Effect of Ni(OH)$_2$ on the photocatalytic activity of δ-FeOOH nanoparticles to produce hydrogen from water splitting


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Introduction

The development of photocatalytically-based technologies using direct sunlight radiation to produce gaseous hydrogen, via molecular splitting of water, is a real scientific challenge, in the attempt to provide low-cost and environmentally clean fuel or industrial precursors, from naturally abundant or fully renewable natural resources. Heterogeneous photocatalyst materials based on widely available and affordable materials are of particular focus on those development efforts. Among the various materials that have been used for water splitting, the iron-bearing oxides have paid attention because of their small band gap energies, stability in solution, non-toxicity, cheap production and ample material availability, iron being one of the most abundant elements on Earth. Recently, our research group reported that δ-FeOOH nanoparticles are promising photocatalysts to water splitting because of its small band gap energy ($E_g = 2.2$ eV), low cost synthesis, small particle size and interparticle mesoporosity [1]. However, the rapid recombination of photogenerated electrons and holes still limits the efficiency of the δ-FeOOH for hydrogen production.

Herein, we present the development of nanocomposites based on δ-FeOOH/Ni(OH)$_2$ for use as photocatalysts in water splitting processes to produce hydrogen. The effect of Ni(OH)$_2$ nanoparticle loading content on the photocatalytic hydrogen production rate of the as-prepared nanocomposites was investigated.

Materials and Methods

The synthesis of δ-FeOOH with 0 wt.% Ni was carried out by precipitation of an Fe$^{2+}$ solution with NaOH. H$_2$O$_2$ was added immediately after precipitation to form δ-FeOOH. Nanocomposites containing 5, 15 and 20 wt.% Ni were obtained by adsorbing and precipitating a Ni$^{2+}$ solution with NaOH on the δ-FeOOH surface. The precipitates were washed with deionized water, dried and characterized with scanning electronic microscopy (SEM), diffuse reflectance measurements, N$_2$ adsorption-desorption measurements and powder X-ray diffraction (XRD). The release of H$_2$ was monitored by chronoamperometric measurements under a 15 W $\lambda < 300$ nm UV lamp.

Results and Discussion

δ-FeOOH was identified in all samples by its (100), (101), (102) and (110) reflections, which are consistent with JCPDS File #13-87. In addition to δ-FeOOH, sample with 5, 15 and 20 wt.% Ni revealed the presence of Ni(OH)$_2$, which was identified by (002) reflection at around 38.5° (20) (JCPDS File #2-1112). SEM images showed that the Ni(OH)$_2$ changes the δ-FeOOH surface. The BET surface area was determined as 153, 167, 136 and 189 m$^2$.g$^{-1}$ for samples containing 0, 5, 15 and 20 wt.% Ni. The Ni adsorption isotherm of all samples is of type IV, indicating interparticle mesoporosity. The Ni(OH)$_2$ leads to decreasing in the pore diameter from 14 nm in 0 wt.% Ni sample to 12, 9 and 12 nm in 5, 15 and 20 wt.% Ni samples, respectively. Diffuse reflectance spectra showed that the nanocomposites absorb over a wide range of the visible spectrum, so that sunlight can be readily used for water splitting. The band gap energy was determined as 1.9 eV for all samples.

Current-voltage curves were measured in the dark and a 15 W UV lamp in the presence of all samples using 1 M NaOH as electrolyte. The dark current density was negligible in the dark. Under UV radiation the current densities (Figure 1) were 28, 40, 38 and 42 mA cm$^{-2}$ for samples with 0, 5, 15 and 20 wt.% Ni, respectively.

![Figure 1. Current density as a function of time in the presence of nanocomposites, UV light and 10 mg photocatalyst.](image)

Application of Faraday’s law of electrolysis indicates that under the given conditions 11, 26, 24 and 30 μmol h$^{-1}$ of H$_2$ are produced for 0, 5, 15 and 20 wt.% Ni samples, respectively.

In conclusion, the Ni(OH)$_2$ can act as effective cocatalysts to enhance the photocatalytic H$_2$-production activity of δ-FeOOH. The potential of Ni$^{2+}$/Ni is deemed to be lower than the conduction band of δ-FeOOH and more negative than the H$^+$/H$_2$ potential, which favors the electron transfer from conduction band of δ-FeOOH to Ni(OH)$_2$ and the reduction of H$^+$, thus enhancing photocatalytic H$_2$-production activity.

Significance

In this work, we not only show a possibility for the utilization of low-cost Ni(OH)$_2$ cocatalysts as a substitute for noble metals in photocatalytic hydrogen production but also present a facile method for producing highly active H$_2$-evolution photocatalysts by a simple precipitation method.

References