Journal of Molecular Catalysis A: Chemical 396 (2015) 15–22

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Woolen bun shaped CdS microspheres enfolded 1D nanowires for the superior photooxidation of dyes: A comparative case study

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ARTICLE INFO

Article history:
Received 20 February 2014
Received in revised form
13 September 2014
Accepted 21 September 2014
Available online 28 September 2014

Keywords:
Woolen bun shaped CdS morphology
Template synthesis
Crystalline nanowires
Photoactivity
Photoluminescence

ABSTRACT

Woolen bun shaped CdS microspheres (2–5 μm) wrapped by highly crystalline one dimensional CdS nanowires (length = 8–10 μm and diameter ~80 nm) are synthesized via anodic alumina membrane to achieve the best photoactivity for the decomposition of rhodamine B (50 μM) and methylene blue (20 μM) dyes using sunlight (50 mW cm^{-2}) irradiations. The higher number of surface exposed molecules for improved interactions with dye molecules in CdS nanowires led to its excellent photocatalytic performance over its spherical [cubic (~12 nm) and hexagonal (~15 nm) phase] and rod like (170 nm × 10 nm) morphology. Though of having less surface area (35.55 < 76 m^{2}g^{-1}) than nanorods, the crystalline structure with least surface defects, higher spectral response to absorb more light for multiple generation of charge carriers (e^-–h^+), and their superior delocalization for better charge separation as evidenced from its maximum (>80%) photoluminescence quenching and higher photoexcited charge carrier relaxation lifetime (3.6 ns) seems to be the cause of its outstanding performance. Many intermediate products and nearly linear increase in CO_2 production are quantified during rhodamine B degradation by CdS nanowires under different time periods of sunlight irradiation.

1. Introduction

One dimensional (1D) semiconductor nanocrystals (NC) such as nano-rods (NR), tubes (NT) and wires (NW) offers the added benefit of quantum confinement in the lateral dimension in relative to 3D spherical nanoparticles [1–4]. The properties of such anisotropic 1D material are blessed with the availability of different atomic planes on different facets, larger per-particle surface area, length/diameter controlled absorption and emission properties, superior delocalization and longer lifetime of photogenerated charge carriers [5–8]. Firstly, an effective absorption of light, secondly rapid separation of the photogenerated charge carriers and thereafter their transportations in vectored movements are the major requirements, where 1D nanostructure only meets. To sum up, control over their size, shape, composition and structure may in turn control their surface related properties (molecular adsorption and catalysis) with greater distinction and confidence.

Most of the studies in the subject of nanocatalysis involve the use of spherical (NS), nearly spherical and some undetermined shape nanoparticles (NP). However, very few studies are concerned with specific shapes to hold on catalysis, as every shape has different fraction and sequence of atoms that are located at different corners, edges and faces [9,10]. As a result, different reactivity's and selectivity's may be expected on distinct surfaces of NPs with different shapes. For an example, a cube like morphology of Ag NP has been found to be nearly 14 times more active for the oxidation of styrene than its plates like morphology, and 4 times more active than its spherical shape [11]. Zhou et al. exposed that CeO_2 nanorods having (0 0 1) and (1 1 0) planes exhibited higher catalytic activity for CO oxidation than do by nanospheres [12]. Nanowires having constrained (diameter in nanometers) and unconstrained (length up to several tens of micrometers) dimensions show potential in the fabrication of new nanodevices [13,14]. Inspired by this, studying of metallic (Cu, Ag, Au and Pt) and semiconducting (TiO_2, ZnS, ZnO, CdS and $BiFeO_3$) nanowires becomes a popular subject in the current research for their extendable applications [15–18].

Absorption in the UV light (~4% of the solar energy) and fast recombination of photoexcited e^-/h^+ pairs in TiO_2, ZnS, and ZnO like wide band gap (3.0–3.7 eV) semiconductors (SC), impair their applications [19–21] to a greater extent. In contrast, CdS, as a visible light-driven photocatalyst (~2.42 eV) with a suitable band edge positions facilitate CdS based photocatalyst moving forward to the practical application such as hydrogen evolution [22,23] photocatalytic reactions [24,25] and photovoltaic's [26]. So far, various physiochemical methods have been employed for the synthesis of 1D CdS nanowires, including hydrothermal [27], solvothermal [28], chemical vapor deposition [29], thermal evaporation [30] etc. Among various fabrication strategies, template assisted synthesis

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http://dx.doi.org/10.1016/j.molcata.2014.09.025
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is one of the most elegant methods for preparation of 1D nanowires through exceptional control on their size, shape, composition, crystallinity, orientation and uniformity [31–33]. In this respect, Xiao et al. have well optimized the reaction conditions like etching time and NaOH solution concentration (0.1–1.2 M) for the optimum production of alumina nanotubes or nanowires from porous alumina membrane [34]. Literature suggests that most of the work has been done on synthesis, optical properties and structural study of CdS nanowires using template approach, but the effect of their high aspect ratio, high crystallinity and exceptional uniformity on its photocatalytic activity is rarely observed [17,35].

In the present study, well growth and crystalline 1D CdS nanowires are synthesized to achieve the best photocatalytic activity for degradation of rhodamine B (RhB) and methylene blue (MB) dyes under direct sunlight. Subsequently, we compared the photoactivity of as synthesized CdS nanowires with its spherical and rod shape-morphology.

2. Experimental

2.1. Materials

Cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$), cadmium chloride ($CdCl_2$), sodium sulfide (Na_2S), ethylenediamine ($H_2NCH_2CH_2NH_2$), thiourea ($SC(NH_2)_2$), dioctyl sodium sulfosuccinate ($C_{20}H_{37}NaO_7S$), heptane (C_7H_{16}), rhodamine B ($C_{28}H_{31}ClN_2O_3$), methylene blue ($C_{16}H_{18}N_3SCl$), sodium hydroxide (NaOH) and ammonium hydroxide (NH_4OH) were purchased from Loba Chemie and used without further purification. The most commonly anodized alumina membrane (AAM) from Whatman of 50 nm pore sizes was used for the growth of nanowires. The advantage of using AAM with fixed pore size as a hard template (high rigidity and resistance to high temperatures) facilitates better control over size, shape and unidirectional aligned nanowires arrays. The membrane was also sonicated in distilled water (DI) for a few minutes prior to use in order to avoid any air bubbles present within the nanochannels. Deionized water was obtained using an ultra filtration system (Milli-Q, Milipore) with a measured conductivity 35 mho cm^{-1} at 25 °C.

2.2. Synthesis of CdS nanowires

CdS nanowires were synthesized using a two-cell electrodeposition method, briefly, a paired cell was assembled using two Teflon half-cells and anodized alumina membrane was mounted between them. In the first compartment or cell an aqueous solution of $CdCl_2$ (0.01 M with a few drops of NH_4OH) was added and allows to diffuse through the membrane for 60 s prior to the introduction of other solution of Na_2S (0.01 M) in second compartment. The cell was then left for 2 h at room temperature. During reaction time, both $CdCl_2$ and Na_2S were dissociated into Cd^{2+} and S^{2-} in an aqueous medium and attracted by the electrostatic force to give CdS inside the AAM template as shown in Scheme 1.

The template was finally removed by dissolving in 1 M NaOH solution for 15 min and the resulting solution was washed several times with ethanol and distilled water and finally dried to collect yellow powder (% yield = 35%). Spherical nanoparticles of CdS with cubic [36] and hexagonal phase [37] and rod-like particles with hexagonal phase [38] were prepared [See supporting information (SI)] for comparison as by reported elsewhere.

2.3. Photocatalytic reactions

The photoactivity of the CdS-NW (amount = 2 mg) was evaluated by the photodegradation of 10 ml of RhB (5×10^{-5} mol L^{-1}) and MB (2×10^{-5} mol L^{-1}) dyes in a 25 ml beaker under continuous magnetic stirring and sunlight (exposed area = 12.56 cm^2 and intensity = 50 mW cm^{-2}) irradiation and analyzed by UV–vis spectrophotometer (λ_{max} = 554 nm for RhB and λ_{max} = 665 nm for MB). The reaction mixture was kept in the dark under stirring for 1 h to attain the adsorption/desorption equilibrium.

2.4. Characterizations

Scanning electron microscopy (SEM) images were taken from JEOL (JSM-7600F) to elucidate the surface topography of sample. Energy-dispersive X-ray spectroscopy (EDS) was carried out on SEM-JEOL for elemental analysis. Microwave Plasma Atomic Emission Spectrometry (Agilent Technologies 4100, MP-AES) was used for quantitative analysis of any aluminum residue/content on the resulting CdS sample. Transmission electron microscope (TEM) photographs were taken on Hitachi 7500 model operating at voltages of 120 kV. The crystallographic studies of CdS nanostructures have been carried out using X-ray diffractometer by PANalytical X'Pert PRO with Cu-Kα (k = 1.54 Å) radiation operated at 45 kV. Optical study was done by UV–vis spectrophotometer (Analytikjena specord-205) and spectrofluorimeter (Perkin-Elmer LS55). The specific surface area was determined by N_2 adsorption method using a Smart Sorb 92/93 instrument after preheating 100 mg of samples at 150 °C for 1 h. For the detection of intermediates, as obtained aqueous solution of RhB after 1 h of sunlight exposure with CdS-NW was centrifuged, filtered through cellulose filter (0.22 μm) and then extracted a number of times with dichloromethane. Residue thus obtained of RhB sample was re-dissolved in methanol and analyzed by gas chromatography–mass spectroscopy (Shimadzu, GC-2010 and GC–MS-QP 2010 plus) using RTX-5Sil-MS column (30 m × 0.25 mm × 0.25 μm). Helium was used as a carrier gas with a flow of 1 ml/min through capillary column. Injector was maintained at 240 °C, while transfer line was kept at 260 °C and 1 μl of the sample was injected. Oven was programmed at 60–300 °C @ 6 °C/min rise of temperature. The CO_2 evolution was determined by injecting 1 ml of the gaseous mixture from the reaction vessel (sealed test tube containing RhB solution plus catalyst) into the gas chromatography (NUCON-5765) using Propak-Q column with nitrogen as carrier gas (30 ml/min) and thermal conductivity detector (TCD). Column oven was maintained at 40 °C while injector and detector were at 70 and 80 °C, respectively.

3. Results and discussion

3.1. Morphological and structural analysis

Scanning electron microscopy (SEM) was carried out to elucidate surface morphology of CdS before and after dissolution in 1 M NaOH aqueous solution. Monodisperse spherical morphology of CdS having size of 2–5 μm is observed as shown in the image of Fig. 1a. The enlarge view shown in Fig. 1(b–d) confirms that this microsphere is actually composed of several haphazard nanowires arranged like a spinning wool. Notably, all CdS nanowires are not emerge to be originated from a single point, which state that nanowires grown in different pores might be arranged together in densely packed spherical bundles as depicted in Scheme 1. After dissolution of AAM with 1 M NaOH solution resulted in uniform fashion of CdS nanowires with length in the range of 8–10 μm and diameter of 80 nm as shown in Fig. 1e. Dense grass likes vertically or parallel texture of many CdS nanowires are also observed in Fig. 1f and g. Nanowires with much uniformity in diameter are clearly distinctive in the image 1 h. The EDS spectrums of pure alumina membrane (template), alumina membrane trapped CdS and resulting CdS powder after dissolution of alumina membrane with NaOH are shown in images i (1-3) of Fig. 1 and that confirms the presence of corresponding Al, O, Cd and S elements with their appropriate atomic percentage. In order to further confirm any residue or