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Water photoreduction with Cu_2O quantum dots on TiO_2 nano-particles

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Abstract

Photocatalyst TiO_2/Cu_2O made by depositing Cu_2O quantum dots on TiO_2 nano-particles, photoreduces water under sacrificial conditions as a result of efficient separation of electrons and holes into TiO_2 and Cu_2O, respectively. Although oxidations take place at Cu_2O sites, these quantum dots remained stable towards oxidation.

Keywords: Water; Photoreduction; Nano-particles

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1. Introduction

Semiconductor particles loaded with fine islets of metals or other semiconductors continue to attract much attention as photocatalysts [1–5]. The catalyst TiO_2/Pt prepared by deposition of fine specks of platinum on the surface of TiO_2 particles greatly promotes photoreduction of water under sacrificial conditions. Band gap light falling on TiO_2 generate electron–hole pairs and Pt specks act as sinks for the electrons. Rapid transfer of electrons to Pt suppresses electron–hole recombination. Islets of Pt could also electrocatalyse hydrogen liberation in water reduction. Again, when two semiconductor particles are in contact, energetically favorable interband electron transfer leads to separation of charges thereby delaying the recombination. More recently interface controlled nucleation and growth of semiconductor nanostructures and their quantum size effects and confinement have attracted much attention [6]. These structures could also have profound implications on design of advanced catalytic systems. We deposited quantum sized Cu_2O on TiO_2 nano-particles to produce the catalyst TiO_2/Cu_2O and found that this composite system photogenerate hydrogen from water under sacrificial conditions. Unlike in the TiO_2/Pt system, there is good evidence that in TiO_2/Cu_2O the TiO_2 surface acts as the reduction site. On illumination of TiO_2/Cu_2O with TiO_2 (Cu_2O) band gap light, the holes (electrons) transfer to Cu_2O (TiO_2) sites while the electrons (holes) accumulate in TiO_2 (Cu_2O). The activity of the catalyst depends on inter-particle charge transfer that suppresses recombination.

2. Experimental

A colloidal solution of Cu_2O consisting of quantum-sized particles was prepared by the following method. Copper(I) iodide (6 mg) was digested with few drops of diethyl sulfide to dissolve it completely and diluted with methanol to 25 ml. Solution was kept purged with nitrogen adding 0.01 M NaOH dropwise to reach a pH ∼9. The resulting transparent yellowish green colloidal solution of Cu_2O coagulates on further addition of NaOH enabling separation by centrifugation. Separated gel was repeatedly washed with 75% methanol and again dispersed in methanol by sonication. The composite catalyst TiO_2/Cu_2O was prepared by the following procedure. Degussa P25 TiO_2 (60 mg) was dispersed in deoxygenated water (35 ml) by sonication and mixed with the Cu_2O colloidal solution (5 ml) by purging nitrogen. The resulting

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dispersion of TiO_2/Cu_2O in aqueous methanol (12.5% volume) was magnetically stirred and irradiated with a xenon lamp at intensity $750\,Wm^{-2}$ using a Tabletop Sunset Exposure System. A filter was used to cut-off wavelengths <300 nm. Hydrogen evolution was monitored by gas chromatography. In some experiments TiO_2 was mixed with the transparent Cu_2O colloidal solution produced in the first step and after sonication the catalyst separated by centrifugation was dispersed in the methanol solution. The main reaction product detected the in solution phase after few hours irradiation (Sunset Xenon Lamp) was formaldehyde. On prolonged irradiation, formic acid (in solution phase) and carbon dioxide (in gaseous phase) were also detected. When a tungsten filament lamp or a xenon lamp with a cut-off filter ($\lambda < 400$ nm) was used, formaldehyde was again detected.

3. Results and discussion

Diethyl sulfide reacts with CuI to form a Cu(I) complex soluble in methanol. Hydrolysis of the solution of the complex with NaOH yields colloidal Cu_2O. Diethyl sulfide molecules liberated in the reaction anchors to Cu_2O surface (S to Cu) arresting crystal growth. The absorption in the pale yellow colloidal solution is blue-shifted with respect that of larger particles (Fig. 1, inset) owing to the quantum size effect and suggest a crystallite of 2–3 nm corresponding to a band gap ∼2.4 eV compared to 2.1 eV for the bulk material [7]. On mixing TiO_2 powder with the colloidal solution, Cu_2O crystallites adhere to the TiO_2 surface. Fig. 2 shows a plot of the volume of H_2 evolved versus time on irradiation of deoxygenated suspension of TiO_2/Cu_2O. In the above experiment Cu_2O loading (1 wt.% TiO_2) corresponded to the optimum activity. The catalyst shows sensitivity to light absorbed by TiO_2 as well as Cu_2O. However, when light of wavelengths <400 nm was cut-off using a filter or if a tungsten filament lamp is used instead of a xenon lamp, rate of H_2 evolution ($R[H_2]$) diminished (Fig. 2), as the light absorbing cross-section of Cu_2O happens to be very small compared to that of TiO_2 (TiO_2:Cu_2O surface area ∼0.05).

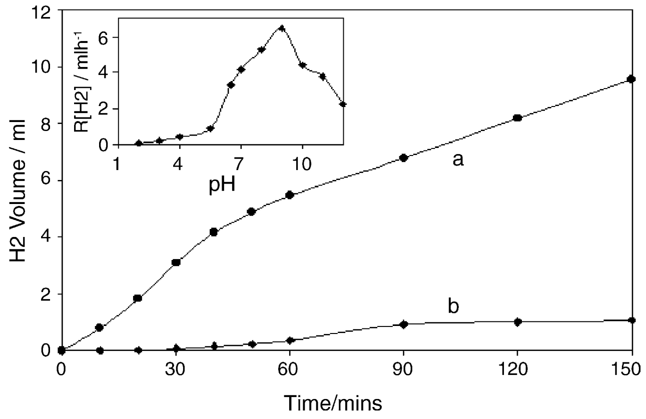

Fig. 2. Plot of volume of H_2 evolved vs. time (60 mg of the catalyst TiO_2/Cu_2O suspended in 40 ml of 12.5% aqueous methanol, Cu_2O loading 1 wt.% of TiO_2); (a) Xe lamp, (b) tungsten lamp. Inset: pH variation of $R[H_2]$ (ml/h).

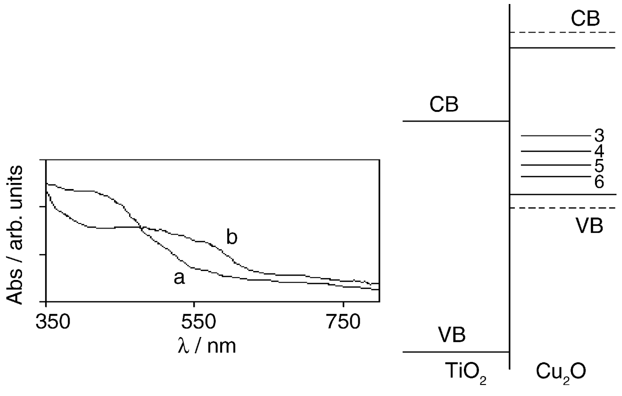

Fig. 1. Schematic diagram showing band positions of TiO_2 and Cu_2O (Cu_2O bulk (solid lines), Cu_2O quantum dot (dotted lines)). Lines marked with numbers corresponds to the redox levels of reactions (3), (5), (4), (6). Inset: absorption spectrum of a (a) colloidal suspension of Cu_2O quantum dots; (b) suspension of larger (∼100 nm) Cu_2O particles.

An energy level diagram showing the positions of the bands of TiO_2 and Cu_2O is presented as Fig. 1. The relative positions of the valence band (VB) edges of Cu_2O and TiO_2 permit transfer of holes created in TiO_2 (by light of frequency ν_1) to Cu_2O. However, positioning of the conduction bands (CBs) does not permit translocation of electrons in TiO_2. We summarize the hydrogen evolution reaction as follows:

$$h\nu_1 + TiO_2 \rightarrow e^-(CBTiO_2) + h^+(VBTiO_2) \rightarrow e^-(CBTiO_2) + h^+(VBCu_2O) \qquad (1)$$

$$h\nu_2 + Cu_2O \rightarrow e^-(CBCu_2O) + h^+(VBCu_2O) \rightarrow e^-(CBTiO_2) + h^+(VBCu_2O) \qquad (2)$$

$$2e^-(CBTiO_2) + 2H_2O \rightarrow H_2 + 2OH^- \qquad (3)$$

$$2h^+(VBCu_2O) + CH_3OH \rightarrow HCHO + 2H^+ \qquad (4)$$

The band edge positions of Cu_2O (Fig. 1) permit reduction and oxidation of Cu_2O via following reactions:

$$Cu_2O + H_2O + 2e^- \rightarrow 2Cu + 2OH^- \qquad (5)$$

$$Cu_2O + H_2O + 2h^+ \rightarrow 2CuO + 2H^+ \qquad (6)$$

When band gap light (frequency $\nu_{2)}$ falls on Cu_2O, electrons generated will move to TiO_2 and therefore reduction of Cu_2O [reaction (5)] will not take place. Fast hole consumption via (4) will suppress (6). The other factor that needs to be considered is the dependence of the band positions with the crystallite size. As the Cu_2O crystallite size decreases conduction and valence band edges move upwards and downward, respectively [8] (Fig. 1). An upward shift in the CB position of Cu_2O will favor electron transfer to TiO_2 suppressing (5). Again a downward shift in the VB edge will facilitate hole-consuming reactions.

During irradiation the catalyst developed a bluish hue. This coloration bleached on exposure to atmospheric oxygen indicating that a reductive process imparted the color. If the suspension irradiated for 1 h is purged with N_2 and irradiated again, the rate of H_2 evolution ($R[H_2]$) reduced slightly. However, suspensions decolorized by exposure to O_2 retained the same activity and readily detectable decrease in $R[H_2]$ became noticeable on continuing irradiation for 2–3 h. We attribute this change in $R[H_2]$ accumulation of reaction products. Irradiation of deoxygenated suspension of TiO_2 in a reducing environment imparts a blue color to TiO_2, which has been understood as originating from the electron accumulation and formation reduced species in bulk and/or surface of TiO_2. In TiO_2/Cu_2O under identical conditions the blue color developed more intensely and rapidly. Furthermore in TiO_2/Pt, blue color development is absent or much less pronounced compared to pure TiO_2. Here, as the electrons rapidly transfer to Pt islets without accumulating in TiO_2 the color development is not observed. Therefore, we confirm that in TiO_2/Cu_2O, holes created in TiO_2 moves to Cu_2O islets leaving electrons in TiO_2. Thus, in the catalyst TiO_2/Cu_2O, reduction site has to be TiO_2 in contrast to TiO_2/Pt where it is the oxidation site. Both TiO_2/Pt and TiO_2/Cu_2O are more efficient than TiO_2 alone because in these systems interparticle charge transfer suppress recombination. However, oxidation and reduction sites are opposite in the two cases. Further evidence for the above conclusion follows from pH variation of the ($R[H_2]$). Fig. 2 inset shows the variation of $R[H_2]$ with pH for TiO_2/Cu_2O (Cu_2O loading 1 wt.% TiO_2) under experimental conditions described previously. Optimum rate occurs at a pH of about 9 and rapidly decreases when the pH is raised. The rapid drop in $R[H_2]$ at lower pHs seems originate from dissolution of Cu_2O under acidic conditions. Situation with respect to TiO_2/Pt is different. Here, a lowering of $R[H_2]$ at higher pHs is not seen. The pH dependence of $R[H_2]$ in sacrificial water photoreduction of water depends on many factors. Higher pHs promote the association of OH^- ions with the TiO_2 surface thereby increasing the rate of oxidation of the sacrificial agent, which is the rate determining step. Thus, in TiO_2/Pt a higher pH favors the oxidation reaction as holes accumulate in TiO_2. Whereas in TiO_2/Cu_2O water reduction takes place at the TiO_2 surface and a low pH favors interaction of H^+ ions with the TiO_2 surface.

When the Cu_2O loading in the catalyst is well above the optimum, the suspension acquires a deeper bluish-violet color on irradiation for about 1 h. Here again the oxidizing agents bleaches the color but cyanide (which dissolves Cu and Cu oxides) turns it pale blue, the characteristic of reduced TiO_2. The absorption spectrum shows a peak around 550 nm, which is a signal of plasmon absorption in fine particles of Cu [9]. Presumably, when the TiO_2 is over crowded with Cu_2O crystallites, some of it get reduced. The chemically reactive intermediates formed on the TiO_2 surface may be mobile [10]. Although oxidations and reductions occur at different points on the catalyst particle; species formed by electron acceptance could migrate towards Cu_2O islets. If the coverage of Cu_2O on the TiO_2 surface can be increased, the catalyst would become more responsive to wavelengths absorbed by Cu_2O. Unfortunately because of the above constraint, the optimum activity occurs at low coverage Cu_2O. Liberation of detectable quantities of H_2 and O_2 in photolysis and mechanical agitation of aqueous suspensions of Cu_2O powder has been reported [11,12] however; we did not see a signal for H_2 or O_2 on irradiation TiO_2/Cu_2O suspensions in water. Furthermore, the wok of Sakata et al. [13] confirms some of our observations. They have observed that copper ion containing TiO_2, photogenerate H_2 from methanolic solution after an induction period when illuminated with visible light. The result was attributed to formation Cu_2O on the TiO_2 surface. It is amazing, why H_2 did not evolve via sacrificial oxidation of Cu_2O to CuO (process thermodynamically allowed). Plausible explanation is passivation of the Cu_2O surface by a thin layer of CuO preventing further oxidation. This also explains the stability of the catalyst TiO_2/Cu_2O against oxidation. Reports in literature have also suggested that, Cu_2O quantum dots are stabilized by a passivating thin film of CuO [7].

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