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Photocatalytic splitting of water on $NiO/InTaO_4$ catalysts prepared by an innovative sol–gel method

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ABSTRACT

$InTaO_4$ is a photocatalyst with visible-light response that is used to split water and produce hydrogen. $InTaO_4$ is traditionally prepared by solid-state fusion of In_2O_3 and Ta_2O_5 at ≥1100 °C. A sol–gel procedure was developed to synthesize $InTaO_4$ from $In(NO_3)_3$ and $Ta(OC_4H_9)_5$ precursors. A uniform crystalline $InTaO_4$ phase was easily obtained on calcination at 1100 °C because the sol–gel method allows homogeneous liquid-phase mixing. The method yields small $InTaO_4$ particles with a high specific surface area. $InTaO_4$ catalysts with different Ni loading were prepared by incipient wetness impregnation. Ni loading greatly enhanced the initial rate of H_2 production during photocatalytic splitting of water. Ni metal within Ni–NiO core/shell nanoparticles can efficiently transfer photoelectrons on the $InTaO_4$ surface and thus reduce H^+ to hydrogen. $NiO_x/InTaO_4$ was deactivated due to the formation of $Ni(OH)_2$. Overall, $NiO_x/InTaO_4$ prepared by the sol–gel method had higher activity than catalysts prepared by solid-state fusion. Among all the photocatalysts, 3.0 wt.% $NiO_x/InTaO_4$ exhibited the highest photoactivity, with an initial rate of H_2 production of 2.10 μmol/g h.

1. Introduction

The production of CO_2-free fuel by direct conversion of solar energy into chemical energy is still a fascinating task for researchers. Among other reactions, the splitting of water into hydrogen and oxygen by sunlight is one of the best ways to achieve photochemical storage of solar energy. Photocatalytic processes on semiconductors occur via the direct absorption of photons with energy greater than or equal to the bandgap to generate electron–hole pairs. Water splitting can then occur on the surface according to Eq. (1). In 1972 Fujishima and Honda [1] first reported the use of semiconductor catalysts for water splitting using ultraviolet radiation. Since then, photocatalysis has attracted much attention and the conversion of solar energy to clean hydrogen energy has been widely investigated.

$$2H_2O \xrightarrow{\text{Catalyst}/h\nu} 2H_2 + O_2 \qquad (1)$$

The efficiency of photocatalytic activity can be enhanced by improving the support material and/or the properties of impregnated metals. Various researches have explored more efficient materials for water splitting using various semiconductors such as TiO_2, TaON, WO_3, Nb_2O_5, Ta_2O_5, In_2O_3 and $InTaO_4$ [2–9]. Various metals, such as Sr, Cr, Fe, Ni and Cu, have been used on semiconductors as co-catalysts to improve the photocatalytic activity for water splitting [3,10–13]. In comparison to other metals and metal oxides, NiO is very effective for water splitting [14–16].

The catalytic potential of NiO–Ni–$InTaO_4$ photocatalysts has been demonstrated for water splitting to produce hydrogen and oxygen. Recently a series of catalysts with visible-light activity was prepared by loading of indium (In) on various transition metal oxides ($InMO_4$; M = V^{5+}, Nb^{5+}, Ta^{5+}) [8]. Vanadium, niobium and tantalum belong to the 3d, 4d and 5d transition series, respectively, so they have different bandgaps. $InVO_4$ has the narrowest gap, at only 1.9 eV; $InNbO_4$ is intermediate at 2.5 eV; $InTaO_4$ has the greatest bandgap of 2.6 eV. It has been demonstrated that NiO promotes the activity of different photocatalysts for water splitting [12,17,18]. Metallic Ni within Ni–NiO core/shell nanoparticles can trap photoelectrons generated by light irradiation. These photoelectrons can be efficiently transferred to split water into H_2 and O_2.

$InTaO_4$ photocatalysts have been synthesized by high-temperature solid-state fusion of In_2O_3 and Ta_2O_5 at ≥1100 °C [19]. However, it is not easy to obtain a uniform $InTaO_4$ phase by solid fusion. We have successfully prepared a uniform $InTaO_4$ phase using an aqueous-phase sol–gel method [20]. The objective of the present study was to demonstrate the improved photoactivity of sol–gel-derived $NiO/InTaO_4$ in water splitting. In addition, the

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influence of different NiO loading situations was investigated to identify the most favorable conditions.

2. Experimental

2.1. Materials and characterization

$InTaO_4$ photocatalysts were prepared by sol–gel and solid-state fusion methods. In the sol–gel method, $InTaO_4$ was prepared by mixing equimolar amounts of $In(NO_3)_3 \cdot H_2O$ and $Ta(OC_4H_9)_5$. First, 2 mmol (0.782 g) of $In(NO_3)_3 \cdot H_2O$ and 2 mmol (1.093 g) of $Ta(OC_4H_9)_5$ were dissolved in 50 ml of methanol. Then 0.5 ml of conc. HNO_3 was added to maintain the solution at $pH < 2$. After the solution was stirred for 30 min, 3 ml of acetic acid was added and the mixture was continuously stirred slowly in a glove box at <40% humidity and 25 °C for 36 h. The sol obtained was dried at 80 °C in air, ground and calcined at 1100 °C in a furnace for 12 h at a rate of 3 °C/min. The powder obtained was ground well to obtain a uniform particle size. These catalysts are denoted $InTaO_4$-SG (i.e., sol–gel). The procedure is described in detail elsewhere [20]. For comparison, $InTaO_4$ was also prepared by solid-state fusion. Equimolar amounts of solid In_2O_3 and Ta_2O_5 powders were mixed and the mixture was calcined at 1100 °C for 12 h at a rate of 3 °C/min [19]. These samples are denoted $InTaO_4$-SS (i.e., solid-state).

A series of catalysts with Ni loading of 0.1, 0.5, 1.0, 2.0, 3.0, 5.0, and 10 wt.% on $InTaO_4$ was prepared by incipient wetness impregnation. The desired amount of nickel nitrate solution was dropped slowly onto $InTaO_4$ powder, then the catalyst was dried and calcined in air at 350 °C for 1 h. These catalysts were further reduced in 26.3% hydrogen (balance N_2) for 2 h at 500 °C, and then oxidized in 13.2% O_2 (balance N_2) at 200 °C for 1 h [17].

A diffusive reflectance UV–Vis spectrophotometer (Varian Cary 100) was used to measure the UV–Vis absorption and to estimate the bandgap of the catalysts. Powder X-ray diffraction (XRD) analysis of the catalysts was performed on a Philips X'Pert instrument. The X-ray (wavelength $\lambda = 1.5405$ Å) tube was equipped with a copper target operated at 40 kV and 30 mA. The scanning rate was 3°/min from 20° to 70°. The crystal size was calculated using Scherrer's equation. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Theta Probe instrument. The catalyst was pressed into a pellet and then stuck to the sample holder using carbon tape. Carbon (1 s, 284.5 eV) was used as an internal standard for binding energy calibration. The specific surface area of catalysts was measured on a Micromeritics ASAP 2000/C5-05 system. Field-emission scanning electron microscopy (FE-SEM) was carried out on a Hitachi model S-800 instrument. The catalyst was sputtered with a thin film of gold to prevent surface charging and to protect the surface material from thermal damage by the electron beam. Transmission electron microscopy (TEM) of the catalysts was carried out on a Hitachi model H-7100 instrument.

2.2. Photocatalytic splitting of water

The photocatalytic splitting of water to hydrogen and oxygen was carried out using the system shown in Fig. 1. In a typical reaction, 0.2 g of catalyst was added to 140 ml of deionized water in the Pyrex reactor. Before photocatalytic reaction, the reactor was heated and evacuated at 50 °C for 30 min with continuous stirring to remove air evolved from the water. Next the reactor was purged with high-purity argon gas and evacuated again. This Ar purge/evacuation process was carried out five times, and then the residual air content was checked by GC. The reactor was irradiated using a 500-W halogen lamp after GC analysis confirmed that the amount of air in the reactor was negligible. The light intensity was measured in front of the reactor using a Lumen meter (Goldilux, GRP-1 70234). The intensity of incident visible light (>420 nm) was 1.68 W/cm^2, which was projected onto the reactor-side surface of 96 cm^2. Cooling water was circulated inside the reactor to maintain the reaction at 25 °C. The reaction was carried out for 6–8 h and the reaction products were analyzed by GC using an on-line sampling loop (1 ml) at intervals of 1 h. A China Chromatography 2000 GC system was equipped with a 3.5-m Molecular Sieve 5A column and a thermal conductivity detector, with Ar at 20 ml/min as the carrier gas. To check the catalyst reproducibility, we repeated reactions with previously used catalyst samples. Blank reactions were carried out without catalyst in the presence of light and with catalyst in the dark. In both cases no production of hydrogen was observed.

3. Results and discussion

3.1. Catalyst characteristics

Data for the particle sizes, specific surface areas and bandgaps of different catalysts are listed in Table 1. The specific surface area

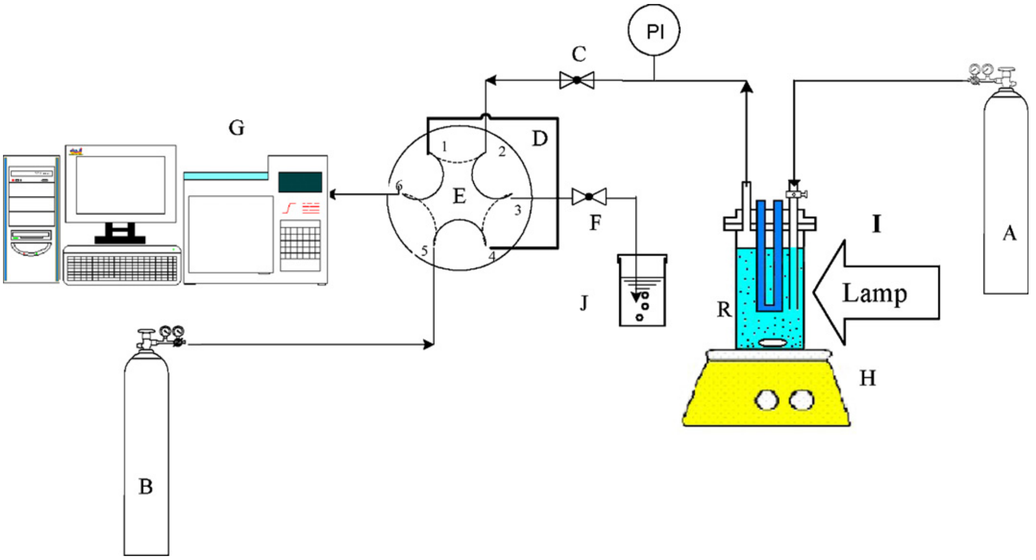

Fig. 1. Apparatus for photocatalytic water splitting. A, Ar for purging; B, ultra-high-purity Ar; C, on/off valve; D, sampling loop; E, six-way valve; F, on/off valve; G, GC; H, magnetic stirrer; I, 500-W halogen lamp; J, water lock; PI, pressure gauge; R, Pyrex reactor.