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Thermocatalytic Syntheses of Highly Defective Hybrid Nano-catalysts for Photocatalytic Hydrogen Evolution

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Defects play important roles in many catalytic processes, particularly for photocatalytic processes in semiconductors as they can alter band structures and affect excited electron-hole recombination pathways/lifetimes of semiconductors. In this report, we described the development of a facile route to the production of highly defective photocatalysts. Firstly, organic species were bound onto the surface of a metal oxide semiconductor catalyst, followed by a relatively low temperature ageing in N2, to remove the organics and to attract oxygen molecules from the surface, generateing oxygen vacancies. In particular, we introduced a co-catalyst during the syntheses, which acted as a thermocatalyst to promote a full oxidation of the organics, leaving more oxygen vacancies at surface and to form intimate heterojucntions with host-catalyst to further drive the photocatalytic hydrogen evolution. The hydrogen evolution rate for our developed NiO-TiO2 defective heterojucntions in a sacrificial system was measured at ca. 1.41 mmol/g/h, which was much higher than comparable catalysts reported in the literature (that generally display hydrogen evolution rates < 0.4 mmol/g/h). Computational simulation, together with other analytical techniques, suggested that the generated surface oxygen vacancies could induce a series of impurity energy levels within the VBM and CBM of TiO2 that narrowed the electron transmission gap in the TiO2 and acted as active sites for the reaction between adsorbed H2O and photoinduced trapped electrons to produce H2。

Introduction

With the rapid growth in urbanization and industrialization, development and deployment of energy delivery technologies to meet human needs, has become increasingly critical.1 Hydrogen fuel is considered to be a renewable and clean energy source, offering high energy density and is an attractive alternative to using polluting fossil fuels.2,3 Consequently, sustainable methods to generate hydrogen, are attractive, e.g. via direct photocatalysis and electrocatalysis with energy provided from a solar cell or renewable source.4-8 Photocatalysis is particularly attractive as it is relatively simple as long as sufficiently robust and appropriate materials can be found.9 In 1972, Fujishima and Honda developed a cell with TiO2 electrode and platinum black electrode for photo-electrochemical water splitting, in which an electrical bias was needed in the system. Since this work, a significant development of new catalysts for photocatalytic hydrogen evolution, has occurred.10 After many years of exploration, such as TiO2-based catalysts, metal sulfides, carbonaceous compounds and some other photocatalysts have been widely used in laboratory-scale tests for photocatalytic hydrogen evolution from water.11-17 Among these catalysts, TiO2-based catalysts have been explored due to their non-toxicity, high stability, low cost and good availability. However, due to the large band gap (ca. 3.2 eV for anatase TiO2) which is not optimum to straddle the water splitting potentials and sometimes with substantial electron-hole recombination, the photocatalytic activity of stoichiometric TiO2 under UV-Vis irradiation, is generally low (e.g. typically at ca. 65 μmol/h/gunder the concentration of TiO2 in the reaction system of ca. 1.0 g/L and the ratio of sacrificial agent (methanol or ethanol) at 10-30%).18-20 Therefore, modification of the TiO2 to improve through various approaches including element doping or surface loading, dye sensitization, as well as using one or more semiconductors synergistically, have been explored with aims to narrow the band gap and to increase excitation lifetimes.

Defects, referred as imperfect arrangement of atoms or molecules in crystalline materials, can strongly affect the band structure of semiconductors and have a significant influence on the activity of photocatalysts.21 Oxygen vacancies that are point defects, can suppress the recombination process of photo-generated electrons and holes by increasing the electron density to cause band bending.22-28 For the well-reported photocatalyst TiO2, the oxygen vacancies are often accompanied with Ti3+ species that can be produced by treating TiO2 in a reducing atmosphere (H2, Ar, NaBH4, etc.) at certain temperatures and pressures, which greatly promoted their photocatalytic activities in many photo catalysis applications.29,30

Herein, we proposed a facile approach to synthesize defective TiO2 photocatalysts; first a well-reported supercritical water, sc-H2O (which has a critical temperature and pressure of Tc = 374 oC and Pc = 22.1 MPa, respectively) flow system was used to make TiO2 nanoparticles with surface bound species.31-33 Thereafter, a N2 treatment of the particles at ca. 300 oC, was carried out to oxidize the bonded organic species into CO or CO2, which resulted in the creation of oxygen vacancies at the particle surface. The generation of such defects has been known to narrow the band gap and increase electron-hole lifetimes of TiO2, which can enhance the reaction rates for photocatalytic reactions.34,35

In particular, this report innovatively introduced a cocatalyst, NiO36, during the syntheses, the introduction of which was expected to act as a thermocatalyst during the oxidative removal (heat-treatment step in N2) of bound organic species, which could promote a full oxidation of the organics and result in more oxygen vacancies on the TiO2 surfaces. Moreover, such a thermal-treatment was also expected to result in the formation of intimate NiO-TiO2 heterojunctions possessing an electric field at the NiO-TiO2 interface. If such a thermocatalytic syntheses approach could be shown to be effective for production of highly defective heterojunctions, then this approach might find more general application for the scalable syntheses of similar mixed oxide photocatalysts. A range of analytical techniques were used in this report to investigate the materials including High Resolution Transmission Electron Microscopy (HR-TEM), Electron Spin Resonance (ESR) spectroscopy, etc. where Temperature Programmed Surface Reduction (TPSR), were employed to elucidate the function of the NiO, in the promotion of oxygen vacancy formation in the anatase TiO2; XPS, UV-Vis and computational simulation were utilized to explore the influence of defects and NiO-TiO2 heterojunction on the band structure of TiO2 and photocatalytic activity for hydrogen evolution.

Experimental Section

Materials

Dihydroxybis(ammonium-lactato)titanium(IV) (50 %w/w, aqueous, TiBALD) was purchased from Alfa Aesar China (Beijing, China). Nickel nitrate hexahydrate (99.8%) was supplied by Shanghai Macklin Biochemical Co. Ltd (Shanghai, China). Methanol was bought from Sinopharm Chemical Reagent Co. Ltd (Beijing, China). All chemicals were of analytical pure grade and used as obtained. 10 megaohms deionized water was used in all experiments.

Fabrication of NiO-TiO2 heterojunction powders

Ultrafine TiO2 and NiO nanocrystallites were separately prepared by using a three-pump continuous hydrothermal flow system (CHFS, see supplementary **Fig. S1**). Typically, to fabricate the TiO2 (denoted as sc-TiO2), an aqueous solution of TiBALD (0.1 M) was pumped at 7.5 mL/min to meet a flow of deionized water (using a T-mixer). This mixture was then pumped to meet a flow of superheated water (pumping rate at 30 mL/min) at a confined jet mixer, whereupon rapid precipitation of TiO2 nuclei occurred. For NiO preparation (denoted as sc-NiO), solutions of Ni(NO3)2·6H2O (0.05 M) and NaOH (2.0 M), were pumped separately into the system at the pumping rate of 7.5 mL/min and mixed at room temperature in flow. Then, the mixture was brought into contact with a flow of superheated water (pump rate at 30 mL/min) in a confined jet mixture, whereupon the NiO particles formed. The temperature of all superheated water feeds was set to be 450 oC. A band heater (set as 450 oC) placed on the outside of the confined jet mixer was also added to provide additional heating. In all reactions, the newly formed nanoparticles were cooled down to near room temperature in flow and passed through a 7 μm filter before being collected from the exit of a back pressure regulator (that was used to maintain the system pressure at 23 MPa). The as-prepared precipitates were then centrifuged and then frozen at -55 oC prior to being freeze-dried for 24 h at 50 Pa.

To fabricate the NiO-TiO2 hybrids (denoted as sc-NiO-TiO2), pure CHFS made sc-TiO2 and CHFS made sc-NiO particles were mixed in a 10:3 mass ratio and ground carefully by hand for 15 min. The mixed powder was then heat-treated in N2 for 2 h using a heating rate of 3 oC/min. The obtained brown powder (denoted as sc-NiO-TiO2-N2) was directly used as catalyst for photocatalytic hydrogen evolution from water.

Characterizations

XRD patterns were recorded using a XRD-6000 diffractometer (Shimadzu, Japan) with Cu-K*α* radiation (λ= 0.1542 nm). The accelerating voltage of which was set at 40 kV while the current remained to be 30 mA. The diffraction patterns were obtained at diffraction angles in the 2 theta ranging from 10 to 80 o with a scanning rate of 4 o/min and a slit size of 1 degree. To analyze the morphology of the crystals, a high-resolution transmission electron microscope, HR-TEM (model FEI Tecnai F20, US), equipped with an energy-dispersive X-ray spectroscope (EDS) was employed. Prior to the analysis, powders were dispersed in ethanol with sonication and then cast onto the formvar stabilized with carbon support film, and tested at an accelerating voltage of 200 kV. The BET specific surface areas were acquired from the N2 adsorption and desorption isotherm at 77 K (model JW-BK132F analyzer, JWGB Sci & Tech Co. Ltd, China). Pretreatment were conducted at 80 oC for 2 h under vacuum to dry and clean the sample surfaces. Electron spin resonance (ESR) spectra at 130 K (JEOL JES-FA200 ESR spectrometer, Japan) was conducted to detect oxygen vacancies in the catalysts. The microwave power during the testing was set 1 at mW (sweep width in the range 223 to 423 mT) with a modulation frequency and modulation amplitude of 100 kHz and 0.35 mT, respectively. The valence band and valence state of surface elements were evaluated using an X-ray photoelectron spectrometer (XPS, Thermo ESCALAB 250, US), with the Al-K*α* radiation (h*v* = 1486.6 eV) operated at 150 W. After calibrating the binding energy scale using the signal of adventurous carbon (a binding energy of 284.8 eV), the curves were fitted using a Shirley background and a Gaussian peak shape with 20 % Lorentzian character. Transmission IR spectroscopic data was acquired using a Vertex 70 spectrometer (Bruker, Germany) at 4 cm-1 resolution (100 co-added scans) at atmospheric pressure. Photoluminescence Spectroscopy (PL) measurements were taken using a fluorospectrophotometer (Fluorolog-3-Tau, France) with a Xe lamp (320 nm) as the excitation source at room temperature. Transient photocurrent measurements were recorded by using a CHI 660E electrochemical workstation. A three-electrode system was used for producing photocurrent, consisting of platinum electrode, Ag/AgCl reference electrode and the thin film electrode with the sample, was applied. UV-Visible Diffuse Reflection Spectra (UV-Vis. DRS) were obtained using a UV-Vis spectrophotometer (TU-1901, China) with an integrating sphere assembly. The spectra were recorded at room temperature in the range of 200 to 800 nm, with a BaSO4 pellet as the standard reflectance sample. Temperature programmed surface reaction (TPSR) data was processed and collected automatically using a multipurpose adsorption instrument (model Tianjin TP-5089, Xianquan, China) equipped with a mass spectrometer (MS, HIDEN QGA portable MS, UK). Typically, catalysts containing 0.06 g of sc-TiO2 or sc-NiO-TiO2 were pretreated at 30 oC for 2 h with a pure flow of helium (He), heated to 300 oC (heating rate of 3 oC/min) and then kept at 300 oC for 2 h. During the process, the amount CO and CO2 released from the system was recorded and analyzed by the MS.

Computational Simulation

To evaluate the effect of oxygen vacancy on the band structure of TiO2, a computational simulation based on density-functional theory was applied. Due to the limit license of VASP, the generalized gradient approximation proposed by Perdew, Burk and Ernzerhof (GGA-PBE) settled in CASTEP (Cambridge Serial Total Energy Package) was selected herein. Parameters during the simulation were set referred to the literature reported by Wu. *et al*.37 and our experimental results. Defective and defect-free anatase TiO2 models using (2×3×1) supercells (containing 47 titanium atoms and 70 oxygen atoms for defect-free anatase TiO2 model, and 47 titanium atoms and 69, 67 or 60 oxygen atoms for defective anatase TiO2 models) were built up for the simulations of band structure and density of states (DOS). Moreover, a norm-conserving pseudopotential was chosen for its high accuracy and the energy cutoff and k-point set were 400.0 eV and 1×1×2, respectively. More details on the computational simulation were provided in supplementary data.

Photocatalytic activity measurements

Photocatalytic hydrogen evolution activity measurements were conducted in a quartz reactor equipped with a magnetic stirrer. Typically, 0.05 g of powder was dispersed into 35.0 mL deionized water, and then bubbled by a flow of high purity argon (Ar) for 15 mins to remove the residual oxygen in the system. Thereafter, 15.0 mL of methanol (99.5 %) was added as the sacrificial agent during the reaction. A 300 W Xe lamp placed 12 cm above the reactor was provided as the light source and the testing temperature was controlled through a flow of water in the jacket around the reactor. The amount of hydrogen evolved during the process was evaluated using a gas chromatograph (GC, Agilent 7890A, US) with a thermal conductivity detector (TCD). The temperature of the column oven, injection port and detector was 45, 110 and 250 oC, respectively. For cycling tests, a flow of Ar was purged into the bottom of the system to remove residual H2 and O2 in the solution before each test, and ca. 2 mL methanol was reloaded to equalize the sacrificial agent in each test. After each test, the reactor containing the catalysts was stored in darkness until the next test.

Results and Discussion

XRD and BET analyses

Phase identities of the catalysts were first elucidated using X-ray powder diffraction (XRD). As shown in supplementary **Fig. S2(a)**, the sc-TiO2 had a tetragonal anatase structure (similar to reference pattern JCPDS No. 78-2486) with diffraction patterns at 2*θ* = 25.3, 37.8, 48.0, 53.9, 55.1 and 62.7 o and the sc-NiO showed a characteristic pattern for NiO (similar to reference pattern JCPDS No. 78-0643) with peaks at 2*θ* = 37.3, 43.4, 63.0, 75.6 and 79.6 o. Both the sc-NiO-TiO2 and sc-NiO-TiO2-N2 revealed peaks due to isolate TiO2 and NiO phases in their XRD profile. Rietveld refinement (see supplementary **Table S1** and **Fig. S2(b)**) was applied to the XRD data using a tetragonal structure (for TiO2) and cubic structure (for NiO) as starting models which gave a fit for the TiO2 phase as being I41/amd (Rp = 0.0169) and the NiO phase as Fm-3m (Rp = 0.0195). The sc-TiO2 was found to best fit to fully stoichiometric TiO2 with an oxygen occupancy value of 1. In contrast, the sc-NiO-TiO2-N2 sample however, appeared to fit best with the oxygen occupancy of ca. 0.84 (i.e. ca. 16% oxygen vacancies, i.e. a formula of TiO1.68). This refinement result is promising as it evidences that the oxidative approach used herein was effective to obtain the highly defective TiO2 material.

**Table 1.** BET surface area, pore volume and pore size of each catalyst.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | SBET (m2/g) | Pore volume (cm3/g) | Pore size (nm) |
| sc-TiO2 | 194.2 | 0.39 | 7.2 |
| sc-NiO | 38.0 | 0.27 | 25.3 |
| sc-TiO2-NiO | 135.3 | 0.35 | 7.5 |
| sc-TiO2-NiO-N2 | 146.8 | 0.35 | 7.4 |

After subjected to BET surface area measurements (see **Table 1**), the sc-TiO2 and sc-NiO revealed a specific surface area (SSA) of ca. 194.2 and 38.0 m2/g, respectively. Upon mixing of the individual powders (forming sc-NiO-TiO2), the products had a SSA of ca. 135.2 m2/g, whilst that of the sc-NiO-TiO2-N2 was at ca. 146.8 m2/g. The adsorption isotherms of sc-TiO2, sc-NiO-TiO2 and sc-NiO-TiO2-N2 (see supplementary **Fig. S3**) displayed an isotherm shape in-between type IV and type I isotherms; the hysteresis loops of all these catalysts tended to be similar to type H3, indicating the presence of “ink-bottle” like micropores and mesopores in sc-TiO2, sc-NiO-TiO2 and sc-NiO-TiO2-N2.38 For sc-NiO, however, a type IV with H2-type hysteresis loop was observed, which suggested the existence of slit-shaped mesopores in the catalyst.39 The inner pore size and pore volume for sc-NiO-TiO2 and sc-NiO-TiO2-N2 catalysts were almost kept invariant (see **Table 1**), suggesting that structure of the pores in sc-NiO-TiO2 nearly remained unchanged during the heating process. This revealed that the slightly increased SSA in the sc-NiO-TiO2-N2 catalyst might be originated from the presence of surface exposed oxygen vacancies (i.e. open pore) due to N2 ageing.

FT-IR and He-TPSR analyses

To understand how the oxygen vacancies were formed at the TiO2 surface during the N2 ageing, FT-IR and He-TPSR measurements were then conducted.



**Fig. 1** FT-IR spectra of sc-TiO2, sc-NiO-TiO2 and sc-NiO-TiO2-N2 catalysts.

As shown in **Fig. 1**, the FT-IR spectrum of sc-TiO2 and sc-NiO-TiO2 catalysts both revealed the peaks at ca. 3404, 1630, 1453, 1386, 1118 and 1057 cm-1, whilst peaks at 3404 and 1630 cm-1 were attributed to the stretching vibrations of surface water molecules.40 Peaks at 1118 and 1057 cm-1 were assigned to the C-CH3 and C-O stretching vibrations, respectively.41 The peak at 1453 cm-1 was due to the C-O stretching mode of surface carbonate, whilst the peak at 1386 cm-1, was attributed to the formed inner-sphere chemical bonds between lactate anions and Ti cations of TiO2.42,43 These groups most likely arose from organic surface species or their decomposition products. Thus, from the FT-IR spectra, we could deduce that there were many organic species present in the CHFS-made sc-TiO2 and sc-NiO-TiO2 catalysts. These organics were believed to be lactate species (or derived from them) that were originated from the TiBALD precursor.32 After N2 heat-treatment at 300 oC for 2 h, the sc-NiO-TiO2-N2 catalyst only revealed adsorption peaks due to water, which suggested that the bounded organic groups were mostly removed during the N2 heat-treatment.

The thermocatalytic role of NiO in breaking down the organics and creating oxygen vacancies (from the N2 heat-treatment) was evaluated by using He-TPSR, in which both of the sc-TiO2 and sc-NiO-TiO2 were subjected to a heat-treatment in the flow of He at elevated temperatures. The desorbed CO and CO2 were monitored simultaneously using the MS. As shown in **Fig. 2**, both of the TPSR plots for sc-NiO-TiO2 and sc-TiO2 samples exhibited CO and CO2 desorption peaks at ca. 240 oC, which was assigned as the onset temperature for decomposition of bonded lactate. When the TPSR temperature was then maintained at 300 oC for 2 h, the sc-NiO-TiO2 catalyst showed much higher CO desorption (two distinct CO desorption peaks observed at 20 and 50 mins) than that of the sc-TiO2 sample. The TPSR data thus verified that the introduction of NiO indeed allowed more efficient thermocatalytic oxidation of the residual organics (i.e. lactate), which resulted in higher CO production for the sc-NiO-TiO2-N2 catalyst and would lead to more surface oxygen vacancies in the catalyst.



**Fig. 2** He-TPSR spectra of sc-TiO2 and sc-NiO-TiO2 catalysts.

ESR Analyses

Indeed, low-temperature ESR measurements suggested that significant oxygen vacancies did exist in the sc-NiO-TiO2-N2 catalyst (see **Fig. 3**). The ESR signals of the catalyst at g = 2.002 was assigned to oxygen vacancies in TiO2 cells, which contributed to the distinct intensity in the signal compared to the sc-NiO-TiO2.44 Such intensities of g signals were also much higher than those of the sc-TiO2-N2 as reported in our previous work.31 Because the oxygen vacancies on the surface of anatase could work as shallow traps for electrons to enhance the electron-hole separation,29,45 the presence of which would be much beneficial for the photocatalytic activity of sc-NiO-TiO2-N2 catalyst towards hydrogen evolution in a sacrificial system.



**Fig. 3** ESR spectra of sc-NiO-TiO2 and sc-NiO-TiO2-N2 catalyst.

Photocatalytic activity measurements

Fig. 4(a) shows the photocatalytic activities of sc-TiO2, sc-TiO2-N2, sc-NiO, sc-NiO-N2, sc-NiO-TiO2 and sc-NiO-TiO2-N2 catalysts (see section 2.5 for details of the precise reaction conditions). It was noted that the sc-NiO alone did not produce any hydrogen during the test. This implied that the NiO in the sc-NiO-TiO2 and sc-NiO-TiO2-N2 catalysts only acted as a cocatalyst to enhance the electron trapping, creating active sites for hydrogen evolution.46 The addition of NiO effectively increased the Hydrogen Evolution Rate (HER) to ca. 0.84 mmol/g/h and the 5 h Total Hydrogen Evolution (THE) to ca. 4.2 mmol/g for the sc-NiO-TiO2 catalyst. After N2 treatment, the sc-NiO-TiO2-N2 catalyst displayed the highest hydrogen evolution rate (HER) at ca. 1.41 mmol/g/h. The 5 h Total Hydrogen Evolution (THE) of this catalyst was measured at approximately 7.00 mmol/g, which was nearly double the value for sc-NiO-TiO2 and ca. seven-fold higher than the sc-TiO2-N2 catalyst (at 0.2 mmol/g/h).31 By comparison with the relevant literatures, the THE contents typically reported are ca. 0.4 mmol/g/h 47-49 or less (for similar NiO-TiO2 catalysts tested under full spectrum irradiation), the sc-NiO-TiO2-N2 catalyst herein showed exemplary photocatalytic performance for hydrogen evolution. Furthermore, by adding ca. 0.1 wt% Pt onto the surface of the catalysts (via a photo-deposition route), the HER could further increase to approximately 2.61 mmol/g/h and the THE value after 5 h was 13.10 mmol/g (see Fig. S4), both of which were higher than many of best known catalysts in the literature.19, 50-52



**Fig. 4**  (a) Photocatalytic activities of sc-TiO2, sc-TiO2-N2, sc-NiO, sc-NiO-N2, sc-NiO-TiO2 and sc-NiO-TiO2-N2 catalysts for hydrogen evolution from the water; (b) Repeated activity measurements on the sc-NiO-TiO2-N2 catalyst.

The stability of the sc-NiO-TiO2-N2 catalyst was also evaluated via a repeated testing; in each test, the sacrificial agent methanol was re-loaded to compensate the loss in each run. A high purity Ar gas was purged for 15 min prior to each test to completely remove residual oxygen in solution. As shown in **Fig. 4(b)**, the photocatalytic activity of the sc-NiO-TiO2-N2 catalyst did not show obvious change after 5 runs, showing that the catalyst had a very stable performance for photocatalytic hydrogen evolution.

Band structure analyses

Valance band X-ray photoelectron spectroscopy (VB-XPS) was applied to study the band structure of investigated catalysts. As shown in **Fig. 5**, the sc-NiO-TiO2 catalyst revealed a valence band maximum (VBM) at ca. 0.35 eV, which was much lower than that of the sc-TiO2 (at ca. 2.71 eV). This is because the sc-NiO-TiO2 was with the NiO of lower VBM of ca. 0.30 eV.53 For the sc-NiO-TiO2-N2, the VBM was measured at ca. -0.05 eV, which was much lower than that of NiO alone, indicating that there should be additional mid-gap state existed in the catalyst. To elucidate the causes of such a low VBM in the sc-NiO-TiO2-N2 catalyst, a computational simulation based on density-functional theory (DFT) was applied in which (2×3×1) anatase supercells of defect-free anatase TiO2 and defective anatase TiO2 with different oxygen occupancy were utilized to calculate their density of states (DOS) (see models of defective anatase TiO2 in **Fig. S5**). According to **Fig. 6(a)**, the valence band maximum, VBM, of defect-free TiO2 was calculated to be 2.75 eV with the conduction band minimum (CBM) of -0.16 eV. This led to the band gap of the TiO2 to be 2.91 eV. In contrast for defective TiO2 (e.g. x = 0.143, containing 47 Ti atoms and 60 O atoms see **Fig. 6(a)** and **Fig. 6(b)**), a mid state of ca. 0.10 eV below the conduction band of TiO2 was observed, which was reported due to the introduced oxygen vacancies.54 Two additional states located at ca. -0.2 and -1.3 eV, were also observed. As reported by Chen *et al*.,55 who first obtained the defective black TiO2 through treating the anatase TiO2 in H2 at 200 oC for 5 days, the higher-energy mid-gap states were derived from the Ti3d orbitals only; the lower energy states were hybridized from both O2p orbitals and Ti3d orbitals.

Herein, our calculation results suggested that the higher-energy one was from the hybrization of O2p and Ti3d orbitals and the lower-energy one was from the O2p, Ti3p and Ti3d orbitals. Nevertheless, these additional states on the top of VBM of TiO2 should be mainly caused by the defective structure that redistributed the electrons among the nearest neighbour Ti atoms around the oxygen vacancy site.54 As such, electron migration between these mid-gap states and the conduction band tail (due to oxygen vacancy) would require less energy as compared with the transition from the valence band to the conduction band of defect-free TiO2. The calculation result also explained why the sc-NiO-TiO2-N2 catalyst had a very low VBM of ca. -0.05 eV from VB-XPS measurement.



**Fig. 5** Valance Band X-ray Photoelectron Spectra for sc-TiO2 and sc-NiO-TiO2 catalysts that were before and after heat treatment unter N2 300 oC for 2 h.



**Fig. 6.** (a) Band structure and density of states (DOS) calculation for defect-free TiO2 and different defective TiO2 and (b) diagram of band structure of defective TiO2 (x=0.143).

Although the calculated value might not be completely consistent with the measured one (e.g. the band gap of sc-TiO2 was calculated at 2.91 eV but measured at 3.11 eV by using the Kubelka-Munk theory,56 see supplementary **Fig. S6**), we can still conclude that the defective sc-TiO2 (herein sample sc-NiO-TiO2-N2) displayed more band gap narrowing for electron migration compared to the defect-free one (herein sample sc-NiO-TiO2). By further calculating the DOS of TiO2 with various amounts of oxygen vacancy (e.g. x = 0.014 and 0.043, containing 69 and 67 O atoms respectively, see **Fig. 6(a)**), we also found that the TiO2 with higher amounts of defects would pull the VBM closer to the conduction state, which led to a more band gap narrowing for the highly defective TiO2. The narrowed band gap in the sc-NiO-TiO2-N2 was also confirmed by transient photocurrent analyses (see **Fig. S7**), which revealed that the electron and hole in the catalyst could be excited even under the visible light irradiation (>420 nm). This explained why the sc-NiO-TiO2-N2 that was with more defects had a much higher photocatalytic activity than the sc-TiO2-N2 (as illustrated in our previous publication 31) although the NiO in the former catalyst would surely contribute to such an enhanced activity for photocatalytic hydrogen evolution.

Transient photocurrent and PL analyses

The amounts of photo-generated electrons under a full spectrum were measured using transient photocurrent spectroscopy. As shown in **Fig. 7(a),** the sc-TiO2 catalyst initially generated a photocurrent of ca. 0.41 μA. However, this current rapidly decreased and eventually settled at ca. 0.13 μA after 50 s. The attenuation of the current was mainly ascribed to the recombination of electron-hole pairs during irradiation, which was consistent with a previous report. 57 The sc-NiO-TiO2 catalyst retained a photocurrent of ca. 0.41 μA after 50 s of irradiation, which was much higher than that of the sc-TiO2 catalyst. This might be attributed to the formation of heterojunction, which provided longer migration distance for photogenerated holes and electrons in the hybrid.58 After the 4th cycle (with the time interval of 100 s, see the inset of **Fig. 7a**) in the sacrificial system, the intensity of the photocurrent for sc-NiO-TiO2 decreased to 0.25 μA, while that for sc-NiO-TiO2-N2 maintained a photocurrent of 0.6 μA. This indicated that the migrated photoinduced electrons and holes were very stable in the sc-NiO-TiO2-N2 catalyst and the recombination of electron-hole was inhibited, even under repeated irradiation cycles. As mentioned above, the oxygen vacancies were most likely to serve as electron trapping sites to enhance the separation of photoinduced charge carriers, which hence led to high photocurrents for the sc-NiO-TiO2-N2 catalyst.

The inhibited recombination behavior in the sc-NiO-TiO2-N2 catalyst was also verified by the PL measurements. As shown in **Fig. 7(b)**, the sc-TiO2 catalyst emitted a very intense PL signal in the range 400 to 550 nm, indicating that high electron-hole recombination occurred. The PL signal for sc-NiO-TiO2 catalyst was much lower than that of the sc-TiO2 material, suggesting that electron-hole recombination was effectively reduced in the catalyst. In contrast for sc-NiO-TiO2-N2 catalyst, the PL signal was further lowered in the range 350 to 450 nm but an additional hump in the range 480 to 580 nm was observed. The latter was believed due to the presence of surface oxygen vacancies that trapped the photo-generated electrons during the irradiation,59 as after subjected to photocatalytic oxidation of toluene (see **Fig. S8**) under visible light irradiation (>420 nm), the sc-NiO-TiO2-N2 had yielded a distinct activity. This suggested that there were photo-generated holes (originating from the electron trapping by oxygen vacancies) functioned for toluene oxidation in the catalyst.



**Fig. 7** (a) Transient photocurrent (12 cm) and (b) PL measurements on sc-TiO2, sc-NiO-TiO2 and sc-NiO-TiO2-N2 catalysts under the full spectrum irradiation of a 300 W Xe lamp.

Proposed Mechanism

On the basis of the aforementioned results, the route for defect formation in the sc-NiO-TiO2-N2 catalyst and the mechanism for photocatalytic hydrogen evolution, were proposed. When the sc-NiO-TiO2 hybrid catalyst was treated in N2 at 300 oC for 2 h, surface oxygen, was most likely to be extracted from the TiO2, leading to the release of active oxygen (O-) and electrons (e-), as well as the formation of oxygen vacancies (*V*o) [reaction (a)]. The electrons (e-) were then captured by the Ti4+ in TiO2 lattice, resulting in the generation of bulk Ti3+ [reaction (b), see supplementary **Fig. S9(b)** for the XPS result that demonstrated the existence of Ti3+ in the sc-NiO-TiO2-N2 catalyst]. The active oxygen (O-) would be expected to oxidize residual organic species, leading to the formation of CO and CO2 [reaction (c) and reaction (d)]. In addition, the produced CO can also react with the NiO to partially reduce it into metallic Ni (Ni0) [reaction (e)]. The presence of Ni metal was suggested from XPS results of the sc-NiO-TiO2-N2 catalyst (see supplementary **Fig. S9(a)**) in which, a distinct gap of ca. 17.4 eV was observed between the Ni2p3/2 and Ni2p1/2 peaks.60-62

|  |  |
| --- | --- |
| 2 O2- → 2 O- + 2 e- + 2 *V*o | (a) |
| Ti4+ + e- → Ti3+ | (b) |
| 2 CH3CH(OH)COO- + 5 O- → 6 CO + 5 H2O + 7 e- | (c) |
| 2 CH3CH(OH)COO- + 11 O- → 6 CO2 + 5 H2O + 13 e- | (d) |
| NiO + CO → Ni0 + CO2 | (e) |

The photocatalytic mechanisms for the sc-NiO-TiO2-N2 catalyst are given in **Scheme 1**. The N2 heat-treatment resulted in the formation of heterojuctions (as verified by EDX-mapping in supplementary **Fig. S10**) between the NiO and TiO2, which facilitated the migration of photo-generated holes from the VBM of sc-TiO2 (at 2.71 eV) to that of NiO (at 0.30 eV) and the electrons from the CBM of sc-NiO (at -3.30 eV) to that of sc-TiO2 (at -0.70 eV). 53 This led to promoted electron/hole transmission in the sc-NiO-TiO2 catalyst (see transient photocurrent results in **Fig. 7**). When irradiated by light, photo-generated electrons (e-) and holes (h+) were formed at surface and in the bulk of sc-NiO-TiO2 hybrid [reaction (f)]; with the existence of h+, H2O molecules could split into hydroxyl radicals (·OH) and H+ [reaction (g)].63 The generated ·OH would then oxidize the sacrificial agent, CH3OH, leading to the production of methanol radicals (·CH2OH) [reaction (h)];64 due to the large negative potential, ·CH2OH could induce electron injection into TiO2 in the hybrid accompanied by the formation of surface-trapped electrons and formaldehyde (HCHO) [reaction (i)].65 The H+ ions in the solution were eventually reduced by e- to produce the H2 [reaction (j)]. After N2 heat-treatment, the breakdown (oxidation) of organic residues led to the formation of significant oxygen vacancies at TiO2 surface (see XRD refinement in **Fig. S2(b)** and ESR results in **Fig. 3**). According to the DOS calculation (see **Fig. 6**), these oxygen vacancies effectively introduced a series of impurity energy levels within the VBM and CBM of TiO2, which narrowed the electron transmission gap to be 1.78 eV (while for the defect-free TiO2, the gap was at ca. 2.91 eV based on DOS calculation), hence enhancing the light adsorption ability of the sc-NiO-TiO2-N2 catalyst.

|  |  |
| --- | --- |
| photocatalyst + *hv* → h+ + e- | (f) |
| H2O + h+ → ·OH + H+ | (g) |
| CH3OH + ·OH → ·CH2OH + H2O | (h) |
| ·CH2OH → HCHO + H+ + e- | (i) |
| 2 H+ + 2 e- → H2 | (j) |



**Scheme 1.** Proposed mechanism for photocatalytic hydrogen evolution (in a sacrificial system) over sc-NiO-TiO2-N2.

In the process of photocatalytic H2O splitting in the sacrificial system, H2O was mainly adsorbed onto the surface oxygen vacancy of TiO2.66-68 Since these vacancies can also trap the photoinduced electrons during the irradiation (see the distinct PL hump in the range 480 to 580 nm in **Fig. 7b**), these sites were most likely to have been active sites for the reaction of adsorbed H2O and electrons that hence profoundly improved the photocatalytic activity of sc-NiO-TiO2-N2 catalyst (see **Fig. 4** for activity measurements). Moreover, the oxygen vacancies on the surface of TiO2 could effectively promote the separation of electrons and holes under irradiation, which further improved the photocatalytic activity of the hybrid.69 In addition, the presence of NiO, particularly the presence of some metallic Ni0, would be expected to facilitate electron transfer during irradiation,66, 67, 70 which also acted as active sites for hydrogen evolution and contribute to the enhanced photocatalytic activity of the most active sc-NiO-TiO2-N2 catalyst.

Conclusions

In this article, we demonstrated that a combination of nanoparticles made using a continuous hydrothermal process followed by heat-treatment in nitrogen, which facilitated the production of highly defective and stable nanocomposite NiO-TiO2 heterojunction photocatalysts for hydrogen evolution (in a sacrificial system). During thermal processing in nitrogen, it was suggested that the nano-NiO particles acted as a thermocatalyst to deeply oxidize the residual organic groups on the surface of TiO2, leading to the formation of extensive oxygen vacancies at the surface. The generated surface oxygen vacancies were found to act as active sites for the reaction between adsorbed H2O and photoinduced trapped electrons. This led to remarkable photocatalytic performance for the highly defective heterojunction catalyst assigned as sc-NiO-TiO2-N2. The hydrogen evolution rate for this catalyst in a sacrificial system was ca. 1.41 mmol/g/h and the 5 h total hydrogen evolution was ca. 7.00 mmol/g, which was much higher than comparable catalysts reported in the literature (that generally display hydrogen evolution rates < 0.4 mmol/g/h). In closing, we conclude that the generic thermocatalytic oxidative approach used herein to create oxygen vacancies could also extend to produce other types of defective catalysts for other (non-solar) applications, e.g. CO oxidation, combustion of volatile organic compounds (VOCs), steam reforming, etc. We are currently exploring such ideas and will report the outputs of these endeavors in due course.

Conflicts of interest

There are no conflicts to declare

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