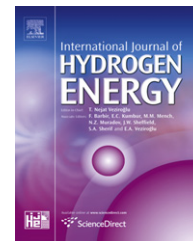


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# Highly efficient TiO<sub>2</sub> nanotube photocatalyst for simultaneous hydrogen production and copper removal from water

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## ABSTRACT

1-D mesoporous TiO<sub>2</sub> nanotube (TNT) with large BET surface area was successfully synthesized by a hydrothermal-calcination process, and employed for simultaneous photocatalytic H<sub>2</sub> production and Cu<sup>2+</sup> removal from water. Cu<sup>2+</sup>, across a wide concentration range of 8–800 ppm, was removed rapidly from water under irradiation. The removed Cu<sup>2+</sup> then combined with TNT to produce efficient Cu incorporated TNT (Cu-TNT) photocatalyst for H<sub>2</sub> production. Average H<sub>2</sub> generation rate recorded across a 4 h reaction was between 15.7 and 40.2 mmol h<sup>-1</sup> g<sup>-1</sup><sub>catalyst</sub>, depending on initial Cu<sup>2+</sup>/Ti ratio in solution, which was optimized at 10 atom%. In addition, reduction process of Cu<sup>2+</sup> was also a critical factor in governing H<sub>2</sub> evolution. In comparison with P25, its large surface area and 1-D tubular structure endowed TNT with higher photocatalytic activity in both Cu<sup>2+</sup> removal and H<sub>2</sub> production.

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## 1. Introduction

Massive global utilization of fossil fuels as energy source has exacerbated worldwide concern on global warming and depletion of natural resources. H<sub>2</sub> has been regarded as an excellent alternative, owing to its high energy content, zero emission of green house gases, and ease of storage and distribution. Currently, majority of H<sub>2</sub> demands are met by steam reforming of natural gases, however this process does not mitigate dependence on fossil fuels, and even produces green house gases. Ever since Fujishima and Honda reported photoelectrochemical water splitting at a TiO<sub>2</sub> electrode, direct photo-splitting of water has been recognized as a promising method for renewable H<sub>2</sub> production [1]. However, H<sub>2</sub> generation efficiency over bare TiO<sub>2</sub> is low, mainly due to the fast recombination of electron/hole pairs [2]. Recently, Cu incorporated TiO<sub>2</sub> (Cu–TiO<sub>2</sub>) was reported to be cost-effective and possess excellent H<sub>2</sub> generation activity under sacrificial conditions [3–9]. Several Cu species (Cu/

Cu<sub>2</sub>O/CuO) have been reported to be active [10–13], and various facile methods, like in-situ photo-deposition, are able to produce efficient Cu–TiO<sub>2</sub> [14], underlining the potential of Cu–TiO<sub>2</sub> in photocatalytic H<sub>2</sub> production.

Cu is widely used in electrical industries, transportation, industrial machinery and military supplies, leading to fast depletion of limited Cu reserves and severe contamination of industrial wastewaters [15]. Thus, waste metal recovery from water can contribute towards resource conservation and mitigation of metal pollution. Common methods employed for Cu recovery today include chemical or electrolytic precipitation, activated carbon adsorption, ion exchange and membrane separation, but they are either too costly or inefficient for low concentration levels [16]. Recently, photocatalytic reduction of Cu<sup>2+</sup> over TiO<sub>2</sub> has been investigated [17–19], and shows lower cost with higher efficiency. Moreover, this method is also applicable in fabrication of Cu deposited TiO<sub>2</sub> photocatalyst, which could potentially be an active photocatalyst for H<sub>2</sub> production. However to date,

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major reports about  $\text{Cu}^{2+}$  reduction over  $\text{TiO}_2$  have merely focused on  $\text{Cu}^{2+}$  removal, and no study about simultaneous  $\text{H}_2$  production with  $\text{Cu}^{2+}$  removal has been reported.

1-D  $\text{TiO}_2$  nanotube has attracted considerable attention since its discovery by Kasuga et al. [20] using a simple hydrothermal treatment of  $\text{TiO}_2$  powder in NaOH aqueous solution. Many efforts have been devoted into understanding the formation mechanism [21], optimizing fabrication conditions [22], and studying the properties of TNT [23]. It is known that TNT possesses large specific surface area, mesoporous structure, and efficient electron conductivity [24]. TNT has exhibited immense potential in a wide variety of applications, ranging from environmental purification [25,26], photocatalysis [27], energy storage [28], and gas sensing [29], however little is known about its performance in photocatalytic  $\text{H}_2$  production. Furthermore, no report about utilization of TNT in simultaneous metal ions removal and  $\text{H}_2$  production could be found in open literature. Herein we report for the first time, an effective  $\text{Cu}^{2+}$  removal and  $\text{H}_2$  production being simultaneously achieved over highly efficient TNT. This may offer a potential and meritorious solution for treatment of metal containing wastewater with concurrent  $\text{H}_2$  production.

In this study, TNT was successfully fabricated by a hydrothermal reaction followed by calcination process, and then employed in photocatalytic reaction to evaluate its performance in simultaneous  $\text{Cu}^{2+}$  removal and  $\text{H}_2$  generation. The experimental results revealed that  $\text{Cu}^{2+}$  can be recovered readily from water by TNT to produce a highly active Cu-TNT photocatalyst for  $\text{H}_2$  production, and  $\text{H}_2$  evolution was largely governed by  $\text{Cu}^{2+}$  reduction process. In addition, initial  $\text{Cu}^{2+}/\text{Ti}$  ratio was proved to be critical in  $\text{H}_2$  production, and its effect was also discussed in this paper.

## 2. Experimental

### 2.1. Synthesis and characterization of TNT

TNT was fabricated via a typical hydrothermal method followed by calcination process. Degussa P25 (Germany) powder was added to 10 M NaOH (Merck, AR) 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 (Milli-Q, ultrapure), and then dispersed under continuous stirring into 0.1 M HCl (Merck, AR) for 24 h. The acid treatment was repeated for 3 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 for 2 h to obtain the final TNT photocatalyst.

X-ray diffraction (XRD) pattern of the fabricated TNT was obtained using a Bruker D8 Advance X-ray diffractometer with monochromated high-intensity  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Element composition of the photocatalyst was analyzed using an energy dispersive X-ray spectrometer (EDS) attached to a scanning electron microscope (Jeol JSM-6360). Sample morphology was studied using a field-emission scanning electron microscope (FESEM, Jeol JSM-6340F), and 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. Diffuse-reflectance spectra were recorded by a Thermo Scientific Evolution 300 UV–visible spectrophotometer, equipped with an integration sphere. X-ray photoelectron spectroscopy (XPS) analysis was carried out in an ultrahigh vacuum chamber with a base pressure below  $2.66 \times 10^{-7} \text{ Pa}$  at room temperature. Photoemission spectra were recorded by a Kratos Axis Ultra spectrometer equipped with standard monochromatic Al  $\text{K}\alpha$  excitation source ( $h\nu = 1486.71 \text{ eV}$ ). All binding energies were referenced to C 1s at 284.8 eV.

### 2.2. Photocatalytic reaction

The photocatalytic reaction was performed in an inner-irradiation type Pyrex reactor (volume: 270 ml) equipped with a 400 W high pressure Hg lamp (Riko, UVL-400HA) as the light source. 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.  $\text{Cu}(\text{NO}_3)_2$  (Merck, GR) was first dissolved in 10 volume% methanol (Fisher, HPLC) water mixture with  $\text{Cu}^{2+}$  concentrations of 8, 80, 400 and 800 ppm, and TNT was then dispersed into the above solution at a dosage of  $1 \text{ g L}^{-1}$ . Cu/Ti atom ratio was controlled at 1%, 10%, 50% and 100%, and the corresponding results were respectively denoted as TNT-1%, TNT-10%, TNT-50% and TNT-100%. A magnetic stirrer was placed at the bottom of the reactor to homogenize the suspension throughout the reaction. Prior to irradiation, the photocatalyst suspension was de-aerated thoroughly for 30 min by nitrogen gas purging.

To investigate the competition of  $\text{Cu}^{2+}$  reduction and effect of re-oxidation of reduced Cu species on  $\text{H}_2$  generation, control experiments were carried out as follows: after normal TNT-10% reaction for 2 h, the fabricated Cu-TNT was collected and washed thoroughly with de-ionized water, and then dispersed in fresh methanol solution with (or without) presence of  $\text{Cu}^{2+}$  ( $\text{Cu}^{2+}/\text{Ti} = 10 \text{ atom\%}$ ) prior to the photocatalytic reactions.

To evaluate the activity of TNT, P25, with an initial  $\text{Cu}^{2+}/\text{Ti}$  ratio of 10%, was chosen as a benchmark, and denoted as P25-10%. Control experiment for  $\text{H}_2$  generation over bare TNT was also conducted without addition of Cu precursor.

$\text{Cu}^{2+}$  concentration in solution was quantified at stated time intervals by an inductively coupled plasma emission spectroscopy (ICP, Perkin Elmer Optima 2000DV). Gas produced via the photocatalytic reaction was analyzed using an off-line TCD-type gas chromatography (Agilent 7890A, HP-PLOT MoleSieve/5A). pH value of the solution was determined by a Horiba F-53 pH meter.

## 3. Results and discussion

### 3.1. Characterization of TNT

XRD pattern and EDS spectrum of the fabricated TNT are shown in Fig. 1. XRD pattern of as-prepared TNT exhibited characteristic features of anatase  $\text{TiO}_2$  (JCPDS 21-1272). No vague peaks associated with other crystal structures were observed. In the EDS spectrum, peaks of C, O, Au and Ti were

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