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Fe_2O_3–TiO_2 core–shell nanorod arrays for visible light photocatalytic applications

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ABSTRACT

By using the glancing angle deposition technique and post-deposition annealing, Fe_2O_3–TiO_2 core–shell nanorod arrays with specific crystalline states can be designed and fabricated. The Fe_2O_3–TiO_2 core–shell samples annealed at temperatures greater than 450 °C formed α-Fe_2O_3 and anatase TiO_2, and showed higher catalytic efficiency for the degradation of methylene blue (MB) under visible light illumination when compared with pure anatase TiO_2 or α-Fe_2O_3 nanorod arrays. Solar conversion of carbon dioxide and water vapor in the presence of Fe_2O_3–TiO_2 core–shell nanorod arrays was also investigated. Carbon monoxide, hydrogen, methane, and methanol along with other hydrocarbons were produced after only several hours' exposure under ambient sunlight. It was determined that the core–shell structure showed greater efficiency for solar CO_2 conversion than the pure TiO_2 nanorod arrays.

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1. Introduction

In recent years, researchers have spent considerable effort in developing methods to use solar energy more efficiently in order to achieve a sustainable solution to the world's long term energy crisis. One promising strategy is to design and fabricate highly efficient photocatalysts that use solar illumination to facilitate chemical reactions that produce a fuel, reduce pollution, or both [1–3]. Among the materials studied and proposed, metal oxides nanostructures have attracted the most attention as photocatalysts due to their large surface-to-volume ratio, adjustable band gap E_g, and superior stability [4–8]. Particularly, TiO_2 photocatalysts have been investigated extensively for solar water splitting, CO_2 conversion, environmental decontamination, among others [9–11]. Its non-toxicity, low cost, and high stability make TiO_2 suitable for those applications. However, the large E_g value of TiO_2 ($E_g = 3.2$ eV) inhibits the absorption of the visible light, the largest part of the solar spectrum, which significantly limits the solar conversion efficiency. Therefore, in order to efficiently utilize most of the solar spectrum, current research has focused on designing novel complex nanostructures with a broad wavelength range for light absorption in the UV–vis–near infrared region [12–16]. There are two common approaches to increasing the visible light absorption of TiO_2: coupling with a lower band gap material (Fe_2O_3, Cu_2O, CuO, CdSe, CdTe, etc.) to create a semiconductor junction [3,17,18] or doping or co-doping with non-metals (carbon, sulfur, fluorine, nitrogen, etc.) [6,19] and metals (silver, gold, platinum, etc.) [20]. Among these two approaches, coupling TiO_2 with smaller band gap semiconductors has distinct advantages: the band gap can easily tuned by selecting different semiconducting materials, the semiconductor junction can spatially separate electron–hole pairs and thereby decrease recombination rates, and finally, combining two or more semiconductors is a relatively simple process that is compatible with many different fabrication techniques.

Hematite, α-Fe_2O_3, is an active nanocatalyst material that makes an interesting companion to TiO_2 due to its narrow band gap ($E_g = 2.2$ eV), low cost, and high stability. Recent studies show that TiO_2–Fe_2O_3 multi-layered thin films and other composite structures (e.g., α-Fe_2O_3 particles coated TiO_2 nanosheets, core–shell structured TiO_2–Fe_2O_3 nanocomposites) are active in the UV–vis

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region of the spectrum and can be more efficient photocatalysts than pure TiO_2 toward degradation of a variety of organic compounds [7,21–26]. The higher catalytic efficiency results from greater visible light absorption, and enhanced charge separation of the electron–hole pairs. Particularly, under visible light, electron–hole pairs only generate in Fe_2O_3 but not in TiO_2. Thus electrons could be transferred from to conduction band of Fe_2O_3 to TiO_2, while the holes remain in the valence band of Fe_2O_3 [22,24,26–28]. The nature of the contact between TiO_2 and Fe_2O_3 is also critical in determining the efficiency of the charge separation process and overall catalytic efficiency. Recently, it was reported that the enhanced photocatalysis of Fe_2O_3–TiO_2 nanocomposites is mainly due to the junction or co-catalyst effect for reactions [3]. There are also a number of other factors that affect the photocatalytic processes, including the surface area, nanoparticle's size and shape, crystallinity, electron–hole recombination rate, heterojunction and synergistic effects between materials, as well as adsorbent–adsorbate interaction [22,24,26–28].

Therefore, it is interesting to explore new architectures and fabrication techniques in order to further study and optimize the TiO_2–Fe_2O_3 system for highly efficient photocatalysts.

Glancing angle deposition (GLAD) is a simple and well-known technique in which the incident material vapor is directed toward a substrate at large incident angles with respect to substrate surface normal (>70°), while the substrate is rotated azimuthally at a constant speed, resulting in self-organized vertically align nanorod arrays [13,29–31]. Our previous work has proven that this is a versatile method in fabricating TiO_2-WO_3 core–shell structured photocatalysts [13,32]. Additionally, the dynamic shadowing growth (DSG) technique has several advantages for metal oxide nanostructure fabrication: simplicity, flexibility, and compatibility with other microfabrication techniques.

In this work, we design and fabricate Fe_2O_3–TiO_2 core–shell nanorod arrays using the GLAD technique. The core–shell architecture is chosen to maximize the interfacial contact between Fe_2O_3 and TiO_2 and is expected to increase charge separation and catalytic efficiency. A post-deposition annealing treatment is developed in order to obtain a structure with twofold active crystalline phases, α-Fe_2O_3 and anatase TiO_2. In addition to their morphological, structural, and optical properties, the visible light photocatalytic activities of the Fe_2O_3–TiO_2 core–shell samples for methylene blue destruction and CO_2 conversion are investigated. It is found that the α-Fe_2O_3–TiO_2 core–shell nanorods arrays are more efficient photocatalysts for both of these processes under visible light illumination than either of the pure material photocatalysts, TiO_2 and Fe_2O_3.

2. Materials and methods

The source materials used in this study, Fe_2O_3 (99.85+%, metal base), and TiO_2 (99.9%) were purchased from Alfa Aesar (Ward Hill, MA) and Kurt J. Lesker (Clairton, PA), respectively and were used as received. Cleaned glass microscope slides (Gold Seal® Catalog No. 3010) and Si (1 0 0) wafers (Montco Silicon Technologies Inc.) were used as substrates for material deposition. High purity methylene blue (MB, C16H18ClN3S; CAS No. 122965-43-9) was obtained from Alfa-Aesar (Ward Hill, MA).

2.1. Fe_2O_3–TiO_2 core–shell nanorod arrays preparation

The nanorod arrays were fabricated in a custom designed electron-beam deposition system (Torr International, Inc.) [13,33]. Fe_2O_3 nanorods was first deposited onto Si and/or glass substrates with the incident angle $\theta = 86°$, with the substrate rotating azimuthally at 0.5 rev/s. The deposition proceeded until a nominal thickness of 3 μm, as determined by a quartz crystal microbalance (QCM), was achieved. Based on the nanorod separation and height measured using scanning electron microscopy, the vapor incident angle for the TiO_2 shell deposition was determined to be $\theta = 6.1°$. Further details describing this calculation and the GLAD core–shell deposition method can be found in Ref. [13]. Using the same substrate azimuthal rotation rate of 0.5 rev/s, the TiO_2 shell was deposited to a nominal thickness of 50 nm. The as-deposited Fe_2O_3–TiO_2 nanorod samples were then annealed in a quartz tube furnace (Lindberg/Blue M Company) in open air for 3 h, at different preset temperatures from 350 °C to 750 °C.

2.2. Characterization

The morphologies of the samples were examined by a field-emission scanning electron microscope (SEM, FEI Inspect F) equipped with an energy dispersive X-ray spectrometer (EDX). The structural properties of the samples were characterized by a PANalytical X'Pert PRO MRD X-ray diffractometer (XRD) with fixed incidence angle of 1.5°. The XRD patterns were recorded with Cu $K\alpha$ radiation ($\lambda = 1.5405980$ Å) in the 2θ range from 20° to 80° at step size of 0.014°. The optical properties of the samples were measured by a double beam UV–visible light (UV–vis) spectrophotometer (JASCO V-570) over a wavelength range from 300 to 800 nm. The photocatalytic activities of the samples were evaluated by the photocatalytic degradation of a 10 ppm (~31 μM) methylene blue (MB) aqueous solution (of pH value ~6.2) under visible light irradiation. The TiO_2, Fe_2O_3, or Fe_2O_3–TiO_2 samples on glass substrates were placed into a 10 mm × 10 mm × 45 mm clear methacrylate cuvette filled with 4.0 ml of MB solution. The cuvettes were illuminated for a total time of 4 h by a 250 W quartz halogen lamp (UtiliTech) covering wavelength range from 400 to 800 nm. The incident light intensity on sample was kept constant at 65 mW/cm^2, as measured by an optical power meter (Thorlabs PM100D/S310C). A rectangular mask (2.4 cm^2) was placed in front of the all samples to keep the light power the same for all photodegradation experiments. A water filter was placed in front of the cuvette to absorb the IR light. The photodegradation the MB solution were measured by examining the in-situ UV–vis transmission spectra of the MB solution using an Ocean Optics spectrophotometer (USB 2000). The absorbance peak at $\lambda = 664$ nm was monitored at regular time increments of 20 min and were used to evaluate the photodegradation rate of MB. For the CO_2 photoconversion study, a syringe-type chamber (volume of 20 ml) was designed as solar-gas convertor reactor with gas inlets/outlets, optical window and sample stage holder. It was loaded with three 1 × 1 cm^2 Fe_2O_3–TiO_2 core–shell nanorod array samples (or control samples of TiO_2 nanorod arrays) in CO_2 and H_2O gas mixture in ambient light and atmospheric conditions. The evolving gas in this system was probed by micro gas-chromatograph (GC) instrumentation equipped with OV1 and pora-plot columns.

3. Results and discussion

3.1. Morphology and composition of the core–shell structures

The Fe_2O_3 nanorod samples, which serve as the "core" template in the core–shell structure, were analyzed using scanning electron microscopy (SEM). As shown in Fig. 1a, the arrays consist of well separated and vertically aligned nanorods with tetrahedral facets. The overall array morphology is consistent with GLAD growth. The morphologies of the individual nanorods is consistent with a fiber texture resulting from a preferred growth direction, where the exposed facets are the low energy crystalline planes, most likely [34,35]. Quantitative measurements of the SEM images reveal that the average height of the Fe_2O_3 nanorods is $h = 1220 \pm 30$ nm, and

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