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Optimization hydrogen production over visible light-driven titania-supported bimetallic photocatalyst from water photosplitting in tandem photoelectrochemical cell

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ABSTRACT

Solar hydrogen production was investigated over a Cu-Ni doped TiO_2 photocatalyst from water photosplitting in a tandem photoelectrochemical cell, which was made up by connecting a modified photoelectrochemical cell to dye solar cell in a series. A mathematical representation for preparation parameters for hydrogen production was successfully generated. Optimization of hydrogen production was conducted with varying preparation parameters of Cu-Ni doped TiO_2 photocatalyst including molar ratios of water, acetic acid and Cu to titanium tetraisopropoxide. The optimum preparation parameters of photocatalyst was obtained at molar ratios of water, acetic acid and Cu to titanium tetraisopropoxide of 32, 4.9, and 5.9, respectively. Physical and photoelectrochemical characterization revealed that low content of water and Cu decreased the charge transfer resistance and charge carrier recombination rate on Cu-Ni/TiO_2 surface. This is attributed to the better crystallinity and less degree of agglomeration which led to obtain optimum particle size at this condition. Maximum hydrogen production rate of 2.12 mL/cm^2. h was achieved under the optimum condition using the tandem photoelectrochemical cell in the aqueous KOH and glycerol solution under visible light irradiation ($\lambda > 400$ nm).

1. Introduction

Hydrogen is an environment-friendly energy source that is used to counteract the growing rate of fossil fuel product combustion, which is a major threat to the environment and human health [1,2]. The conventional hydrogen production from carbon-containing materials has raised questions on how hydrogen might be produced to solve problems related to energy security, air pollution, and climate change in the future. Fujishima and Honda established to produce hydrogen and oxygen from water photosplitting by irradiating light over a semiconductor in a photoelectrochemical (PEC) cell in accordance with Eq. (1) [3–5],

$$H_2O \xrightarrow[\text{semiconductor}]{h\nu \geq E_{band\ gap}} H_2 + 1/2O_2 \qquad \Delta G^{\circ} = 273\ \text{KJ/mol} \qquad (1)$$

This technique is relatively simple, cheap, and without undesirable by-products; unlike gasoline production, this technique only requires water and sunlight as renewable resources in both small and large scales [6,7]. However, the photoconversion efficiency of this technique is still low for it to be economically feasible. A single PEC cell should have an optimal photocatalyst with high water stability, maximum solar spectrum absorbance, and sufficient negative conduction band (CB) to provide enough potential (~1.9–2 V) for water photosplitting [7,8]. The tandem configuration of two photovoltaic cells is a practical approach to unassisted water photosplitting [9]. In tandem configuration, a PEC cell connected to a dye solar cell (DSC) provides photoelectrons, injects them to the DSC to increase their electrochemical potential, and then feeds

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them back to the PEC cell to reduce water to hydrogen [8]. An extensive literature review of water photosplitting has shown that WO_3 and Fe_2O_3 are the main photocatalysts in PEC cell of tandem configuration [10–13]. Different metal oxides (i.e., TiO_2, $SrTiO_3$, ZnO, α-Fe_2O_3, WO_3, Ta_2O_5, VO_2, $KTaO_3$, and Fe_2O_3) have been studied as photocatalysts; TiO_2 is considered a better photocatalyst than WO_3 and Fe_2O_3 owing to its photochemical stability, low cost, environmental friendliness, and suitable CB (−0.29 V) level to split water in large-scale applications [14]. However, its wide bandgap energy and ability to harvest only the UV region of a solar spectrum restrict its photocatalytic application [15–17].

Some investigators have modified TiO_2 by creating a new energy state of the metal dopant in the electronic structure of TiO_2 to extend the absorbance to the visible region [18,19]. Many researchers have modified TiO_2 by using single metal dopants, such as Fe [20], Cr and Fe [21], Ag [22,23], and Cu [24] for photocatalytic water photosplitting reaction in PEC cell. Incorporating two metals in the TiO_2 support can improve the photocatalytic performance of TiO_2 compared with single metal-doped TiO_2. Results showed that Cu-Ni/TiO_2 [25], Pt-Cu/TiO_2 [26], and Cu-Ag/TiO_2 [27] perform better than single metal-doped TiO_2 in removing Orange II, reducing nitrate, and producing hydrogen from water photosplitting, respectively. Previous investigations on TiO_2 modification illustrated that the photocatalytic hydrogen production of TiO_2 can strongly be controlled by the type of metal and its total loading, preparation techniques, and experimental conditions [28,29]. The sol–gel process of molecular doping is effective in preparing new TiO_2-based photocatalysts that either absorb visible light or display enhanced conducting characteristics. In addition, the inexpensive sol–gel hydrothermal method can improve the crystalline phase and the number of surface states at low temperatures because the charge transfer process is expected to be sensitive to the crystal structure and morphology of the exposed lattice planes at the electrode/electrolyte interface [30,31].

This research aims to optimize solar hydrogen production over a new bimetallic Cu-Ni/TiO_2 photoanode by controlling the photoelectrochemical behavior in a tandem PEC cell. A hydrogen production model was established, and preparation variables, including the molar ratios of water, acetic acid and Cu to titanium tetraisopropoxide, were optimized for maximum hydrogen production in the tandem PEC cell.

2. Materials and methods

2.1. Materials

Titanium tetraisopropoxide (TTIP), anhydrous ethanol (EtOH) and glacial acetic acid (ACA), $Ni(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ was purchased from Merck. The chemicals for fabrication of PEC cell and DSC were polyethylene glycol 20000 (Merck), ethylcellulose (Aldrich), α–Terpineol (Aldrich), potassium hydroxide (Merck), glycerol (Merck) Iodide/triiodide (I^-/I_3^-), Ruthenium (N719), Epoxy resin, conductive silver paste and platinum (PT1) from Dyesol, Australia. All chemicals were used as received without further purification.

2.2. Experimental design

The experimental design matrix was established by coupling the response surface methodology with the central composite design (CCD) using the Design-Expert software version 8.0.7.1 (Stat-Ease, Inc.). The molar ratios of H_2O:TTIP, ACA:TTIP, and Cu:TTIP were considered as parameters to synthesize different bimetallic Cu-Ni/TiO_2 photocatalysts. The total metal loading was fixed at 10 mol%; thus, Ni amount was varied from 1 to 5. Table 1 shows the coded and actual values of the parameters in CCD for the three variables (n = 3) in five levels ($-2 \leq \alpha \geq 2$).

Table 1
The real and coded values of the independent process parameters in CCD.

Variables	Parameter code	Level (α)				
		−2	−1	0	+1	+2
H_2O:TTIP	A	16	32	48	64	80
ACA:TTIP	B	1	2	3	4	5
Cu:TTIP	C	5	6	7	8	9

2.3. Photocatalyst preparation

A mixture of TTIP, EtOH, and ACA (1:4:X) was prepared in a glove box at room temperature under argon flow for 1 h, and then Cu and Ni solutions were added to the prepared mixture. The prepared solution was added dropwise to a mixture of water and EtOH (Y:4) under vigorous stirring. Accordingly, ACA (X), water (Y), and Cu and Ni ratios were chosen with respect to the experimental design. The obtained hydroxide precipitates were directly transferred to a Teflon-lined stainless steel vessel for hydrothermal treatment at 180 °C for 12 h. The products were separated by centrifugation at 4000 rpm for 15 min and then rinsed with deionized water and EtOH until neutral pH was achieved. The raw photocatalyst was dried at 105 °C overnight and then calcined at 450 °C for 2 h.

2.4. Experimental setup

Fig. 1 shows the six-series DSC fabrication that was initiated by glass marking, labeling, washing, and sintering at 500 °C. The working electrode (WE) was printed twice with TiO_2 paste on the surface of fluorine-doped tin oxide (FTO) substrate, dried, and then sintered to achieve maximum efficiency. The counter electrode (CE) was drilled to make a hole on the surface, where electrolyte will be later injected. The CE was then printed with platinum paste and sintered at 400 °C. Silver paste was also printed on the surfaces of the WE and CE before sintering process. The sintered WE was immersed in 0.5 mM N719 dye in the EtOH solution and then stored at room temperature overnight. A sandwich layer of the CE and the dye-sensitized WE electrodes was sealed with a hot-melt thermoplastic gasket. The iodide/triiodide redox couple solution was injected through the hole drilled on the CE and then sealed with aluminum tape. The fabricated DSC had an open circuit voltage (VOC) of ~0.7 V.

Fig. 2 illustrates the screen-printed four-layered thin film of the interconnected Cu-Ni/TiO_2 which was applied as a photoanode in the PEC cell of the tandem PEC cell. The first layer of the prepared Cu-Ni/TiO_2 paste was printed on the FTO glass substrate with an active surface area of 2 cm^2 by using polyester screen material (48 T and 6 μm thickness) [22].

The first layer of printed paste was dried and sintered in a high-temperature belt furnace at 400 °C for 30 min to decompose the organic compounds. The printing step was repeated four times (24 μm) to enhance the adhesiveness of the paste in the FTO substrate and improve its stability in the highly alkaline solution [32]. A small strip of conductive silver paste was also printed on top of the printed thin film as an ohmic contact before the last step of sintering. The silver strip and backside of the glass substrate were covered using a non-conductive and non-corrosive epoxy resin sealant for protection from the electrolyte.

Fig. 3 displays the multiple layers of the thin film in the FTO substrate as a WE and the platinum (Pt) rod as a CE in the PEC cell. All electrodes were immersed in the fabricated glass reactor vessel