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Structural evolution of cobalt oxide–tungsten oxide nanowire heterostructures for photocatalysis

Yuan Li[a], Nitin Chopra[a,b,c,*]

[a] Metallurgical and Materials Engineering Department, Center for Materials for Information Technology (MINT), The University of Alabama, Tuscaloosa, AL 35487, USA
[b] Department of Biological Sciences, The University of Alabama, Tuscaloosa, AL 35487, USA
[c] Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, USA

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ABSTRACT

Tungsten oxide (WO_3) and cobalt tungstate ($CoWO_4$) decorated one-dimensional cobalt oxide (Co_3O_4) nanowire heterostructures were fabricated through a facile and cost-effective approach. The process includes vapor–solid growth of cobalt oxide nanowires *via* a thermal oxidation method and sputtering coating of tungsten oxide on the standing Co_3O_4 nanowires. To further modulate the structure and/or morphology and improve the crystallization of tungsten oxide, the product was subjected to a post-annealing process, which resulted in free-standing Co_3O_4–WO_3/$CoWO_4$ multi-component nanowire heterostructures. The crystal structures, morphologies, and chemical composition at each fabrication stage were studied in detail using microscopy and spectroscopy. The investigation for the first time showed the dry processing route for formation of such novel nanowire heterostructures. The photocatalytic performance and behavior of such nanowire heterostructures were further demonstrated for the degradation of water-contaminating organics (*via* a phenol photodegradation process). The photocatalytic efficiency of the final nanowire heterostructures was estimated to be increased by ∼30% for both visible and UV illumination as compared with the as-produced Co_3O_4 nanowires.

1. Introduction

Environmental remediation technologies for efficient water cleaning *via* the photocatalytic methods are of particular interest [1,2]. The demands are for using cheap catalyst with suitable energy and electronic structures. Compounds such as phenol, textile dyes, and poly chloro-biphenyls (PCBs) contaminate water through domestic sewage, industrial wastewater, and agriculture wastewater. Even low concentration of such contaminants ($<1\ mg\ L^{-1}$) is hazardous since they prevent the growth of aqueous organisms and reduce the photosynthesis activity of the marine flora [3]. Various physical and chemical methods for the removal of these contaminants from water have been studied, including absorption (using activated carbon), thermal degradation, and wet-air oxidation/ozonation [4,5]. However, these processes are cost- or energy-intensive and suitable for higher-concentration contaminants [5,6]. Thus, catalytic or photocatalytic degradation of organic pollutants is critical and holds potential for efficient, cost-effective, and environmental-friendly decontamination strategy [3,7–9]. Furthermore, photocatalytic degradation of organics can be conducted at room temperature and atmospheric pressure, which makes this approach commercially viable [3,10].

Various metal oxide semiconductors such as TiO_2, ZnO, Fe_2O_3, and sulfides (CdS, ZnS) exhibit photocatalytic behavior attributed to their suitable electronic, surface, and crystal structure [6,10,11]. Among these oxides, TiO_2 is the best known photocatalyst due to its high photocatalytic activity and good photostability in aqueous medium [12,13]. However, its sustainable application is largely limited due to the wide energy band gap (only UV-active) and high charge recombination [14]. Meanwhile, ZnO and Fe_2O_3 are unstable in various industrial wastewater streams [6]. Metal sulfides will release toxic sulfides under illumination and thus their suitability for water decontamination was also constricted [6]. Out of several material choices, Co_3O_4 and WO_3 are earth-abundant catalytically active materials with relatively narrow band gap energies [4,15]. These two oxides present advantages such as extended photosensitivity in the visible region, long-term physical/chemical stability, and/or ease of preparation [15]. However, band gap engineering of such oxides is a challenge and mainly depends on their morphology, size, and configuration. If the aim was to develop a photocatalyst that can also survive

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* Corresponding author at: Metallurgical and Materials Engineering Department, Center for Materials for Information Technology (MINT), The University of Alabama, Tuscaloosa, AL 35487, USA.

E-mail addresses: nchopra@eng.ua.edu, nchop2@gmail.com (N. Chopra).

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multiple processing or treatment cycles then catalysts based on single component nanostructure or oxide cannot surpass the advantages of heterostructured photocatalysts. The latter implies nanoscale systems combining two or more materials or nanostructures, where the synergistic effect of all the components results in a multifunctional catalytic architecture.

Nanowire heterostructures are novel one-dimensional nanoarchitectures that possess unique surface functionality, chemical and electrical properties [16,17]. Such heterostructures can exhibit anisotropic light-matter interactions and thus are promising for photocatalysis processes [18,19]. For instance, one-dimensional geometry (e.g., core–shell nanowires) can allow for greater absorption of light in longitudinal direction and result in efficient charge transport (or charge carrier generation) in radial direction [19,20]. However, such merit exhibition shows significant dependence on the structure, morphology, size, and material selection. Meanwhile, another challenge for photoactive nanostructures is to eliminate or mitigate the use of noble metals [21]. This further narrows down the materials selection criteria for photoactive systems. In this regard, we propose an interesting and novel photocatalyst design through the hybridization of cobalt oxide and tungsten oxide, which can result in one-dimensional multi-component heterostructures with specific structure and tunable band gap energies [19,22,23]. Moreover, tungsten oxide (WO_3) is n-type semiconductor with band gap energy of ~2.8 eV while cobalt oxide (Co_3O_4) is a p-type semiconductor with band gap energy ~1.6 eV for O^{2-} to Co^{3+} charge transfer and ~2.2 eV for O^{2-} to Co^{2+} charge transfer [19,24,25]. Recently Chakraborty et al. [26] studied their combination of Co_3O_4 and WO_3, which has been proved to be able to form a stable p–n junction at the interface and further generate a constant electric field at equilibrium [12,27]. Under illumination, the photo-excited electrons are prone to move to the positive field and the holes flow into the negative field. As a result, the electron–hole pairs can be separated in an efficient manner, leading to significantly improved photocatalytic activity [28].

The major goal of this work was to develop novel oxide-based nanowire heterostructures with controlled morphology, chemical composition, and interfaces. The fabrication of the cobalt oxide-tungsten oxide nanowire heterostructures was achieved in a surfactant-free and dry processing route. Free-standing Co_3O_4 nanowires were grown in a water vapor-assisted thermal oxidation process [29,30]. Further sputtering coated with WO_3 thin shell, and annealed in air. The resulting nanowire heterostructures remained standing on the substrate after multiple processing steps. The morphology, interfaces, chemical composition, and crystal structure of the heterostructures were characterized by various microscopic and spectroscopic techniques. The photocatalytic performance and kinetics of the same were also studied for the degradation of phenol.

2. Experimental section

2.1. Materials and methods

Cobalt (Co) foil was purchased from Alfa Aesar (Ward Hill, MA). Tungsten oxide (WO_3) target (99.99%) was provided by AJA International, Inc. Phenol was purchased from Sigma–Aldrich (St. Louis, MO). DI water (18.1 MΩ-cm) was obtained using a Barnstead International DI water system (E-pure D4641). All chemicals were used without further purification. Branson 2510 Sonicator (Danbury, CT) was used to assist the surface cleaning of Co foil/powders in acetone and DI-water. ATC ORION sputtering system (AJA international, Inc., North Scituate, MA) was used. 5% O_2/Ar gas cylinders were purchased from Airgas South (Tuscaloosa, AL).

2.2. Growth of Co_3O_4 nanowires

Roughened Co foil with a thickness of ~0.2 mm was used as the initial substrate [29]. Before the thermal growth, the pre-treated samples were first cleaned in acetone and then in DI-water. The samples were further treated with 10% HNO_3 solution for 15 s to remove pristine surface oxide layers. The growth of Co_3O_4 nanowires was carried out in a quartz tube furnace (at ~450 °C for 10 h) in the presence of humidity (flow rate ~12 mg/min) and 5% O_2 in Ar (flow rate ~12 SLM).

2.3. Fabrication of Co_3O_4–WO_3 nanowire heterostructures

The as-produced Co_3O_4 nanowire was pre-coated with WO_3 in a RF sputtering process directly using the commercial tungsten oxide (WO_3) as the target. The sputtering was carried out at 50 W for 10 min at chamber pressure of $\sim 3 \times 10^{-3}$ Torr. The measured sputtering rate of WO_3 was ~0.02 nm/s. This should result in a WO_3 thickness of ~12 nm on a flat substrate. In the following, this as-sputtered Co_3O_4–WO_3 nanowire heterostructures were further subjected to a high-temperature (450 °C) air-annealing process for 30 min, which leads to the formation of final annealed nanowire heterostructures.

2.4. Photodegradation of phenol

To test the photocatalytic performance of the nanowire heterostructures, degradation of phenol (~3 mM in DI-water) was carried out under visible light or UV illumination. Standing nanowire heterostructures on the Co foil ($2 \times 2\ cm^2$) were immersed in ~3 mL phenol solution. This was followed by further addition of ~100 μL H_2O_2 (37%) as the sacrificial agent [31,32]. Either UV illumination lamp (~254 nm, 8 W) or visible illumination lamp (~360 nm, 8 W) was utilized as the light source. The solution was gently stirred during the photodegradation. UV–vis absorbance spectra of the phenol solution were recorded every 30 min for estimating the concentration of phenol. This photodegradation process was continued for ~8 h.

2.5. Characterizations

Scanning Electron Microscopy (SEM) images were obtained using FE-SEM JEOL-7000. Tecnai F-20 was used to collect Transmission Electron Microscopy (TEM) images and Energy Dispersion Spectroscopy (EDS) line-profiles in the Scanning Transmission Electron Microscopy (STEM) model. Philips X'Pert-MPD X-ray Diffraction (XRD) System was used for the phase analysis. Raman spectra were collected using Bruker Senterra system (Bruker Optics Inc. Woodlands, TX) equipped with 785 nm laser source. Kratos Axis 165 X-ray photoelectron spectroscopy (XPS) with a mono-aluminum gun was used. Full range XPS spectra were collected at 160 eV pass energy for high-resolution spectra which were collected at 40 eV pass energy. UV–vis reflectance spectra of the cobalt oxide nanostructures were obtained using DH-2000 UV–VIS-NIR light source. The optical transition energy value can be determined using Eq. (1) as follows:

$$ah\upsilon = A(h\upsilon - E_g)^n, \qquad (1)$$

where a is absorption coefficient, A is a constant, $h\upsilon$ is the energy of light and n is a constant depending on the nature of the electron transition (n assumes the values 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively). Since the absorption coefficient (a) is proportional to Kubelka–Munk function ($F(R)$),

$$F(R) = (1 - R)^2/2R = a/s, \qquad (2)$$