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Simultaneous copper ion removal and hydrogen production from water over a TiO₂ nanotube photocatalyst

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ABSTRACT

A one-dimensional (1-D) mesoporous TiO₂ nanotube (TiNT) was successfully synthesized via a hydrothermal-calcination process, and employed in simultaneous photocatalytic Cu²⁺ removal and H₂ production. Under irradiation, Cu²⁺ in the wide concentration range of 8–800 ppm, could be reduced rapidly, and the reduction was not severely impacted by co-existing inorganic ions in solution. Simultaneous with Cu²⁺ reduction, noticeable H₂ was produced over the in-situ fabricated Cu incorporated TiNT (Cu–TiNT) photocatalyst, while H₂ evolution rate was controlled by the Cu²⁺ reduction process, due to competition of electron capture between protons and Cu²⁺. In addition, H₂ generation activity of Cu–TiNT depended on the initial Cu²⁺/Ti ratio, and could be depressed by coexisting ions in solution. Fast Cu²⁺ reduction and remarkable H₂ evolution confirmed the feasibility of simultaneous Cu²⁺ removal and H₂ production over a TiNT photocatalyst.

Keywords: copper ion removal; hydrogen production; TiO₂ nanotube

INTRODUCTION

Copper is widely used in the electrical industry, for transportation, and in industrial machinery and military supplies, and this use leads to fast depletion of limited Cu reserves and severe contamination in industrial wastewater (Foster *et al.* 1993). According to USEPA

recommendations, the maximum contaminant level of Cu^{2+} is 1.3 mg L^{-1} , and exposure to excess Cu^{2+} may cause gastrointestinal disturbance, and liver or kidney damage. Thus, waste metal recovery from wastewater can contribute to both resource conservation and metal pollution prevention. Common methods for Cu recovery from the liquid phase are chemical or electrolytical precipitation, ion exchange, activated carbon adsorption, and membrane separation, but they have proven to be costly or not applicable to low concentration conditions (Troupis *et al.* 2002). Recently, photocatalytic reduction of Cu^{2+} by TiO_2 under illumination has been investigated (Yamazaki *et al.* 2001; Barakat *et al.* 2004; Vinu & Madras 2008), and has proved to be cost effective and efficient over a relatively large Cu^{2+} concentration range. Moreover, this method also finds an application in the preparation of Cu deposited TiO_2 photocatalyst, which could be active in photocatalytic reactions.

Photocatalytic water splitting has been considered as one of the most promising approaches for renewable H_2 production, ever since the discovery of photoelectrochemical water splitting at a TiO_2 electrode by Fujishima and Honda (Fujishima & Honda 1972). However, the H_2 generation rate over bare TiO_2 is low, mainly due to the fast recombination of electron/hole pairs (Ni *et al.* 2007). Recently, Cu incorporated TiO_2 (Cu- TiO_2) was proved to be cost effective and to possess excellent H_2 generation activity under sacrificial conditions (Bandara *et al.* 2005; Sreethawong & Yoshikawa 2005; Choi & Kang 2007; Xu & Sun 2009), and various methods, including in-situ photo-deposition, were able to produce efficient Cu- TiO_2 (Xu *et al.* 2010). This situation ensures the potential for simultaneous Cu^{2+} reduction and H_2 production; however, no information about this aspect could be found in the available literature to date.

The one-dimensional TiO_2 nanotube has attracted considerable attention due to its large specific surface area, mesoporous structure, and efficient electron conductivity (Bavykin & Walsh 2009). In this study, highly efficient TiNT was fabricated by a hydrothermal-calcination process, and was employed in a photocatalytic reaction to evaluate simultaneous Cu^{2+} reduction and H_2 production activity. This study revealed that Cu^{2+} could be reduced readily by TiNT under irradiation, and formed highly active Cu-TiNT photocatalyst for H_2 generation. As Cu^{2+} in industry wastewater is usually found over a wide concentration range, and co-exists with substantial amounts of inorganic ions, the effect of initial Cu^{2+} concentration and co-existing ions on simultaneous Cu^{2+} reduction and H_2 production was also investigated in this study.

MATERIALS AND METHODS

Materials

Degussa P25 (Germany) was utilized as a precursor in the preparation of TiNT. It is a mixture of 80% anatase and 20% rutile, with a BET surface area of $50 \text{ m}^2 \text{ g}^{-1}$ and an average particle size of 30 nm, according to the manufacturer's specifications. NaOH (AR), HCl (AR), $\text{Cu}(\text{NO}_3)_2$ (GR), CuCl_2 (GR), CuSO_4 (GR), NaNO_3 (GR), $\text{Ca}(\text{NO}_3)_2$ (GR), and $\text{Al}(\text{NO}_3)_3$ (GR) were purchased from Merck, and used without further purification. Methanol (HPLC) was obtained from Fisher. De-ionized water was produced by a Milli-Q system and used systematically

Synthesis and characterization of TiNT

TiNT was fabricated by a typical hydrothermal method followed by the calcination process. P25 powder was added to 10 mol L^{-1} NaOH aqueous solution, followed by an ultrasonic process and thorough mixing. The homogeneous suspension was then hydrothermally treated in a Teflon-lined autoclave at 150°C for 48 h. The obtained precipitate was first washed with de-ionized water, and then dispersed under continuous stirring into 0.1 mol L^{-1} HCl for 24 h. The acid treatment was repeated three times, and the product was washed thoroughly with de-ionized water until the resulting pH was neutral. After drying in a freeze dryer, the product was calcined at 400°C to obtain the final TiNT photocatalyst.

An X-ray diffraction (XRD) pattern of the fabricated TiNT was obtained using a Bruker D8 Advance X-ray diffractometer with monochromated high-intensity Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Element compositions of photocatalyst were detected using an energy dispersive X-ray spectrometer (EDS) attached to a scanning electron microscope (Jeol JSM-6360). Sample microstructure was observed by a high-resolution transmission electron microscope (HRTEM, Jeol JEM-2010) at 200 kV. BET surface area and pore size distribution were determined using a Micromeritics ASAP 2010 system. The diffuse-reflectance spectrum was recorded by a Thermo Scientific Evolution 300 UV–visible spectrophotometer, equipped with an integration sphere.

Photocatalytic reaction

The photocatalytic reaction was performed in an inner-irradiation type Pyrex reactor (volume:

270 ml) with a 400 W high pressure Hg lamp (Riko, UVL-400HA) as the light source. The peak wavelength of the Hg lamp is centred at 365 nm. To maintain a constant reactor temperature of 25 °C, a quartz water jacket, which was cooled by recycled water, was utilized to cover the lamp. TiNT was first dispersed in 10 volume % methanol water mixture at a concentration of 1 g L⁻¹; the Cu precursor was then dissolved into the above suspension with certain concentration to control the Cu/Ti atom ratio. A magnetic stirrer was placed at the bottom of the reactor to homogeneously churn the suspension during the reaction. Prior to irradiation, the photocatalyst suspension was de-aerated thoroughly for 30 min by nitrogen gas purging.

To investigate the applicable concentration range of Cu²⁺ by photocatalytic reduction over TiNT, Cu²⁺ concentrations of 8, 80, 240, 400, 560 and 800 ppm were studied, to control the Cu/Ti atom ratio at 1, 10, 30, 50, 70 and 100%, respectively. The corresponding situations were respectively denoted as Cu/Ti-1%, Cu/Ti-10%, Cu/Ti-30%, Cu/Ti-50%, Cu/Ti-70% and Cu/Ti-100% in the paper.

The effect of co-existing anions (NO₃⁻, Cl⁻ or SO₄²⁻) on Cu²⁺ reduction and H₂ production was studied by employing different Cu²⁺ precursors (Cu(NO₃)₂, CuCl₂, or CuSO₄); the effect of cations (Na⁺, Ca²⁺ or Al³⁺) was evaluated by adding NaNO₃, Ca(NO₃)₂, or Al(NO₃)₃ into the reaction solution before addition of photocatalyst, with Cu(NO₃)₂ as the Cu²⁺ precursor. Amount of cation was determined by equalizing the charges with initial Cu²⁺ in solution.

Cu²⁺ concentration in solution was quantified at the stated time intervals by an inductively coupled plasma emission spectroscope (ICP, Perkin Elmer Optima 2000DV). Gas produced via the photocatalytic reaction was analyzed using an off-line TCD-type gas chromatograph (Agilent 7890A, HP-PLOT MoleSieve/5A). The pH value of the solution was determined by a Horiba F-53 pH meter.

RESULTS AND DISCUSSION

Characterization of TiNT

Characterizations of the fabricated TiNT are summarized in Figure 1. The XRD pattern of TiNT (Figure 1(a)) exhibited features typical of anatase TiO₂ (JCPDS 21-1272), without peaks associated with other crystal structures. In the EDS spectrum, peaks of C, O, Au and Ti were clearly observed. As C and Au were induced by the carbon tape and gold coating required by the EDS test, the as-prepared sample was expected to contain only O and Ti elements. The HRTEM image of TiNT (Figure 1(b)) revealed that the as-prepared

photocatalyst possessed a multilayered nanotubular structure, and the tubes could be long, up to hundreds of nanometers. The N₂ adsorption/desorption isotherm of the as-prepared TiNT (Figure 1(c)) exhibited a typical type IV curve with a hysteresis loop, indicating the mesoporous structure of the photocatalyst (Gregg & Sing 1982). The mesoporous nanotubular structure endowed the fabricated TiNT with large BET surface areas, 279 m² g⁻¹, which is attractive for photocatalytic reaction. The pore size distribution curve of the fabricated TiNT comprised two distinct portions, with peak values of ca. 2–3 nm and 20–30 nm, respectively; the two portions were assigned to pores inside and between the nanotubes, respectively (Bavykin *et al.* 2004). The UV–visible absorption spectrum of TiNT (Figure 1(d)) exhibited a strong absorption band at around 350 nm, attributed to excitation of electrons in the O 2p orbital to the Ti 3d level. The band gap of TiNT was calculated at 3.25 eV based on the Kubelka–Munk function, where P25 was 3.15 eV under the same conditions. Characterization of TiNT revealed that alkaline hydrothermal treatment followed by the calcination process completely transformed P25 to anatase TiO₂ nanotube, with large BET surface area and excellent UV light absorption ability.

Photocatalytic reactions under different initial Cu²⁺ concentrations

Simultaneous photocatalytic Cu²⁺ reduction and H₂ production were investigated under six initial Cu²⁺ concentrations over TiNT, and the results are summarized in Figure 2.

From Figure 2(a), it can be found that Cu²⁺ could be reduced readily under irradiation over TiNT. In the first 10 min, removal efficiency of Cu²⁺ in Cu/Ti–1%, Cu/Ti–10%, Cu/Ti–30%, Cu/Ti–50%, Cu/Ti–70% and Cu/Ti–100% reached 93, 97, 78, 63, 36 and 22%, respectively. A removal efficiency of 99% in Cu/Ti–70% and Cu/Ti–100% cases could also be achieved within 90 min. XRD, EDS and XPS analyses (data not shown) were carried out on TiNT samples after photocatalytic reaction, and confirmed that the removed Cu was combined with TiNT and removed from the liquid phase. However, it should be mentioned that Cu²⁺ could not be eliminated completely via photocatalytic reaction; minute amounts of Cu²⁺ (0.5–2 ppm) still remained in solution after 4 h reaction; in addition, after major Cu²⁺ was reduced, Cu²⁺ concentration in solution increased slightly with reaction progress. This factor is related to the cyclic redox transformation of Cu during photocatalytic reaction (Xu *et al.* 2010): Cu²⁺ was reduced by electrons to form metallic Cu; Cu metal could be oxidized back to Cu oxide by holes, and dissolved into solution with the help of methanol decomposition by-products, CO₂ and HCOOH, and closed the Cu transformation cycle. This redox deposition–dissolution of Cu proceeded during the entire photocatalytic reaction; nevertheless, the magnitude of the Cu²⁺ concentration remaining in the cycle was

minuscule. Considering the fast elimination rate and broad application concentration range (8–800 ppm in this study), photocatalytic reduction over TiNT still held great potential for Cu^{2+} containing wastewater treatment.

From Figure 2(b), it can be seen that, pure TiNT exhibited negligible H_2 generation activity; nevertheless, with Cu^{2+} reduction, noticeable H_2 was generated over TiNT. Average H_2 evolution rate over 4 h reaction was recorded in the range of $15.7\text{--}40.2 \text{ mmol h}^{-1} \text{ g}_{\text{catalyst}}^{-1}$. Once Cu^{2+} reduction commenced, the deposited Cu species over TiNT served as an electron reservoir, preventing electron-hole recombination in TiO_2 and providing reduction sites for H_2 formation. It was found that H_2 evolution related closely to the Cu^{2+} reduction process, which was clearer in cases with high initial Cu^{2+} concentrations. Taking Cu/Ti– 100% as an example, in the first 120 min, Cu^{2+} reduction was dominant, and captured most of the electrons from TiNT; the corresponding H_2 evolution was slow. After the majority of Cu^{2+} was reduced, the protons began to successfully compete with Cu^{2+} for electrons, and H_2 generation rate ascended and finally stabilized at a relatively high value over mature Cu–TiNT photocatalyst. This is applicable to Cu/Ti–1%, Cu/Ti–10%, Cu/Ti–30%, Cu/Ti–50% and Cu/Ti–70% cases, with difference only in the transformation time. In addition, H_2 generation activity of mature Cu–TiNT photocatalysts depended on the Cu/Ti ratio. Cu/Ti–10% exhibited the greatest activity, followed by 1, 30, 50, 70 and 100%, which is consistent with our previous study (Xu & Sun 2009). Higher Cu/Ti ratio provided more active sites for H_2 formation, but enhanced light blockage to TiNT as well; Cu/Ti ratio at 10% optimized the balance between the two factors, and gave rise to the highest activity.

In comparison with P25 (data shown in inset of Figure 2), TiNT exhibited greater activity in both Cu^{2+} reduction and H_2 generation. The superiority of TiNT was credited to the large BET surface area and unique 1-D tubular structure, whose large surface area provided a more active site for reaction, and the 1-D tubular structure facilitated fast electron transfer and improved charge separation in TiO_2 (Khan & Yang 2009). In addition, Cu–TiNT possessed excellent settling ability. Without agitation, more than 90% of Cu–TiNT could be settled down and separated from solution in 5 min.

Blank experiments without UV light or TiNT were also conducted, and no Cu^{2+} reduction and H_2 production were observed. This indicated that both UV light and TiNT were prerequisites for photocatalytic reactions.

Effect of ions on photocatalytic reactions

Photocatalytic reactions were carried out with various inorganic ions in solution (anions:

NO_3^- , Cl^- or SO_4^{2-} ; cations: Na^+ , Ca^{2+} , or Al^{3+}) to investigate the effect of ions on photocatalytic Cu^{2+} reduction and H_2 production; initial Cu^{2+}/Ti ratio was controlled at 10%. The results are shown in Figure 3.

From Figure 3(a), it can be seen that, Cu^{2+} reduction in the presence of various ions still progressed very fast; reduction efficiency in all cases exceeded 80% in the first 10 min. As a counteranion, NO_3^- was more beneficial for Cu^{2+} reduction, compared with Cl^- and SO_4^{2-} . Maximum Cu^{2+} reduction efficiencies in the presence of NO_3^- , Cl^- and SO_4^{2-} were 99%, 93%, and 97% respectively. Inferiority of Cl^- and SO_4^{2-} might be mainly due to the big pH drop during photocatalytic reaction. After 2 h reaction, solution pH with Cl^- and SO_4^{2-} dropped from 5.4 to 2.9 and 3.2, respectively, which was much lower than the NO_3^- case (4.8). Lower pH facilitated re-dissolution of reduced Cu, and increased Cu^{2+} concentration in the Cu transformation cycle, exhibiting inhibition to Cu^{2+} reduction. In addition, under reaction pH conditions, TiNT was positively charged; Cl^- and SO_4^{2-} could be easily adsorbed on the TiNT surface (stronger than NO_3^-) (Abdullah *et al.* 1990; Wang *et al.* 2004), and methanol was block adsorbed (lone-pair electron donor) (Sreethawong *et al.* 2007). This factor might also limit Cu^{2+} reduction, as methanol adsorption was crucial for scavenging holes in TiO_2 . Conversely additional cations (Na^+ , Ca^{2+} and Al^{3+}), showed no obvious inhibition of Cu^{2+} reduction. This might be due to the more negative redox potential of these cations ($E_{\text{Na}^+/\text{Na}}^\theta = -2.714 \text{ V}$, $E_{\text{Ca}^{2+}/\text{Ca}}^\theta = -2.87 \text{ V}$, $E_{\text{Al}^{3+}/\text{Al}}^\theta = -1.66 \text{ V}$), which could not compete with Cu^{2+} for electrons from TiNT. In addition, cations could not adsorb on to TiNT to restrain holes scavenging, owing to the electrostatic repulsion between cations and the positively charged TiNT.

H_2 production (Figure 3(b)) was obviously influenced by the co-existing ions. H_2 evolution rate dropped when Cl^- or SO_4^{2-} was the counteranion for Cu^{2+} , compared with NO_3^- . SO_4^{2-} adsorbed more strongly on to TiO_2 than Cl^- (Wang *et al.* 2004), and exhibited higher inhibition of H_2 generation. This indicated that the disadvantage of Cl^- and SO_4^{2-} might be mainly due to the depression of holes scavenging, which has been discussed above. Presence of Ca^{2+} or Al^{3+} confined H_2 generation to a certain extent. This might result from coverage of Cu–TiNT by CaCO_3 or $\text{Al}(\text{OH})_3$ precipitate. Methanol decomposition product, CO_2 , was inclined to precipitate Ca^{2+} , under nearly neutral pH conditions in this study; while solution pH in the presence of Al^{3+} increased from 4.3 to 6.9 after 2 h reaction, which promoted hydrolysis of Al^{3+} to produce $\text{Al}(\text{OH})_3$. CaCO_3 and $\text{Al}(\text{OH})_3$ precipitates might aggravate light blockage to TiNT, and limit methanol adsorption over the TiNT surface, leading to depression of H_2 generation activity. It is interesting that the presence of Na^+ promoted H_2

generation. This situation might be credited to electrostatic repulsion between Na^+ and Cu^{2+} on the TiNT surface, which facilitated formation of more highly dispersed Cu species over TiNT, and produced more active Cu–TiNT photocatalyst. For real wastewater, the influence of inorganic components was complicated. Further investigation should be carried out to optimize the reaction conditions for efficient H_2 production.

CONCLUSION

Simultaneous Cu^{2+} removal and H_2 production were proved to be feasible over 1-D TiNT photocatalyst. Under irradiation, Cu^{2+} in a wide concentration range could be reduced rapidly by photo-induced electrons, and deposited on the TiNT surface, serving as an excellent promoter for H_2 production. However, minuscule Cu^{2+} still remained in solution after prolonged reaction, especially when Cl^- or SO_4^{2-} served as counteranion for Cu^{2+} . This situation is caused by redox deposition–dissolution transformation of Cu in photocatalytic reactions. Simultaneous H_2 production over Cu–TiNT was related closely to the Cu^{2+} reduction process: initially, rapid Cu^{2+} reduction limited H_2 generation; while, after major Cu^{2+} it was reduced, H_2 evolution rate ascended and was maintained at a relatively high value. H_2 generation activity of Cu–TiNT depended on the initial Cu^{2+}/Ti ratio as well. In addition, co-existing inorganic ions in solution showed a slight influence on Cu^{2+} reduction, but reduced H_2 evolution to a certain extent.

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- Fig.1 Characterizations of TiNT: (a) XRD pattern (with P25 as comparison) and EDS spectrum (inset); (b) HRTEM images; (c) N₂ adsorption/desorption isotherm and pore volume distribution (BJH desorption); (d) UV–visible absorption spectrum (with P25 as comparison) and corresponding spectra expressed as a Kubelka–Munk function.
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- Fig.3 Effect of ions on Cu²⁺ reduction (a) and H₂ production (b) during photocatalytic reactions over TiNT.

Figure .1

Figure .2

Figure 3