

Research Article

H₂ Fuels from Photocatalytic Splitting of Seawater Affected by Nano-TiO₂ Promoted with CuO and NiO

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To enhance H₂ yields from the photocatalytic splitting of seawater, better photocatalysts such as nanostructured TiO₂ promoted with NiO (2.5%) and CuO (2.5%) have been studied in the present work. The accumulated H₂ yielded from the photocatalytic splitting of seawater containing oxalic acid (50 mM) as the sacrificial reagents on CuO/nano-TiO₂ is 8.53 μmol/g_{cat} after the 5 h radiation. On the NiO/nano-TiO₂ photocatalyst, the H₂ yield is relatively low (i.e., 1.46 μmol/g_{cat}). Note that the hole scavenging with chlorides in seawater may be associated with the less H₂ yielded from the seawater photocatalysis (on CuO/nano-TiO₂) if compared with that from water (42.4 μmol/g_{cat}).

1. Introduction

Utilization of fossil energy which may cause air pollution or global warming has negative impacts on the human health and environment. Today's world is also facing an urgency need in developing alternative fuels. Renewable hydrogen energy (H₂) is becoming one of the better alternatives. Combustion of H₂ for energy does not emit pollutant gases such as CO, NO_x, or SO_x. H₂ has also been widely used in many sectors such as food, metallurgical, electronic, chemical, petroleum, and refinery industries. H₂ has been technically demonstrated for transportation, heating, and power generation [1].

H₂ yielded from the photocatalytic splitting of water has extensively received attention recently [2–4]. Since the H₂ generation by the water electrochemical method was demonstrated, splitting of water photocatalyzed by TiO₂ for the H₂ fuel has been considered to be one of the alternates [5]. The TiO₂-based photocatalysts for H₂ generation could be promoted by codoping of antimony and chromium [6],

nickel and either tantalum or niobium [7], cobalt [8], Pt [9], and nitrogen [10]. During photocatalysis, photo-excited holes can irreversibly oxidize electron donor compounds, and thus facilitate water reduction by conduction band electrons if the bottom of the conduction band of the photocatalyst is located at a more negative redox potential than the reduction potential of water [11]. Inorganic reagents such as Na₂S and Na₂SO₃ are generally used as the sacrificial compounds [12, 13].

In the present work, CuO and NiO were used as the promoters on the nanosize TiO₂ to enhance catalytic splitting of water and seawater. Oxalic acid which may be formed from the photocatalytic reduction of CO₂ in H₂O was used as the sacrificial reagent during photocatalysis.

2. Materials and Methods

The CuO (2.5%) and NiO (2.5%) supported on nanosize TiO₂ (P25) (UR, ITIT001) were prepared by the impregnation method. The samples were dried and calcined at 673 K for two

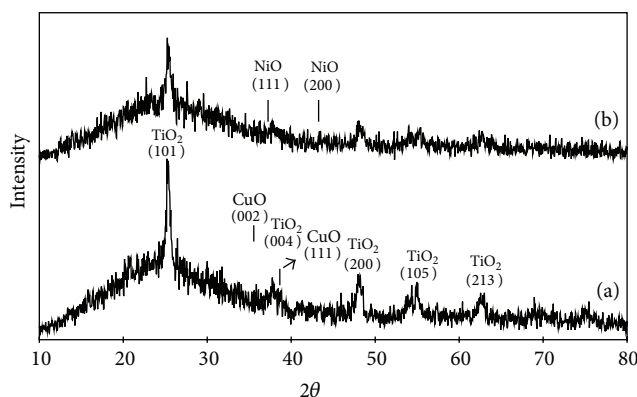


FIGURE 1: XRD patterns of (a) CuO and (b) NiO promoted nano-TiO₂.

hours to form CuO and NiO dispersed on TiO₂ (CuO/nano-TiO₂ and NiO/nano-TiO₂), respectively. The X-ray diffraction (XRD) patterns of the photocatalysts were recorded on a XRD spectrometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) ranged from 10° to 80° (2θ) at the scanning speed of 5°/min.

The XANES spectra of the TiO₂ photocatalysts were also recorded on the Wigler I7C beam line at the Taiwan National Synchrotron Radiation Research Center (NSRRC). The electron storage ring was operated at the energy of 1.5 GeV (ring current = 120–200 mA). A Si(111) double crystal monochromator was used for selection of energy at an energy resolution ($\Delta E/E$ (eV/eV)) of 1.9×10^{-4} . The absorption spectra were collected in ion chambers that were filled with helium and nitrogen mixed gases. Beam energy was calibrated by the adsorption edges of nickel and copper foils at the energy of 8335 and 8979 eV, respectively.

The photocatalytic splitting of water and seawater experiments was carried out in a quartz reactor (45 mL) having a total reflection mirror system. About 100 mg of the catalyst samples were dispersed in the simulated seawater (about 35 g of NaCl in the 1 L of pure water) under magnetic stirring for five hours. A 300 W Xenon arc lamp (Oriental Instruments, Model 6259) equipped with a water filter was used as the photocatalytic light source. The H₂ gas generated from the photocatalytic splitting of water and seawater was analyzed by a gas chromatography (Varian 430-GC) equipped with a thermal conductivity detector. The apparent quantum efficiency (QE) of the photocatalysts was obtained by the equation $QE (\%) = (\text{number of reacted electrons})/(\text{number of incident photons}) \times 100 = (\text{number of evolved H}_2 \text{ molecules} \times 2)/(\text{number of incident photons}) \times 100$.

3. Results and Discussion

The XRD patterns of the CuO/nano-TiO₂ and NiO/nano-TiO₂ photocatalysts are shown in Figure 1. The main diffraction peaks of the photocatalysts at (101), (200), (004), and (105) are observed, suggesting that the photocatalysts have mainly anatase crystallites. The XRD peaks of CuO and NiO are barely observed in the CuO/nano-TiO₂ and NiO/nano-TiO₂, which may be due to the existence of

subnanosize CuO and NiO crystallites that are well dispersed on the nano-TiO₂.

The XANES spectra of nickel and copper in the photocatalysts are shown in Figure 2. Metallic nickel (Ni) and copper (Cu) are not found. The absorption features observed at 8335 and 8979 eV suggest that NiO and CuO are the main nickel and copper species on the TiO₂, respectively.

Figure 3 presents the photocatalytic splitting of water and seawater containing 0.05 M oxalic acid as the sacrificial reagent. On the nano-TiO₂ photocatalyst, a very small amount of H₂ is formed from the photocatalytic splitting of water and seawater. Notably, the accumulated H₂ yielded from the photocatalytic splitting of water on CuO/nano-TiO₂ and NiO/nano-TiO₂ is about 32.4 and 3.07 $\mu\text{mol/g}_{\text{cat}}$ after the 5 h radiation, respectively. Compared to the photocatalytic splitting of seawater on CuO/nano-TiO₂ and NiO/nano-TiO₂, the accumulated H₂ yields are less than those from water by 3.8 and 2.1 times, respectively. Hole scavenging with chlorides may occur during photocatalysis [14, 15]. Many hydroxyl groups such as TiOH₂, TiOH on TiO₂ may absorb Cl[−] to form TiCl, which may decrease the H₂ yield in the photocatalysis [16, 17]. Generally, CuO on TiO₂ can be reduced to Cu⁺ ($E_0 = 0.16 \text{ V}$) or Cu⁰ ($E_0 = 0.34 \text{ V}$) by attracting the excited electrons from the valence band of TiO₂ during photooxidizing [18–21]. The reduction potential of NiO ($E_0 = -0.25 \text{ V}$) is slightly less than the TiO₂ conduction band gap ($E_0 = -0.26 \text{ V}$) [22, 23]. Additionally, the reduction potential of H⁺/H₂ ($E_0 = -0.00 \text{ V}$) is less than that of CuO or NiO. CuO and NiO can thus promote TiO₂ in the photocatalytic H₂ formation.

In the separate experiments, oxalic acid was formed from simultaneously photocatalytic reduction of H₂O and CO₂. It is of great interest to study the behavior of acetic acid as the sacrificial compound for photocatalytic splitting of water and seawater for the H₂ fuel. Note that addition of sacrificial reagents in water or seawater may cause water pollution.

Effects of the oxalic acid sacrificial reagent concentrations on the photocatalytic splitting of water and seawater on CuO/nano-TiO₂ are shown in Figure 4. Without oxalic acid, H₂ may not be formed in the photocatalysis. A small amount of oxalic acid can enhance the H₂ generation. Note that

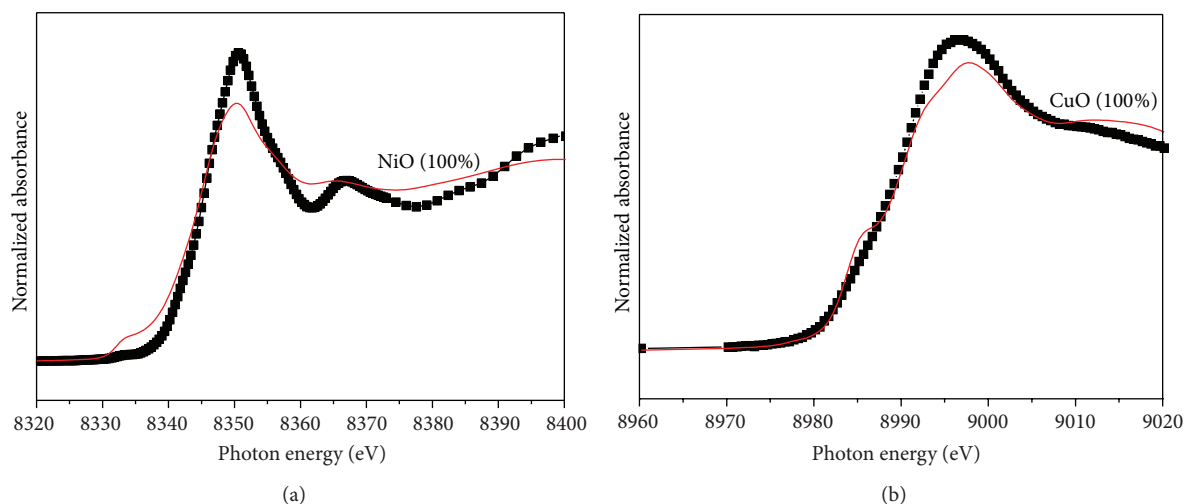


FIGURE 2: Component-fitted XANES spectra of (a) nickel and (b) copper in the NiO/nano-TiO₂ and CuO/nano-TiO₂ photocatalysts, respectively.

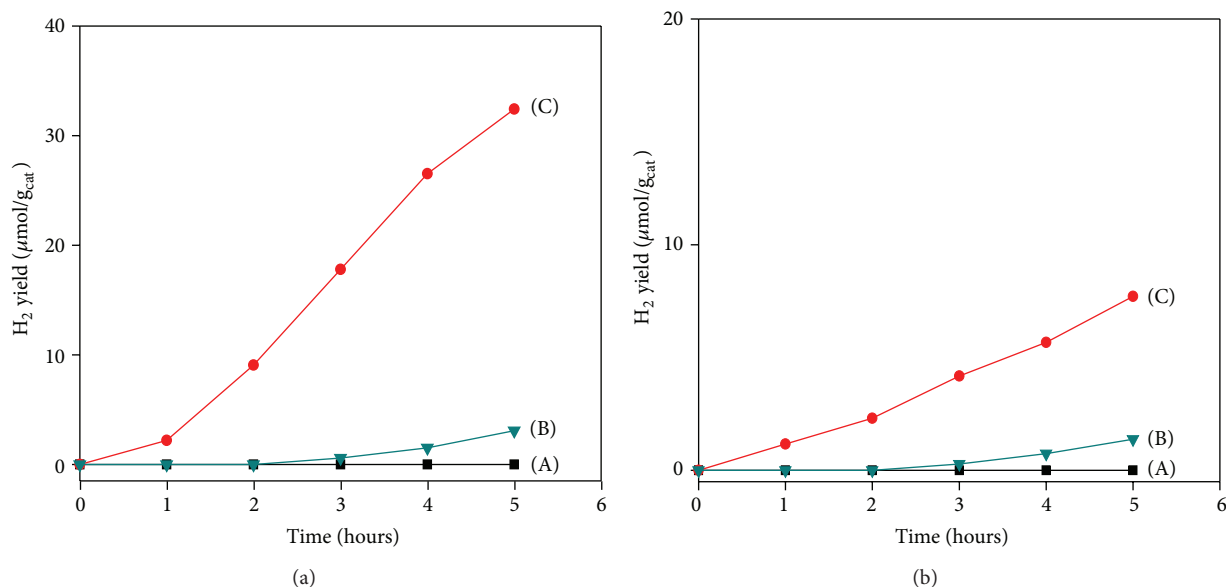


FIGURE 3: Photocatalytic splitting of (a) water and (b) seawater with 50 mM oxalic acid sacrificial reagent affected by (A) nano-TiO₂, (B) NiO/nano-TiO₂, and (C) CuO/nano-TiO₂.

oxalic acid is a strong reductive reagent which may consume the photogenerated holes. After a 5 h UV-Vis irradiation, a better H₂ yield from the photocatalytic splitting of water is about 42.4 $\mu\text{mol/g}_{\text{cat}}$ when the initial concentration of oxalic acid is 12.5 mM. However, the photocatalytic H₂ formation from water and seawater affected by CuO and NiO promoted TiO₂ was less than that of related studies, mainly due to the fact of the much less amount of the sacrificial reagents used in the photocatalysis. With an increase of the initial oxalic acid concentration by two times, the photocatalytic H₂ generation is slightly decreased. As the initial concentration of oxalic acid is increased by four times, the H₂ yields from the photocatalytic splitting of water are decreased by 24%. It seems that excessive oxalic acid sacrificial reagent may

not have a positive effect on the photocatalytic splitting of water.

4. Conclusions

Photocatalytic splitting of seawater for H₂ formation on CuO/nano-TiO₂ and NiO/nano-TiO₂ is feasible experimentally. The sacrificial reagent (oxalic acid) can enhance the H₂ yields in the photocatalytic splitting of seawater. However, the excessive sacrificial reagent may not favor the photocatalysis. It is worth noting that a better H₂ can be yielded from the photocatalytic splitting of seawater affected by CuO/nano-TiO₂ (8.53 $\mu\text{mol/g}_{\text{cat}}$) than that by NiO/nano-TiO₂ (1.46 $\mu\text{mol/g}_{\text{cat}}$). In particular, the hole scavenging with

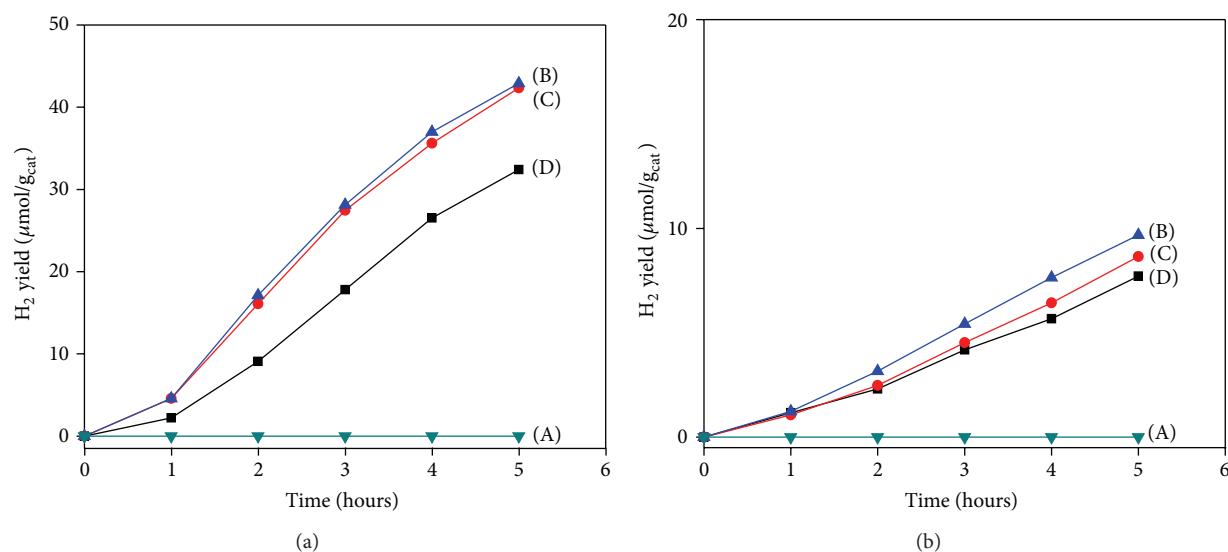


FIGURE 4: Photocatalytic splitting of (a) water and (b) seawater affected by CuO/nano-TiO₂ with (A) 0, (B) 12.5, (C) 25, and (D) 50 mM of the oxalic acid sacrificial reagent.

chlorides in seawater may be associated with the less H₂ yielded from the seawater photocatalysis (on CuO/nano-TiO₂) if compared with that from water (42.4 μmol/g_{cat}).

Acknowledgment

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