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Silver deposited holmium hydroxide nanowires for synthesis of aniline from visible light reduction of nitrobenzene

E.S. Baeissa*

Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

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ABSTRACT

Holmium hydroxide nanowires were prepared by a hydrothermal method, while silver was deposited on the surface of holmium hydroxide nanowires by a photoassisted deposition method. Holmium hydroxide nanowires and silver deposited holmium hydroxide nanowires were characterized by different techniques such as XRD, PL, XPS, UV–vis, TEM and BET surface area measurements. The photocatalytic performance of holmium hydroxide nanowires and silver deposited holmium hydroxide nanowires was measured by studied the visible light reduction of nitrobenzene to aniline. The results reveal that the form of deposited silver is a metallic silver and it well dispersed on the surface of holmium hydroxide nanowires. Band gap of holmium hydroxide nanowires was decreased from 2.92 to 2.64 eV by depositing of silver. Weight percent of deposited silver plays important role in control band gap and photocatalytic activity of holmium hydroxide nanowires. 0.3 wt% silver deposited holmium hydroxide has the lowest band gap and the highest photocatalytic activity for reduction of nitrobenzene.

1. Introduction

One of the most important chemicals and intermediates in the production of dyes, pigments, pesticides and pharmaceuticals is aniline [1,2]. Aniline was prepared by hydrogenation of nitrobenzene. In hydrogenation process, the most common catalysts are noble metals catalysts such as Au, Pd and Pt and transitions metals catalysts such as Ni and Cu [1–3], but, the hydrogenation process needs high hydrogen pressure, high temperature and high reaction time [3,4]. The preparation of aniline was done at room temperature and atmospheric pressure by using photocatalytic process [5–15]. The most famous photocatalyst it titanium dioxide due to its stability, and high photocatalytic activity. But, TiO_2 absorb in UV region and percent of UV light in solar spectrum is about 3–5%, which hinder using of TiO_2 in visible region [16]. Many methods were used to shift absorption of TiO_2 from UV to visible region such as metal and non metal doping and coupling with another semiconductor materials [17–25]. Recently, new photocatalysts which have narrow band gaps were prepared. Perovskites photocatalysts have narrow band gap [26–32]. The drawbacks of perovskites photocatalysts are high electron–hole recombination rate and low surface area. Also, researchers prepare polymer-like semiconductor materials that are considered to be an efficient photocatalyst using visible light for environmental purification and hydrogen production [33–37]. Polymer-like semiconductor materials have many properties, such as high stability, low cost and a controllable surface. Therefore, a polymer-like semiconductor material can be considered as a new material for solar energy and environmental applications. There are three drawbacks for using it as a commercial photocatalyst: a small surface area, high recombination rate of electron–hole pairs and a lack of absorption above 460 nm. Recently, hydroxide-based photocatalysts such as $In(OH)_3$ and InOOH have high photocatalytic activity for photodegradation of benzene [38,39]. To best of our knowledge, there is no reported about preparation of holmium hydroxide or silver doped holmium hydroxide nanowires. Also, there is no published paper about synthesis of aniline by hydroxide photocatalyst. Thus, this work aims to preparation of holmium hydroxide and silver deposited holmium hydroxide nanowires for preparation of aniline from visible light photocatalytic reduction of nitrobenzene.

2. Experimental

2.1. Synthesis of photocatalyst

Holmium hydroxide nanowires were prepared by a hydrothermal method. In a typical procedure, 30 ml of ethylene glycol, 98.8% was mixed with 20 ml of isopropanol, 99% and 5 mmol of holmium nitrate pentahydrate was added dropwise to them and resulting mixture was stirred for 30 min at room temperature. The obtained sol was heated at 80 °C to produce gel and the gel was dried for

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* Fax: +966 2 6952292.
E-mail address: elhambaeissa@gmail.com

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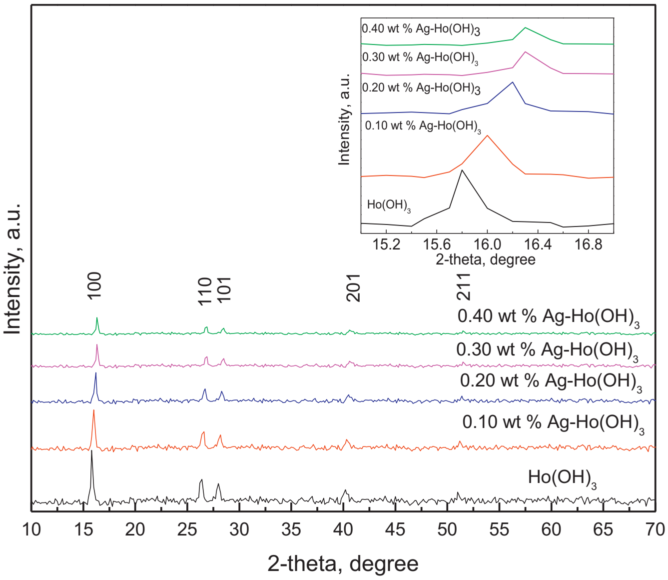

Fig. 1. XRD of holmium hydroxide and silver doped holmium hydroxide nanowires.

24 h at 100 °C. The obtained powders were dispersed in 80 ml of distilled water and heated at 180 °C for 24 h using an autoclave. After cooling temperature of autoclave, the obtained powders were washed many times by distilled water and absolute ethanol, then dried for 24 h at 80 °C. Different weight percents of silver (0.1, 0.2. 0.3 and 0.4 wt% Ag) were deposited on the surface of holmium hydroxide nanowires by a photoassisted deposition method. In a typical procedure, metallic silver was deposited on surface of holmium hydroxide nanowires using strong UV lamp (150 W) and in presence of silver nitrate solution.

2.2. Characterization techniques

Nanostructure morphology and sample dimensions were measured using JEOL-JEM-1230 transmission electron microscopy (TEM). Samples were suspended in ethanol and ultra-sonicated for 30 m. A small amount was then coated with carbon, dried on a copper grid, and loaded into the TEM. Also, N_2-adsorption measurements were taken on treated samples (2 h under vacuum at 100 °C) with a Nova 2000 series Chromatech apparatus at 77 K to calculate surface area. Crystalline phase was determined by powder X-ray diffraction (XRD) using Bruker axis D8 with Cu Kα radiation (λ = 1.540 Å) at room temperature. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-ALPHA spectrometer. Band gap performance was determined by ultra violet–visible diffuse reflectance spectra (UV–vis-DRS), measured using a UV–vis-NIR spectrophotometer (V-570, Jasco, Japan) in air at room temperature to detect absorption over the range 200–800 nm. And photoluminescence emission spectra (PL) were obtained with a Shimadzu RF-5301 fluorescence spectrophotometer.

2.3. Photocatalytic performance

The photocatalytic apparatus consists of two parts: an annular quartz tube and a sealed quartz reactor. A 500-W Xenon lamp (Institute of Electric Light Source, Beijing) with a maximum emission of about 470 nm is the visible light source. A cutoff filter (λ > 420 nm) controlled the light's wavelength. The lamp was in an empty chamber of the annular tube, and running water passed through the tube's inner thimble. Continuous cooling kept the reaction solution at approximately 30 °C. The sealed quartz reactor has a diameter of 8.3 cm and is below the lamp. For each photochemical reaction, we ultrasonically dispersed a sample of the photocatalyst (50 mg) in 10 ml nitrobenzene–CH_3OH solution (1/99, v/v). The initial concentration of nitrobenzene (NB) was 8.13×10^{-4} mol/l. The distance between the light source and the surface of the reaction solution was 11 cm. Nitrogen passed through the solution for 0.5 h before illumination to remove dissolved oxygen in the solution, freeing photoinduced electrons to reduce NB. After 2.5 h of illumination, we took the samples from the reaction suspension, centrifuged them at 7000 rpm for 20 min and finally filtered them through a 0.2-µm millipore filter to remove any residual particles. The filtrate was then analyzed using a gas chromatography Agilent GC 7890A model: G3440A Gas Chromatography using 19091J-413 capillary column (30 m × 0.32 µm × 0.25 µm).

2.4. Radical-trapping experiment

In order to identify the major active species in the reduction of nitrobenzene, radical-trapping experiments were carried out using three chemicals, disodium ethylenediaminetetraacetate (Na_2-EDTA, a hole scavenger), tert-butanol (an $^\bullet OH$ radical scavenger) and benzoquinone (a superoxide anion radical scavenger). The conditions radical-trapping experiments are the same as in photocatalytic test except we add one of chemicals to reaction mixture.

2.5. Transient photocurrent tests

Indium-tin-oxide slices (ITO) were boiled in a 2 M NaOH solution and sonicated successively in acetone, alcohol, and deionized water for 15 min each. Then, the ITO electrodes were rinsed with deionized water and dried at room temperature. The solution with $Ho(OH)_3$ was dropped onto the pretreated ITO (1.0 cm × 1.0 cm) and then dried at room temperature. The photocurrent intensity recorded using electrochemical workstation, Zahner Zennium, Germany. The photocurrent measurements were carried out in 0.1 M Na_2SO_4 solution. The applied potential was 0.2 V and a 500 WXe lamp equipped with a monochromator was used as the irradiation source to produce the monochromatic light at 420 nm.

Table 1
Texture parameters of $Ho(OH)_3$ and Ag–$Ho(OH)_3$ nanowires.

Sample	S_{BET} (m^2/g)	S_t (m^2/g)	S_{micro} (cm^2/g)	S_{ext} (cm^2/g)	V_p (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	r (Å)
$Ho(OH)_3$	40.00	41.00	27.00	13.00	0.200	0.150	0.050	30.00
0.10 wt% Ag–$Ho(OH)_3$	37.00	38.00	26.00	11.00	0.190	0.150	0.040	35.00
0.20 wt% Ag–$Ho(OH)_3$	35.00	35.00	25.00	10.00	0.160	0.130	0.030	40.00
0.30 wt% Ag–$Ho(OH)_3$	33.00	34.00	24.00	09.00	0.155	0.120	0.025	45.00
0.40 wt% Ag–$Ho(OH)_3$	31.00	31.00	23.00	08.00	0.130	0.110	0.020	50.00

Note:
(S_{BET}) ► BET-surface area (S_t) ► surface area derived from V_{l-t} plots.
(S_{mic}) ► surface area of micropores (S_{ext}) ► external surface area.
(V_p) ► total pore volume (V_{mic}) ► pore volume of micropores.
(V_{mes}) ► pore volume of mesopores (r^-) ► mean pore radius.

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