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Isoelectric Point-Controlled Preferential Photodeposition of Platinum on Cu$_2$O-TiO$_2$ Composite Surfaces

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ABSTRACT

Photocatalytic water splitting has been extensively studied as an ideal method to produce hydrogen since the report of the Honda-Fujishima effect of water splitting using a TiO$_2$ electrode [1]. It consists of photoexcitation of semiconductor photocatalyst to generate electrons and holes in the bulk, transfer of photoexcited carriers from the bulk to the surface, and photoexcited carriers-participated water reduction to H$_2$ and photoexcited holes-participated water oxidation to O$_2$ on the surface [2-4]. Among various semiconductor photocatalysts for photocatalytic water splitting, TiO$_2$ is considered as a potential commercial photocatalyst due to the favorable electronic band structure and high photo-chemical stability [5-7]. However, TiO$_2$ photocatalyst suffers from the wide band gap of around 3.2 eV [8-10] and rapid recombination of photoexcited electron-hole pairs [5,6]. Great effort has been thus devoted to suppressing the recombination of photoexcited electron-hole pairs to increase the efficiency of TiO$_2$ in photocatalytic water splitting, and the co-catalyst strategy is very effective. Noble metals (Pt, Pd, Au and Ag) and transitional metal oxides have been demonstrated as efficient co-catalysts for TiO$_2$ to suppress the charge recombination via the transfer of photoexcited electrons and holes from TiO$_2$ to the co-catalyst, respectively [11-20]. Recently space-separated noble metal and transitional metal oxide co-catalysts have been successfully loaded on TiO$_2$ to allow simultaneous transfer of photoexcited electrons and holes from TiO$_2$ respectively to the noble metal and transitional metal oxide co-catalysts [11-13].

Utilizing photoexcited electrons to reduce metal cations, photodeposition emerges as a convenient method to load metal particles on semiconductors [21-28]. Photodeposition was also successfully used for a simultaneous loading of Au and CoO$_2$ respectively on electron-enriched [010] face and hole-enriched [110] face of BiVO$_4$ nanocrystals [11]. However, there are few works reported on photodeposition of metal particles on oxide composite surfaces. Cu$_2$O acts as a nice hole-scavenger co-catalyst for TiO$_2$ [29-31]. In this letter, we report the structures and photocatalytic performances in water reduction of Pt/Cu$_2$O-TiO$_2$ composite photocatalysts prepared by photodeposition of Pt particles on Cu$_2$O-TiO$_2$ composite surfaces. The results reveal an interesting isolectric point-controlled preferential adsorption and photodeposition of Pt species on Cu$_2$O-TiO$_2$ composite surfaces.

Experimental details are described in the Supporting Information. Pt with loadings of about 0.5% was photodeposited on TiO$_2$ and Cu$_2$O-TiO$_2$ composites employing H$_2$PtCl$_6$ aqueous solutions as the Pt precursor. Under the photodeposition process, Pt metal particles are facilely photodeposited on TiO$_2$ support; on Cu$_2$O-TiO$_2$ composite supports, the Cu$_2$O surface is positively charged and enriched with photo-excited holes while the TiO$_2$ surface is negatively charged and enriched with photo-excited electrons. This lead to the preferential adsorption of PtCl$_6^{2-}$ anion precursor on the Cu$_2$O surface of Cu$_2$O-TiO$_2$ composite and the dominant formation of Pt oxide particles on Cu$_2$O surface but few Pt metal particles on TiO$_2$ surface. Consequently, the activity of resulting Pt/Cu$_2$O-TiO$_2$ composite photocatalysts in photocatalytic water reduction decreases as the Cu$_2$O content increases. These results deepen the understanding of photodeposition processes on oxide composite surfaces.
condition, the pH values of the solutions were measured to be 3.6. Table 1 summarizes compositions and BET specific surface areas of various photocatalysts. Both Pt loadings and BET specific surface areas are similar for all photocatalysts. Fig.1 shows photocatalytic H$_2$ productions as a function of reaction time of various photocatalysts in photocatalytic water reduction illuminated with simulated solar light. It can be seen that the photocatalytic H$_2$ production increases linearly with the reaction time for various photocatalysts, indicating the stability of these photocatalysts. The calculated mass-specific photocatalytic H$_2$ production rates of all photocatalysts are summarized in Table 1. 0.5%Pt/TiO$_2$ exhibits a H$_2$ production rate of 4.8 mmol·g$^{-1}$·h$^{-1}$, but the H$_2$ production rate of Pt-Cu$_2$O-TiO$_2$ composite photocatalysts keeps decreasing with the loading of Cu$_2$O. These results suggest that the Pt and Cu$_2$O species in Pt/Cu$_2$O-TiO$_2$ composite photocatalysts exert a negative effect, instead of a synergistic effect, on promoting the photocatalytic performance of TiO$_2$.

Table 1 Compositions, BET specific surface areas and mass-photocatalytic H$_2$ productions of various photocatalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cu loading (wt%)</th>
<th>Pt loading (wt%)</th>
<th>BET (m$^2$/g)</th>
<th>H$_2$ Production (mmol·g$^{-1}$·h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%Pt/TiO$_2$</td>
<td>0.59</td>
<td>76.2</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>Pt/0.005%Cu$_2$O-TiO$_2$</td>
<td>0.01</td>
<td>0.49</td>
<td>69.8</td>
<td>3.9</td>
</tr>
<tr>
<td>Pt/0.05%Cu$_2$O-TiO$_2$</td>
<td>0.07</td>
<td>0.42</td>
<td>70.1</td>
<td>3.2</td>
</tr>
<tr>
<td>Pt/0.5%Cu$_2$O-TiO$_2$</td>
<td>0.70</td>
<td>0.50</td>
<td>77.7</td>
<td>1.6</td>
</tr>
<tr>
<td>Pt/1%Cu$_2$O-TiO$_2$</td>
<td>1.26</td>
<td>0.50</td>
<td>72.5</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Fig. 1. Photocatalytic H$_2$ production as a function of reaction time of various Pt/Cu$_2$O-TiO$_2$ under simulated solar light irradiation.

Fig. 2A shows XRD patterns of various photocatalysts, in which all observed diffraction patterns could be indexed to anatase TiO$_2$ (JCPDS card: 21-1272). No peaks associated with Cu or Pt species could be identified. This may be due to the fine dispersions of copper and platinum species on TiO$_2$ and/or the low loadings of copper and platinum in all photocatalysts. Surface structures of all photocatalysts were characterized with XPS. As shown in Fig. S1, all Pt/Cu$_2$O-TiO$_2$ composite photocatalysts exhibit the same Ti 2p$_{3/2}$ binding energy at 458.8 eV and Cu 2p$_{3/2}$ binding energy at 952.4 eV that respectively correspond to TiO$_2$ and Cu$_2$O [30]. However, they exhibit Cu$_2$O loading-dependent Pt 4f XPS features (Fig. 2B). A peak at around 75.6 eV corresponds to an energy loss peak of TiO$_2$, and other peaks at 70.9/74.3, 72.8/76.1, and 74.2/77.5 eV can be assigned to the 4f$_{7/2}$/4f$_{5/2}$ components of metallic Pt, Pt$^{2+}$, and Pt$^{4+}$ species, respectively [32-34]. Fig. 2C shows the Pt species in various photocatalysts. 0.5%Pt/TiO$_2$ exhibits dominant metallic Pt species with minor Pt$^{4+}$ species. With the Cu$_2$O loading of Pt/Cu$_2$O-TiO$_2$ increasing, the metallic Pt species decreases and could not be observed in Pt/1%Cu$_2$O-TiO$_2$; the Pt$^{2+}$ species increases, reaches the maximum in Pt/0.5%Cu$_2$O-TiO$_2$; and then slightly decreases in Pt/1%Cu$_2$O-TiO$_2$; and the Pt$^{4+}$ species emerges in Pt/1%Cu$_2$O-TiO$_2$. These XPS results demonstrate that the Pt species changes from the metallic Pt to the Pt cations in our Pt/Cu$_2$O-TiO$_2$ photocatalysts prepared by photodeposition as the Cu$_2$O loading increases.

Fig. 2B. (A) Pt 4f XPS spectra with peak-fitting results, and (C) calculated Pt speciation of (a) 0.5%Pt/TiO$_2$, (b) Pt/0.005%Cu$_2$O-TiO$_2$, (c) Pt/0.05%Cu$_2$O-TiO$_2$, (d) Pt/0.5%Cu$_2$O-TiO$_2$ and (e) Pt/1%Cu$_2$O-TiO$_2$ photocatalysts. The red line in Fig. 2A represents the standard XRD pattern of anatase TiO$_2$ (JCPDS Card No. 21-1272). The scatter points and solid lines in Fig. 2B respectively represent the original XPS spectra and peak-fitted XPS spectra.

Representative TEM and HRTEM images of Pt/TiO$_2$ and Pt/Cu$_2$O-TiO$_2$ photocatalysts are shown in Fig. 3, Fig. S2 and Fig. S3. The identified lattice spacings of 0.35, 0.21, 0.23, 0.26 and 0.22 nm arise from TiO$_2$(111), Cu$_2$O(200), Pt(111), PtO(101) and PtO$_2$(011), respectively [29,30,35,36]. Fig. S3 gives Pt-transformed patterns of TRTEM images of individual particles to distinguish nanoparticles with similar observed lattice spacings. As reported in our previous paper [29], TiO$_2$ exhibits a rod shape, and Cu$_2$O forms a thin film on TiO$_2$ in Cu$_2$O-TiO$_2$ composites up to 1%Cu$_2$O-TiO$_2$, forming TiO$_2$(core)/Cu$_2$O(thin film shell) rod structures in which the Cu$_2$O shell thickness increases with the Cu$_2$O loading. Pt/TiO$_2$ and Pt/Cu$_2$O-TiO$_2$ photocatalysts remain rod shapes, and Cu$_2$O exists as thin layers on TiO$_2$ in all Pt/Cu$_2$O-TiO$_2$ photocatalysts, but exposed TiO$_2$ surfaces are always present. This is also confirmed by the DRIFTS results of CO adsorption on Pt/Cu$_2$O-TiO$_2$ photocatalysts (Fig. S4) in which the vibrational band of CO adsorption at Ti(IV) sites is observed for Pt/Cu$_2$O-TiO$_2$ photocatalysts [37]. Thus the original TiO$_2$(core)/Cu$_2$O(thin film shell) rod structures of Cu$_2$O-TiO$_2$ composites get destroyed after the photodeposition processes in H$_2$PtCl$_6$ aqueous solutions.

Metallic Pt nanoparticles of 2-3 nm can be easily identified in Pt/TiO$_2$, Pt/0.005%Cu$_2$O-TiO$_2$ and Pt/0.05%Cu$_2$O-TiO$_2$ but few PtO nanoparticles is found although the XPS results suggest the presence of minor PtO species. This could be attributed to the generally much higher dispersion of Pt oxides than Pt metal supported on oxide surfaces. In Pt/0.5%Cu$_2$O-TiO$_2$ and Pt/1%Cu$_2$O-TiO$_2$ photocatalysts with Pt oxides as the dominant Pt species, PtO and PtO$_2$ nanoparticles of 3-4 nm are easily observed but Pt nanoparticles can only be occasionally found. It is found that the Pt species supported on TiO$_2$ are always metallic Pt nanoparticles while those supported on Cu$_2$O include metallic Pt nanoparticles in Pt/0.005%Cu$_2$O-TiO$_2$ and Pt/0.05%Cu$_2$O-TiO$_2$ but then are exclusively PtO and PtO$_2$ nanoparticles in Pt/0.5%Cu$_2$O-TiO$_2$ and Pt/1%Cu$_2$O-TiO$_2$. Meanwhile, much more Pt species are photodeposited on the Cu$_2$O surface of Cu$_2$O-TiO$_2$ composites than on the TiO$_2$ surface. This agrees with the XPS results of dominant Pt oxides species since the photodeposited Pt species on TiO$_2$ is mainly metallic Pt nanoparticles.

The above spectroscopic and microscopic characterization results demonstrate that the presence of Cu$_2$O layers on TiO$_2$ strongly affects the photodeposition processes of Pt. The photodeposited Pt species is preferentially formed on the Cu$_2$O
surface, and changes from metallic Pt nanoparticles to PtO and PtO2 nanoparticles as the CuO layers thicken. It is reasonable that the synthesized Pt/CuO-TiO2 photocatalysts with dominant PtO and PtO2 nanoparticles on CuO surface and few Pt nanoparticles on TiO2 surface are less active than the synthesized Pt/TiO2 catalyst with Pt nanoparticles in photocatalytic water reduction, as experimentally observed.

During the photodeposition process, the [PtCl6]4− precursor needs to adsorb on the oxide surface prior its photoreduction. Depending on its isoelectric point and the pH value of aqueous solution, an oxide surface in the aqueous solution is negatively, neutrally, or positively charged. We measured Zeta potentials of TiO2, CuO, and various CuO/TiO2 composites as a function of pH values (Fig. 4), from which the isoelectric point of TiO2, 0.005%CuO/TiO2, 0.05%CuO/TiO2, 0.5%CuO/TiO2, 1%CuO/TiO2 and commercial CuO is determined as 3.1, 4.8, 5.3, 5.8, 7.1 and 10.2, respectively. The pH value of employed H2[PtCl6] aqueous solution is measured to be 3.6, thus the TiO2 surface of CuO-TiO2 composites is locally negatively charged while the CuO surface is locally strongly positively charged.

Based on these observations, we proposed a photodeposition mechanism of Pt on CuO-TiO2 composites (Fig. 5). Under the employed photodeposition conditions, the negatively-charged [PtCl6]4− precursor adsorb majorly on the strongly positively-charged CuO surface of CuO-TiO2 composites but minorly on the negatively-charged TiO2 surface, resulting in the preferential adsorption of [PtCl6]4− precursor on CuO surface of CuO-TiO2 composites. Illuminated with light, both CuO and anatase TiO2 are photoexcited to produce the electron-hole carriers, and the excited electrons in the conduction band of CuO tend to transfer to the conduction band of TiO2 at the CuO-TiO2 junction interface while the excited holes in the valence band of TiO2 tend to transfer to the valence band of CuO. This leads to electron-rich TiO2 and hole-rich CuO in CuO-TiO2 composites. Thus, the [PtCl6]4− species on electron-rich TiO2 surface can be facilely reduced to form metallic Pt nanoparticles while those on hole-rich CuO surface cannot be adequately reduced and tend to form PtO nanoparticles and even PtO2 nanoparticles. The reduction extent of [PtCl6]4− species on CuO surface decreases as its thickness on TiO2 increases. Thus, oxide isoelectric point plays an important role in the photodeposition of Pt on CuO-TiO2 composite surfaces via preferential adsorption of [PtCl6]4− precursor. These reveal the important role of surface chemistry in photo-induced chemical processes on solid surfaces [38].
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Supplementary material

Experimental section, Fig. S1, Fig. S2, Fig. S3 and Fig. S4.

Reference