/j.cej.2017.07.156.

1034   [86]   J. Jing, C. Cao, S. Ma, Z. Li, G. Qu, B. Xie, W. Jin, Y. Zhao, Enhanced defect oxygen of

1035   LaFeO3/GO hybrids in promoting persulfate activation for selective and efficient elimination

1036   of bisphenol A in food wastewater, Chem. Eng. J. 407 (2021) 126890.

1037   https://doi.org/https://doi.org/10.1016/j.cej.2020.126890.

1038   [87]   R. Luo, C. Liu, J. Li, C. Wang, X. Sun, J. Shen, W. Han, L. Wang, Convenient synthesis and

1039   engineering of ultrafine Co3O4-incorporated carbon composite: towards practical application

1040   of environmental remediation, J. Mater. Chem. A. 6 (2018) 3454–3461.

1041   https://doi.org/10.1039/C7TA11052A.

1042   [88]   G.P. Anipsitakis, D.D. Dionysiou, Degradation of Organic Contaminants in Water with Sulfate

1043   Radicals Generated by the Conjunction of Peroxymonosulfate with Cobalt, Environ. Sci.

1044 Technol. 37 (2003) 4790–4797. https://doi.org/10.1021/es0263792.

[89] R. Luo, M. Li, C. Wang, M. Zhang, M.A. Nasir Khan, X. Sun, J. Shen, W. Han, L. Wang, J. Li, Singlet oxygen-dominated non-radical oxidation process for efficient degradation of bisphenol A under high salinity condition, Water Res. 148 (2019) 416–424. https://doi.org/https://doi.org/10.1016/j.watres.2018.10.087.

[90] X. Zhou, C. Luo, M. Luo, Q. Wang, J. Wang, Z. Liao, Z. Chen, Z. Chen, Understanding the synergetic effect from foreign metals in bimetallic oxides for PMS activation: A common strategy to increase the stoichiometric efficiency of oxidants, Chem. Eng. J. 381 (2020) 122587. https://doi.org/https://doi.org/10.1016/j.cej.2019.122587.

[91] C. Tan, X. Jian, L. Su, X. Lu, J. Huang, J. Deng, W. Chu, Kinetic removal of acetaminophen and phenacetin during LED-UV365 photolysis of persulfate system: Reactive oxygen species generation, Chemosphere. 269 (2021) 129337. https://doi.org/https://doi.org/10.1016/j.chemosphere.2020.129337.

[92] C. Chen, F. Li, H.-L. Chen, M.G. Kong, Interaction between air plasma-produced aqueous 1O2 and the spin trap DMPO in electron spin resonance, Phys. Plasmas. 24 (2017) 103501. https://doi.org/10.1063/1.4986008.

[93] X. Peng, J. Wu, Z. Zhao, X. Wang, H. Dai, Y. Wei, G. Xu, F. Hu, Activation of peroxymonosulfate by single atom Co-N-C catalysts for high-efficient removal of chloroquine phosphate via non-radical pathways: Electron-transfer mechanism, Chem. Eng. J. 429 (2022) 132245. https://doi.org/https://doi.org/10.1016/j.cej.2021.132245.

[94] X. Tian, P. Gao, Y. Nie, C. Yang, Z. Zhou, Y. Li, Y. Wang, A novel singlet oxygen involved peroxymonosulfate activation mechanism for degradation of ofloxacin and phenol in water, Chem. Commun. 53 (2017) 6589–6592. https://doi.org/10.1039/C7CC02820B.

[95] T. Zhang, Y. Ding, H. Tang, Generation of singlet oxygen over Bi(V)/Bi(III) composite and its use for oxidative degradation of organic pollutants, Chem. Eng. J. 264 (2015) 681–689. https://doi.org/https://doi.org/10.1016/j.cej.2014.12.014.

48

1070   [96]   E.-T. Yun, J.H. Lee, J. Kim, H.-D. Park, J. Lee, Identifying the Nonradical Mechanism in the

1071   Peroxymonosulfate Activation Process: Singlet Oxygenation Versus Mediated Electron

1072   Transfer, Environ. Sci. Technol. 52 (2018) 7032–7042.

1073   https://doi.org/10.1021/acs.est.8b00959.

1074   [97]   Q. Wang, Y. Shao, N. Gao, W. Chu, J. Chen, X. Lu, Y. Zhu, N. An, Activation of

1075   peroxymonosulfate by Al2O3-based CoFe2O4 for the degradation of sulfachloropyridazine

1076   sodium: Kinetics and mechanism, Sep. Purif. Technol. 189 (2017) 176–185.

1077   https://doi.org/https://doi.org/10.1016/j.seppur.2017.07.046.

1078   [98]   Y. Yao, Z. Yang, H. Sun, S. Wang, Hydrothermal Synthesis of Co3O4–Graphene for

1079   Heterogeneous Activation of Peroxymonosulfate for Decomposition of Phenol, Ind. Eng.

1080   Chem. Res. 51 (2012) 14958–14965. https://doi.org/10.1021/ie301642g.

1081   [99]   Y. Yao, Y. Cai, F. Lu, F. Wei, X. Wang, S. Wang, Magnetic recoverable MnFe2O4 and

1082   MnFe2O4-graphene hybrid as heterogeneous catalysts of peroxymonosulfate activation for

1083   efficient degradation of aqueous organic pollutants, J. Hazard. Mater. 270 (2014) 61–70.

1084   https://doi.org/https://doi.org/10.1016/j.jhazmat.2014.01.027.

1085   [100] H. V Lutze, N. Kerlin, T.C. Schmidt, Sulfate radical-based water treatment in presence of

1086   chloride: Formation of chlorate, inter-conversion of sulfate radicals into hydroxyl radicals and

1087   influence of bicarbonate, Water Res. 72 (2015) 349–360.

1088   https://doi.org/https://doi.org/10.1016/j.watres.2014.10.006.

1089   [101] W. Duan, J. He, Z. Wei, Z. Dai, C. Feng, A unique Si-doped carbon nanocatalyst for

1090   peroxymonosulfate (PMS) activation: insights into the singlet oxygen generation mechanism

1091   and the abnormal salt effect, Environ. Sci. Nano. 7 (2020) 2982–2994.

1092   https://doi.org/10.1039/D0EN00848F.

1093   [102] A. Shahzad, J. Ali, J. Ifthikar, G.G. Aregay, J. Zhu, Z. Chen, Z. Chen, Non-radical PMS

1094   activation by the nanohybrid material with periodic confinement of reduced graphene oxide

1095   (rGO) and Cu hydroxides, J. Hazard. Mater. 392 (2020) 122316.

49

1096   https://doi.org/https://doi.org/10.1016/j.jhazmat.2020.122316.

1097   [103]   S. Yang, P. Wu, J. Liu, M. Chen, Z. Ahmed, N. Zhu, Efficient removal of bisphenol A by

1098   superoxide radical and singlet oxygen generated from peroxymonosulfate activated with Fe0-

1099   montmorillonite, Chem. Eng. J. 350 (2018) 484–495.

1100   https://doi.org/https://doi.org/10.1016/j.cej.2018.04.175.

1101   [104]   S. Wang, J. Tian, Q. Wang, F. Xiao, S. Gao, W. Shi, F. Cui, Development of CuO coated

1102   ceramic hollow fiber membrane for peroxymonosulfate activation: a highly efficient singlet

1103   oxygen-dominated oxidation process for bisphenol a degradation, Appl. Catal. B Environ. 256

1104   (2019) 117783. https://doi.org/https://doi.org/10.1016/j.apcatb.2019.117783.

1105

1106

1107

1108   Graphical abstract

1109 Synthesis of novel LaCoO₃/graphene catalysts as highly efficient
1110 peroxymonosulfate activator for the degradation of organic pollutants

1111 Mohaned Hammad[a*], Steven Angel[c], Ahmed K. Al-kamal[c,g], Anam Asghar[b], Amin Said Amin[a],

1112 Haakon T. A. Wiedemann[d], Md Yusuf Ali[c], Paolo Fortugno[c], Cheolyong Kim[b], Torsten C.

1113 Schmidt[b], Christopher W. M. Kay[d,f], Doris Segets[a,e], Hartmut Wiggers[c,e*]

1114
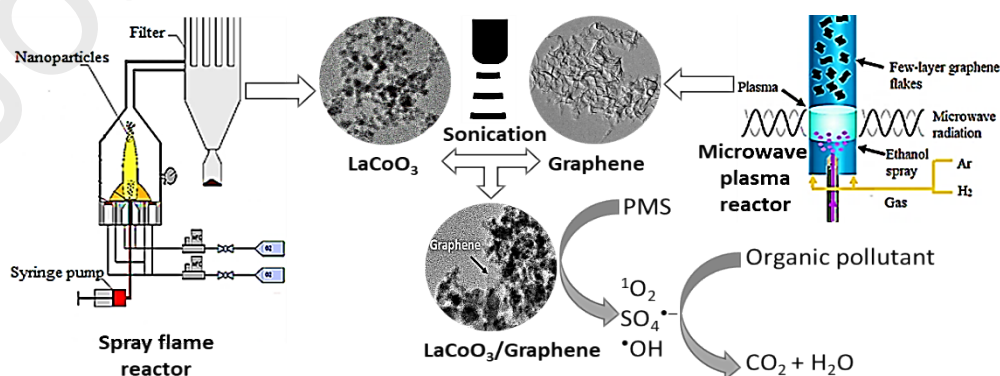
1115

1116

1117

1118

Highlight

1120 • Large-scale synthesis of novel $LaCoO_3$/Graphene material is presented.

1121 • $LaCoO_3$/Graphene composite exhibits outstanding PMS activation efficiency than $LaCoO_3$.

1122 • Co–O–C interactions improve the stability and prevent cobalt leaching.

1123 • $LaCoO_3$/Graphene material has an excellent performance under various environmental

1124   factors.

1125

1126