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A systematic comparative study of the efficient co-catalyst-free photocatalytic hydrogen evolution by transition metal oxide nanofibers

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ABSTRACT

The efficiencies of a series of hydrogen evolving catalysts based on metal oxide nanofibers (NiO, Co_3O_4, Mn_3O_4) are investigated for the photocatalytic hydrogen evolution from water without using any co-catalyst under the visible light irradiation by using triethanolamine (TEOA) as an electron donor and Eosin-Y (EY) dye as a photosensitizer. It is found that the photocatalytic hydrogen evolution activities follow the order as: Mn_3O_4<Co_3O_4<NiO (196 $\mu molg^{-1}h^{-1}$, 5552 $\mu molg^{-1}h^{-1}$, 7757 $\mu molg^{-1}h^{-1}$, respectively). Moreover, the catalytic behavior of these nanofibers on the hydrogen production has been also compared to bulk forms of NiO, Co_3O_4 and Mn_3O_4 by producing hydrogen 937 $\mu molg^{-1}h^{-1}$, 901 $\mu molg^{-1}h^{-1}$ and 135 $\mu molg^{-1}h^{-1}$, respectively. The nanofiber structures demonstrated much higher photocatalytic activity than bulk forms due to the effect of the increased surface to volume ratio deduced from the fibrous character. The photocatalytic plausible pathway for the hydrogen production is also discussed.

Introduction

The dye sensitization of semiconductors for the photocatalytic water splitting has stimulated considerable interest due to the efficient use of solar light to produce hydrogen as a clean and renewable future energy [1]. In dye sensitized semiconductor systems, electrons arising from the excited dye by the visible light absorption are transferred into the conduction band of semiconductor catalyst. In order to increase the hydrogen evolution reaction (HER) efficiency, different kinds of co-catalysts, especially noble metals, such as Pt, Pd, Au [2–9] have been used together with semiconductor catalysts. Investigation into high efficiency and stable noble-metal-free co-catalysts for the photocatalytic hydrogen production has been intensely continued due to the source scarcity and high cost of precious metals [10–20]. Until now, metal oxide semiconductors such as NiO, Co_3O_4, Mn_3O_4

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have been used as catalysts in different hydrogen evolution systems with and without using co-catalyst. For example, the high electrocatalytic activity was observed for the HERs by using Nickel oxide/nickel (NiO/Ni) attached to carbon nanotube (NiO/Ni-CNT) [21]. NiO and CrO_3 double surface-decorate Ni (Ni@NiO@CrO_3) nanofibers were also used as highly effective and stable electrocatalysts for the HER [22]. NiOx@bamboo-like carbon nanotubes hybrids (NiOx@BCNTs) was also designed for the highly active and robust HER electrocatalysts in alkaline solution [23]. Mn_3O_4 supported Pd nanocomposite was used a highly active catalyst on the HER [24]. Pt–Mn_3O_4/C composite was also used as a water electrolysis catalyst and indicated excellent catalytic activity [25]. Li et al. were investigated the electrocatalytic HER activity of Ni–Mn_3O_4 grown on Ni foam (NF) in alkaline solution. Ni–Mn_3O_4–NF was demonstrated outstanding electrocatalytic activity and good stability for the HER [26]. Yan et al. have recently been investigated the catalytic activity for the HER of three-dimensional (3D) reduced graphene oxide-Mn_3O_4 nanosheets [27].

Nanocrystalline Co_3O_4 [28] was used as a co-catalyst for the photocatalytic HER. The urchin-like sphere arrays Co_3O_4 [29], Co/Co_3O_4 core/shell nanosheets [30] was also used in the electrocatalytic HERs.

More recently, co-catalyst free highly efficient and stable photocatalytic hydrogen evolution systems have been also developed especially by using transition metal oxide semiconductor Co_3O_4. For example, Eosin-y-sensitized Co_3O_4 quantum dot system has been reported for photocatalytic hydrogen production without any co-catalyst [31,32]. Gao et al. reported that carbon incorporated Co_3O_4 nanoparticles without loading co-catalysts produce high yield of hydrogen under visible light irradiation [33]. More recently, La_xCo_3-xO_4/Graphene, which is synthesized by the microwave hydrothermal method, has been reported to be highly efficient photocatalyst for the photocatalytic hydrogen evolution [34]. $Ca_3Co_4O_9$ and $MgCo_3O_5$ fabricated by electrospinning method, have been exhibited promising catalytic activity for the electrocatalytic hydrogen evolution [35]. Highly stable and efficient 3D Ni nanodome arrays were used as cathode materials for alkaline water splitting [36]. Nickel oxide/Au porous nanobelts showed high photocatalytic activity for hydrogen evolution from water [37]. NiO nanoflower structure has been investigated for high catalytic activity of the photoelectrochemical hydrogen production [38]. Moreover, nickel oxide and cobalt oxide species were studied for hydrogen generation, such as NiO/$Sr_3Ti_2O_7$ [39], core/shell Ni@NiO cluster on TiO_2 [40], NiO modified silica [41], Ni–NiO/β-Ga_2O_3 [42], CuO_x-NiO bimetallic oxides [43], cobalt oxide (CoO_x) loaded on titanium dioxide/cadmium sulfide [44] and cobalt oxide nanoclusters deposited on titanium dioxide [45]. Furthermore, tube-like yolk-shell Co_3O_4@$NiMoO_4$ structures [46], reduced graphene oxide on Ni–NiO [47], $Ni_{0.3}Co_{2.7}O_4$ nanostructures on Ni-foam [48] and graphene/nickel oxide composite structures [49] have been explored for the supercapacitor applications.

In addition, to the best of our knowledge, there has been no report on the photocatalytic hydrogen evolution system by using Co_3O_4, Mn_3O_4 and NiO nanofiber catalysts in the absence of co-catalysts. Moreover, the utilization of the nanofiber technology in various catalysis applications is an outstanding path. Recently, Aljabour et al. have been reported on the catalytic activity of copper indium sulfide and cobalt oxide nanofibers in the electrochemical CO_2 reduction. The impressive performances of catalysts are attributed to the increased catalytically active sites introduced by the fiber structure and thus the nano-structuring leading to an expansion in the surface to volume ratio [50,51].

Based on these works, in this study metal oxide (Co_3O_4, Mn_3O_4 and NiO) nanofibers have been synthesized by the electrospinning process. The easiness, cost-efficiency and time-saving utility of the electrospinning process make this technique absolutely essential for the production of the nanofiber metal oxide. The as-prepared nanofibers have been characterized by optical, elemental, surface as well as electrochemical characterization techniques. These nanofibers have been used as catalysts for the photocatalytic HER under the visible light irradiation by using triethanolamine (TEOA) as an electron donor and Eosin-y (EY) dye as a photosensitizer in the absence of co-catalysts. The rate of hydrogen generation using different metal oxide nanofibers follow the order as: Mn_3O_4<Co_3O_4<NiO (196 $\mu mol g^{-1}h^{-1}$, 5552 $\mu mol g^{-1}h^{-1}$, 7757 $\mu mol g^{-1}h^{-1}$, respectively). The hydrogen evolution activities of these nanofibers have been also compared to bulk forms of these materials. The plausible photocatalytic hydrogen evolution pathway is also discussed in detail.

Experimental section

Materials

All reagents were studied analytical grade without any purification. Triethanolamine (TEOA) and Eosin-Y (EY) were obtained from Sigma-Aldrich and Alfa Aesar, respectively. Hydrochloric acid (HCl, 37.5%) was purchased from Merck. Following chemicals were involved for the synthesis of the Mn_3O_4 and Co_3O_4 nanofibers in their highly pure quality: manganese (II) chloride dehydrate ($MnCl_2.2H_2O$, 99%, Merck), cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$, 99%, Merck), dimethylformamide (DMF, 99%, Sigma-Aldrich), polyacrylonitrile (PAN, Mw = 150,000, Sigma-Aldrich). Acetonitrile (CH_3CN, 99.9%, Roth) and tetrabutylammonium hexafluorophosphate ($(CH_3CH_2CH_2CH_2)_4N(PF_6)$, 99.00%, Fluka) were used in the electrochemical studies as the electrolyte solution with the corresponding electrolyte salt. Pure water was used throughout all experiments.

Preparation of catalysts

Methods

The nanofiber structuring of the NiO, Mn_3O_4 and Co_3O_4 materials was achieved through the electrospinning technique by using brand DC power supply and Kd Scientific brand syringe pump (New Era Pump System Inc.). The syringe is attached between collectors at optimum conditions for electrospinning. The XRD pattern for the nanofibers was tested in powder mode using a Bruker Advance D8 XRD instrument, equipped with Cu Kα source ($\lambda = 1.5406$). The optical properties of the obtained nanofibrous NiO, Mn_3O_4, and Co_3O_4 were

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