

Photocatalytic splitting of seawater for hydrogen energy

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Abstract

Photocatalytic splitting of seawater with oxalic acid as sacrificial reagents on CuO/TNT and nanosize TiO₂ have been studied. A better H₂ yield (1.26 μmol/g cat.) from photocatalytic splitting of seawater on CuO/TNT is obtained. An economic consideration for electrical power generation with a H₂-internal combustor fueled with H₂ yielded from photocatalytic splitting of seawater has also been studied. The years of return for the small scale solar-derived power generation system are 3.5.

Keywords: nanosize TiO₂, H₂, seawater.

1 Introduction

Fossil fuels which have been the main energy source have had negative impacts on human health and the environment. Air pollution or global warming has been caused mainly by the combustion of fossil fuels. However, fossil energy is fast depleting. Renewable energy is becoming one of the better alternatives. Since Honda and Fujishima demonstrated electrochemical photolysis of water for generation of H₂ in 1972 [1], photocatalytic splitting of water has become one of the active energy research topics. Many efforts have been devoted to enhance activity of splitting of water by promotion with noble metals [2, 3], modification by metal doping [4–6], or adding electron donors on TiO₂ [7, 8]. Generally, the enhancement of photocatalytic activity may be obtained on high surface area



TiO₂-based photocatalysts. It has been found that TiO₂ nanotubes (TNTs) possess higher surface areas as well as more active sites than the conventional nanosize TiO₂ [9]. For instance, Kasuga *et al.* have indicated that TNTs have a higher surface area (400 m²/g) than nanosize TiO₂ by eight times [10].

Oxalic acid and oxalates are widely used in many sectors such as a purifying agent in the pharmaceutical industry, a precipitating agent in rare-earth metal processing, a bleaching agent in the textile and wood industry, a rust-remover for metal treatment, a grinding agent, and a bleaching agent in the textile industry [11, 12]. Oxalate is a detectable intermediate in the mineralization of many pesticides and other organic compounds. Oxalate can be oxidized directly to CO₂ without formation of any stable intermediate of organic products [13].

Thus, the main objective of this work was to prepare a new TNT photocatalyst for the splitting of seawater to yield H₂. Oxalic acid is used as a model compound for pollutants during photocatalytic splitting of water and seawater. Additionally, the economic consideration for electrical power generation with a H₂-internal combustor fueled with H₂ yielded from photocatalytic splitting of seawater has also been studied.

2 Material and methods

2.1 Preparation of copper oxide supported on TNTs

The copper oxide supported TNTs (CuO/TNTs) photocatalysts were prepared by impregnation of Cu(NO₃)₂·3H₂O on nanosize TiO₂. Two grams of the nanosize TiO₂ (P25) (UR, ITIT001) containing 80% of anatase and 20% of rutile were suspended in a solution containing 5% of Cu(NO₃)₂·3H₂O (Merck, 99.5%) under an ultrasonic stirring. About 80 mL of NaOH (10 M) (Mallinckrodt Chemicals, 98%) were well mixed with the slurry for the hydrothermal treatment at 383 K for 24 hours. The pH value of the hydrothermal product was adjusted to 2.0 with a diluted HCl (Sigma-Aldrich, 37%), and was subsequently washed with distilled water to remove NaOH and HCl residues. The powder products were calcined at 773 K for two hours.

2.2 Photocatalytic splitting of seawater

The photocatalytic splitting of seawater experiments were carried out in a quartz reactor (45 mL) having a total reflection mirror system. The seawater was prepared by adding 35 g/L NaCl into water. About 100 mg of the catalysts was dispersed in water under magnetic stirring during photocatalysis. A 300 W Xenon arc lamp (Oriel Instruments, Model 6259) light source with a recycled water filter was used in the photocatalytic experiments which were prolonged for five hours. H₂ gas generation from the photocatalytic splitting of seawater was analyzed by a gas chromatography (Varian 430-GC) equipped with a thermal conductivity detector.



3 Results and discussion

3.1 Characteristic of copper oxide supported on TNT

The XRD patterns of the TNT and CuO/TNT photocatalysts are shown in Figure 1. The main diffraction peaks of photocatalysts are (101) and (200), (105), and (004), suggesting that the photocatalysts have mainly anatase crystallines. CuO having subnanosize crystallines is not found. The images of the TNT and CuO/TNT determined by transmission electron microscopy (TEM) are shown in Figure 2. It is clear that the photocatalysts possess a tubular structure with the lengths and diameters of 70–100 nm and 7.5–8.0 nm, respectively. Diffuse reflectance (DR) UV-Vis spectra of the photocatalysts determined by a UV-Vis spectrophotometer (Cary 100) in the range of 200–800 nm are shown in Figure 3. The blue-shift absorption caused by the quantum size effect for the TNT is not found. The main light absorption of the TNT is in range of 200–400 nm. Nevertheless, for the CuO/TNT, absorption of light is extended to the visible light range (400–550 nm). The band gap of nanosize TiO₂, TNT, and CuO/TNT are 3.02, 3.17, and 2.95 eV, respectively.

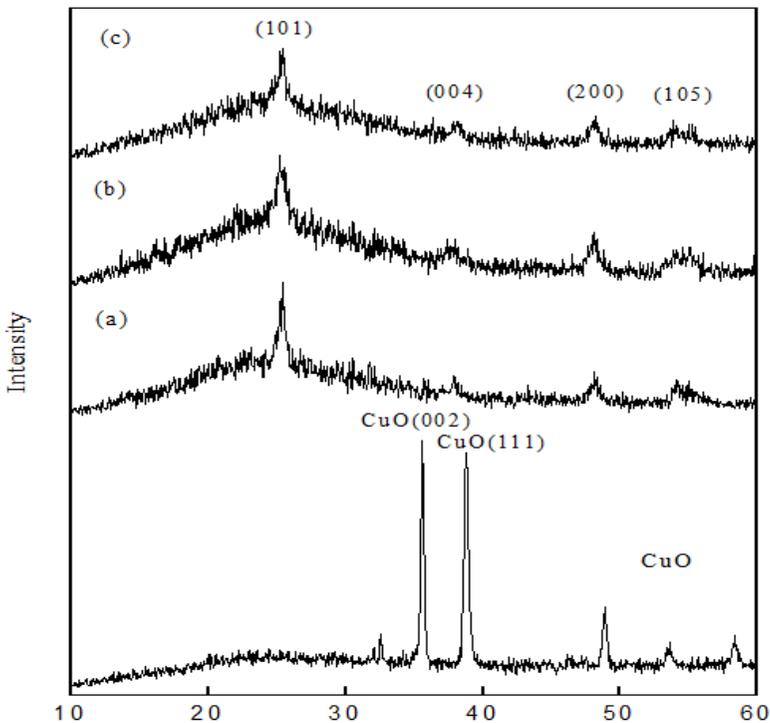


Figure 1: XRD patterns of (a) nanosize TiO₂, (b) TNT, and (c) CuO/TNT.

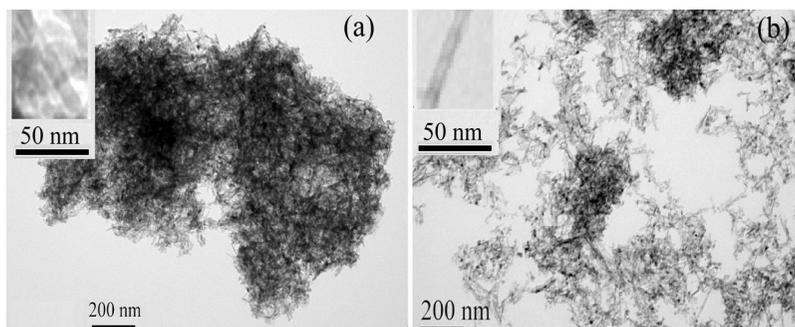


Figure 2: TEM images of (a) TNT and (b) CuO/TNT.

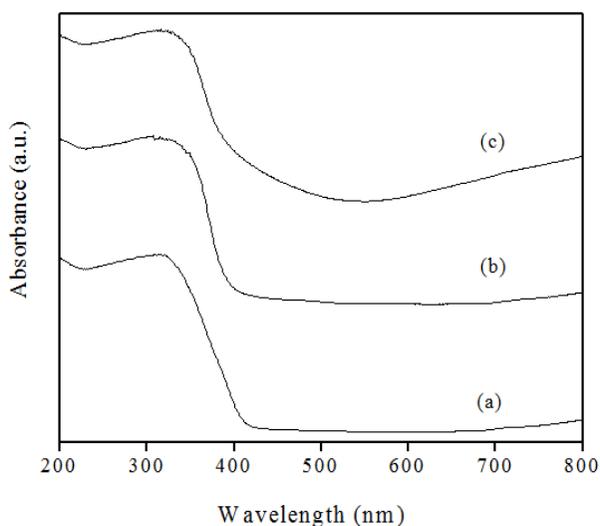


Figure 3: DR UV-Vis spectra of (a) nanosize TiO_2 , (b) TNT, and (c) CuO/TNT.

The Cu K-edge XANES spectra of bulky, nanosize and cluster CuO, and CuO/TNT are shown in Figure 4. The CuO cluster model compound was prepared by impregnation of $\text{Cu}(\text{NO}_3)_2$ on MCM-41, which was calcined at 573 K for four hours [14]. The pre-edge XANES spectra of all copper species exhibit a very weak absorbance feature for the 1s-to-3d transition (8975–8980 eV) which is forbidden by the selection rule in the case of perfect octahedral symmetry of Cu(II). Two intense shoulders at 8985–8988 and 8995–8998 eV can be assigned to the 1s-to-4p transitions allowed for Cu(II) [15]. Figure 4 also shows a small shoulder at 8985–8998 eV for CuO clusters and CuO supported on TNT. Note that the XANES spectrum of the CuO/TNT is very similar to that of the CuO cluster, suggesting that CuO clusters are supported on the surfaces of the TNT.

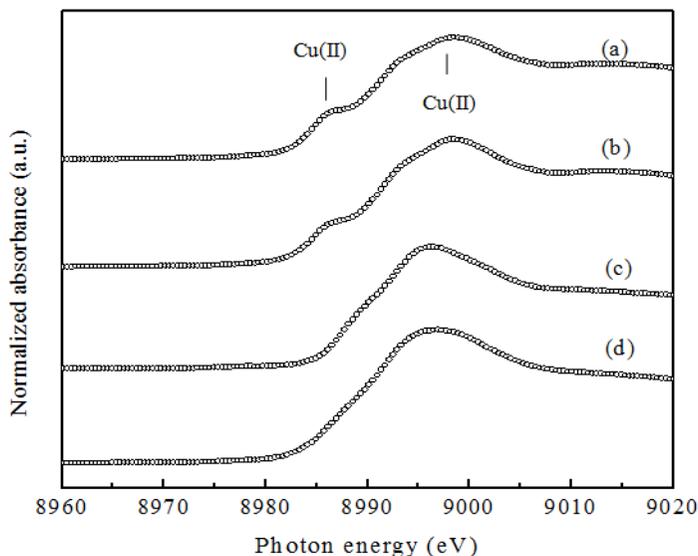


Figure 4: Cu K-edge XANES spectra of (a) bulky CuO, (b) nanosize CuO, (c) CuO clusters, and (d) CuO/TNT.

The EXAFS spectra of the TNT and CuO/TNT were recorded and analyzed in the range of 3.5-14 \AA^{-1} . The best fitted structural parameters are shown in Table 1. The bond distance and coordination number of CuO are decreased as the particles size decreases. The first shell of Cu-O bond distance in the CuO/TNT is 1.94 \AA which is shorter than the Cu-O bond distance of bulky and nanosize CuO, whereas the Ti-O bond distance in the CuO/TNT is 1.93 \AA .

Table 1: Structure parameter of copper and titanium in the CuO/TNT.

	First shell	R (\AA)	CN	σ^2 (\AA^2)
Bulky CuO	Cu-O	1.96	3.8	0.003
Nanosize CuO	Cu-O	1.95	3.2	0.002
CuO/TNT	Cu-O	1.94	2.1	0.003
CuO/TNT	Ti-O	1.93	3.1	0.007

R: Bond distance; σ^2 : Debye-Waller factor; CN: Coordination number.

3.2 Photocatalytic splitting of seawater

Figure 5 presents photocatalytic splitting of seawater containing oxalic acid (0.05 M). On the nanosize TiO_2 photocatalyst, H_2 is not found during photocatalytic splitting of seawater containing 0.05 M oxalic acid. On the contrary, H_2 yielded from photocatalytic splitting of seawater containing oxalic acid on CuO/TNT is about 1.26 $\mu\text{mol/g cat}$. It seems that the CuO/TNT is very active for photocatalytic splitting of seawater with oxalic acid as the sacrificial reagent.

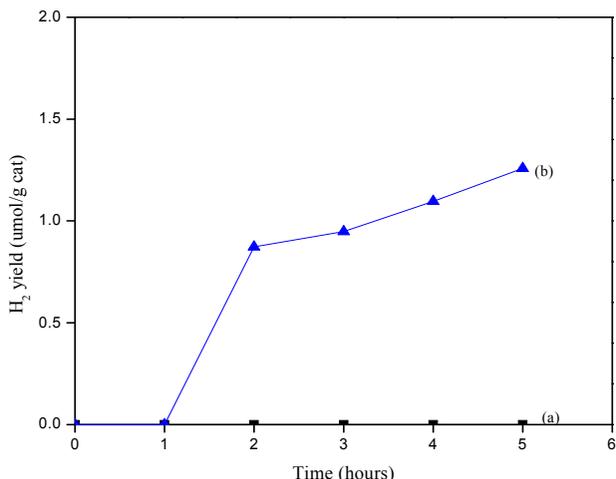


Figure 5: Photocatalytic splitting of seawater containing 0.05 M of oxalic acid on (a) nanosize TiO₂ and (b) CuO/TNT.

3.3 Economic consideration of hydrogen fuel cell

The economic burden for H₂ generation and converting to electricity has been analyzed. Table 2 shows the detailed economic calculation. The cost for operation and maintenance for this system is much less than its capital cost. Note that organic wastewater can be used as a sacrificial reagent during photocatalysis. Assuming the price of electricity is US\$0.1/kWh, the years of return is 3.5 approximately.

Table 2: Total cost for installation of photocatalytic splitting of seawater system integrated with an internal combustor.

Material and equipment	Quantity	Cost/unit (US\$)	Cost (US\$)
Photocatalyst			
TiO ₂	10 kg	2.5	25
Glass	32 units	25	800
Metal frame	25 units	5	125
Water pump	2 units	50	100
Internal combustor	1 unit	150	150
Total cost			1,200

4 Conclusion

Photocatalytic splitting of seawater with oxalic acid as sacrificial reagents on CuO/TNT and nano TiO₂ have been studied. The average effectiveness of the CuO/TNT for photocatalytic splitting of seawater is 1.26 μmol/g cat. An economic consideration for electrical power generation with an internal combustor fueled with H₂ yielded from photocatalytic splitting of seawater has also been investigated. The capital cost of the solar-derived power generation system is US\$ 1,200 approximately with negligible operation cost. The years of return for the small scale photocatalytic H₂ utilization system are 3.5.

References

- [1] Fujishima, A. & Honda, K., Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 238, pp. 37-38, 1972.
- [2] Bamwenda, G.R., Tsubota, S., Nakamura, T. & Haruta, M., Photoassisted hydrogen production from a water-ethanol solution: a comparison of activities of Au-TiO₂ and Pt-TiO₂. *Journal of Photochemistry and Photobiology A: Chemistry*, 89, pp. 177-189, 1995.
- [3] Sreethawong, T. & Yoshikawa, S., Enhanced photocatalytic hydrogen evolution over Pt supported on mesoporous TiO₂ prepared by single-step sol-gel process with surfactant template. *International Journal of Hydrogen Energy*, 31, pp. 786-796, 2006.
- [4] Choi, W., Termin, A. & Hoffmann, M.R., The role of metal ion dopants in quantum-sized TiO₂: correlation between photoreactivity and charge carrier recombination dynamics. *The Journal of Physical Chemistry*, 98, pp. 13669-13679, 1994.
- [5] Wilke, K. & Breuer, H.D., The influence of transition metal doping on the physical and photocatalytic properties of titania. *Journal of Photochemistry and Photobiology A: Chemistry*, 121, pp. 49-53, 1999.
- [6] Xu, A.W., Gao, Y. & Liu, H.Q., The preparation, characterization, and their photocatalytic activities of rare-earth-doped TiO₂ nanoparticles. *Journal of Catalysis*, 207, pp. 151-157, 2002.
- [7] Galinska, A. & Walendziewski, J., Photocatalytic water splitting over Pt-TiO₂ in the presence of sacrificial reagents. *Energy & Fuels*, 19, pp. 1143-1147, 2005.
- [8] Sayama, K. & Arakawa, H., Effect of carbonate addition on the photocatalytic decomposition of liquid water over a ZrO₂ catalyst. *Journal of Photochemistry and Photobiology A: Chemistry*, 94, pp. 67-76, 1996.
- [9] Chen, X. & Mao, S.S., Titanium dioxide nanomaterials: synthesis, properties, modifications, and application. *Chemical Reviews*, 107, pp. 2891-2959, 2007.
- [10] Kasuga, T., Hiramatsu, M., Hoson, A., Sekino, T. & Nihara K., Formation of titanium oxide nanotube. *Langmuir*, 14, pp. 3160-3163, 1998.



- [11] Kosanic, M.M., Photocatalytic degradation of oxalic acid over TiO₂ power. *Journal of Photochemistry and Photobiology A: Chemistry*, 119, pp. 119-122, 1998.
- [12] Xiao, J.B., Determination of nine components in bayer liquors by high performance ion chromatography with conductivity detector. *Journal of the Chilean Chemical Society*, 51, pp. 964-967, 2006.
- [13] Addamo, M., Augugliaro, V., García-López, E., Loddo, V., Marci, G. & Palmisano, L., Oxidation of oxalate ion in aqueous suspensions of TiO₂ by photocatalysis and ozonation. *Catalysis Today*, 107, pp. 612-618, 2005.
- [14] Huang, H.L., *Enrichment and recycling of nanosize copper and zinc pollutants*. Dissertation for Doctor of Philosophy Department of Environmental Engineering National Cheng Kung University, 2007.
- [15] Palomino, G.T., Fisticaro, P., Bordiga, S., Zecchina, A., Giamello, E. & Lamberti, C., Oxidation rates of copper ions in ZSM-5 zeolites. A multitechnique investigation. *The Journal of Physical Chemistry B*, 104, pp. 4064-4073, 2000.

