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ZnO nanonails: Organometallic synthesis, self-assembly and enhanced hydrogen gas production

Siti Nur Haslinda Mohd Daud [a], Choonyian Haw [a], Weesiong Chiu [a,*], Zarina Aspanut [a], Meiyuen Chia [a], Noor Hamizah Khanis [a], Poisim Khiew [b], Muhammad Azmi Abd Hamid [c]

[a] Low Dimensional Materials Research Centre, Department of Physics, Faculty of Science, University Malaya, Lembah Pantai, 50603 Kuala Lumpur, Malaysia
[b] Division of Materials, Mechanics and Structures, Faculty of Engineering, University of Nottingham Malaysia Campus, 43500 Semenyih, Selangor, Malaysia
[c] School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

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ABSTRACT

We report the rational synthesis and characterizations of defect-rich zinc oxide (ZnO) nanonails that were prepared by organometallic approach and their implementation as an efficient photocatalyst for hydrogen (H_2) generation. The ZnO nanonails were prepared from zinc stearate in n-octadecene that serves as non-coordinating solvent without the presence of any capping agent. Transmission electron microscopy (TEM) studies reveal that the individual triangular prismatic nanonail has an average edge length of 50–70 nm and it appears to have preferred growth orientation along [0001] crystal axis. Intriguingly, this nanonails show oriented-attachment along the flat-basal edge and self-assembled into twinned structure. Such structure is interconnected via a narrow-gap to form symmetrical twinned-like nanonails with truncated tips at both ends. In comparison to ZnO commercial nanopowder, ZnO nanonails show significant enhancement in photocatalytic H_2 gas generation rate of 53.33% under UV light for 5 h. These results demonstrate ZnO nanonails to be a substantial potential photocatalyst for efficient photocatalytic applications.

1. Introduction

Photocatalytic hydrogen (H_2) generation by water splitting with the use of suspension-based semiconductor photocatalyst creates virtually no pollution, and has the potential to become an attractive alternative clean fuel for large-scale use [1–3]. In recent years, nanosized semiconductor materials have emerged as an efficient component photocatalyst as a result of their small size and intriguing nanostructure as to increase surface area for better water conversion takes place. Till dates, many nanostructured photocatalysts such as TiO_2 [4], ZnO [5], Ta_2O_5 [6], WO_3 [7], CdS [8] and MoS_2 [9] demonstrated to be effective in stimulating the evolution of H_2 from water molecules, via photocatalytic process. However, the photocatalytic H_2 evolution efficiency is heavily dependent upon the charge separation, charge migration, and charge recombination in photocatalysts by changing the size and shape of semiconductor nanocrystals [10]. Thus, this in turn has compelled many researchers to look for better strategy in synthesizing semiconductor nanocrystals with various size or shape to further improve the photocatalytic activity especially in H_2 generation [11–13].

Zinc oxide is a direct band gap (3.37 eV) semiconductor material from group II–IV which has wide spectrum of applications ranging in versatile fields such as photocatalysis [14], piezoelectric [15], lasing applications [16], etc. Due to its wide range of utilities, the synthetic scheme in controlling the size or shape of ZnO is always in demand and is undergoing enormous changes in order to harness the shape-dependent properties such as photocatalytic [13] and optical properties [14]. It is well-known that the size, shape, surface topology and composition of ZnO can drastically alter their physical and chemical properties. Notably, anisotropic nanostructures are of particular interest owing to the asymmetrical structures of ZnO that often leads to novel, unusual and intriguing physical and/or chemical properties especially in photocatalytic studies. To dates, intense research is mainly endeavored photoelectrochemical (PEC) studies and limited reports are available for its utility in photocatalytic water splitting for the generation of H_2 even though reports are there on photolytic splitting of water using ZnO as catalyst [15–17]. For example, in the study of photocatalytic properties, engineering of ZnO into 1D nanorod with high aspect ratio has been found to significantly boost up the water splitting efficiency due to its excellent charge-carrier dynamic properties resulting from efficient electron-hole separation [18]. Additionally, another work reported on the creation of twin-

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* Corresponding author.
E-mail address: w.s.chiu@um.edu.my (W. Chiu).

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like ZnO nanostructure with tunable polar facets and shape synthesized via hydrothermal route which induced the enhancement of photocatalytic performance [19]. Therefore, there is always an inspiration for researcher that scrupulously maneuvering of morphology for ZnO with novel nanoarchitecture techniques would render a route to contribute for the advancement in photocatalysis technology.

Literally, there are several approaches have been widely employed in the preparation of ZnO nanostructures such as solution [20], gas-phase [21], and solid-state method [22]. Among these techniques, solution-phase synthesis is one of the widely used techniques due to its feasibility, economically and practicability in the preparation of high quality colloidal nanocrystals. In this context, organometallic approach by thermolysis has offer an efficient way to finely tune the shapes and size of nanocrystals. Additionally, the as-synthesized nanocrystals show excellent crystallinity due to sufficient heat is supplied during the course of reaction and thereby promote efficient decomposition of precursor followed by oxidation of cation. Besides, further post-annealing is not required and reliable scaled-up production of nanocrystals can be achieved via this synthetic scheme. Moreover, recent advancement in the similar synthesis approach shows that Zn-terminated (001) facets can be modulated by addition of oleic acid to promote the preferred orientation grow along x- and y-axis for obtaining 2D hexagonal plate-like nanocrystal. Tremendous enhancement of photocatalytic degradation of organic-dyes has been observed for this sample and the improved-performance is attributed to the contribution by enrichment of active surface originated from terminal polar (0001) and $(000\bar{1})$ [20].

We report herein a shape-controlled synthesis of ZnO nanonails via organometallic approach, where a relatively infrequent used zinc stearate has been chosen as single precursor in thermolysis reaction. Recently, we found that zinc stearate can serve as good lipophilic precursor that are highly similar to that of saturated lipid for shape-controlled synthesis [21]. As compared to the preceding reports, the distinguished difference for current synthesis scheme is without the use of capping ligand such as oleic acid and oleylamine [22]. Instead, the stearate monomer that originated from the zinc stearate precursor itself can serve as capping ligand and the results proved the feasibility of shape-modulation in producing nanonails. To our surprise, the as-synthesized nanonails were found to self-assemble into twinned rice-like structure. This so-called nanorices have average edge length of 120–160 nm and exhibit uniformity in terms of size and morphology. The nanonails are bridged by a narrow- and flat-gap which is to be approximately 3.01 Å. Photocatalytic H_2 evolution under UV irradiation of the as-prepared ZnO nanonails was analyzed by gas chromatography (GC). The result indicates that the H_2 production rate of the as-prepared ZnO nanonails reached at 30 µL for 5 h irradiation in the presence of 1-butanol as hole scavenger, which is 53.33% of increment to that of ZnO commercial nanoparticles. A possible mechanistic explanation for the advancement of photocatalytic water splitting H_2 evolution with the use of suspension-based ZnO nanonails has been proposed as well in this study.

2. Experimental

2.1. Synthesis of ZnO nanonails

All the chemicals were used as received without any further purification. ZnO nanonails were prepared by loading 3 mmol (2.11 g) of zinc stearate ($Zn(C_{18}H_{35}O_2)_2$, Meryer Chemical) and 50 ml of n-octadecene, ODE (Sigma-Aldrich, technical grade 90%) into a four-neck flask equipped with a condenser. The mixture was then heated to 120 °C for an hour under a continuous flow of Ar gas to remove the residual amount of oxygen gas and water vapor. Next, the temperature was further increased to 317 °C and the mixture was refluxed for 7 h under constant stirring. During purification stage, the yellowish precipitates were washed alternatively in hexane and acetone and finally the precipitates were dried at 80 °C overnight.

2.2. Characterizations

The morphology of ZnO nanonails were characterized by using high resolution transmission electron microscope (HRTEM, JEM-2100F, operation voltage 200 kV). X-ray diffraction (XRD) pattern of the sample was evaluated by using Siemens D5000 X-ray Diffractometer (scanning rate 0.05°/s, Cu K_α radiation and wavelength, $\lambda = 0.154$ nm). Raman spectra of ZnO were characterized by Renishaw inVia equipped with Argon source at 514 nm. The binding energy of ZnO nanonails were analyzed by using photoemission spectroscopy (PES) beam line (BL3.2a), in which a thermo VG Scientific CLAM2 electron spectrometer (maximum photo energy of 600 eV; energy step of 0.1 eV) was used during the operation. The luminescence characteristics of ZnO were carefully studied by Photoluminescence (PL) spectroscopy with He-Cd laser excited at 325 nm. Finally, the total amount of H_2 produced was quantitatively measured by using gas chromatography (GC-Agilent 7890A) with hourly monitoring.

2.3. Photocatalytic hydrogen production

A quartz-made photocell (Suprasil® 300 Quartz photocell that is equipped with a flat optical window (Window polish, standard: 60/40 scratch/dig) with total internal volume of 7.5 ml) was filled with 3.8 ml boiled deionized water (18.2 MΩ, TOC ≤ 5 ppb) and 0.037 mmol ZnO nanonails precipitates which was firstly dissolved in 0.42 ml 1-butanol. In order to remove the dissolved oxygen, the mixture was purged with nitrogen gas (99.999%) for 15 min. A 300 W Xenon arc lamp (Newport 66983, Collimated output diameter: 3.3 cm, aperture: 3.3 cm) was mounted with UV beam turner (Newport 66245, power intensity: 1.431 W/cm^2) together with full-reflector (Newport 81045). The light was projected perpendicularly into the window of photo-reactor to ensure best collimation. The distance between photocell and arc lamp was kept at 5.5 cm and the mixture was vigorously stirred (600 rpm) by using a magnetic bar during the course of irradiation. In order to quantify the volume of hydrogen gas generated, the accumulated gas sample in the headspace of photocell was withdrawn and channeled into gas-chromatography with every 15 min interval of time. Hydrogen gas production rate was then monitored for five hours duration under constant UV irradiation.

3. Results and discussion

The formation of twinned-like ZnO nanonails can be rationalized through an ingenious model proposed in our previous works in combination with other published reports elsewhere [23–26]. Possible mechanistic formation is represented in Fig. 1 and it shows a progressive built-up from a formation of ZnO pyramidal nanostructure to a self-assembled ZnO nanonail driven by van der Waals and hydrogen bonding of stearic acid formed in the cleavage of the nanostructure. In particular, the formation of twinned-like ZnO nanonails involves two synthetic mechanisms (thermal decomposition and self-assembly) within two reaction stages. In the first stage, ZnO crystal seeds were produced after nucleation via thermal decomposition of zinc stearate at elevated temperature (317 °C) in the presence of n-octadecene as polar solvent (Fig. 1a).