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ScienceDirect
Ceramics International 40 (2014) 1553–1559
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Incorporation of cadmium sulfide nanoparticles on the cadmium titanate nanofibers for enhanced organic dye degradation and hydrogen release

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Received 24 June 2013; received in revised form 7 July 2013; accepted 7 July 2013
Available online 12 July 2013

Abstract

In this study, the effective cadmium sulfide NPs were successfully encapsulated on cadmium titanate electrospun nanofibers. Calcination of electrospun nanofiber mats composed of titanium isopropoxide, poly (vinyl pyrrolidone) (PVP) and cadmium acetate dihydrate with few drops of ammonium sulfide in air at 600 °C led to the production of good morphology of CdS decorated cadmium titanate nanofibers. The morphology and structure of as-synthesized nanocomposites were characterized by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD). As-synthesized nanocomposites exhibited a strong photocatalytic activity for decomposition of methylene blue (MB) under visible light and showed good hydrogen release from hydrolysis of the ammonia–borane complex. The perfect recovery of catalyst after reaction and its unchanged efficiency for cyclic use showed that it will be an economically and environmentally friendly photocatalyst. The results indicated that the $CdS/CdTiO_3$ photocatalysts possess improved photocatalytic activity than that of $CdTiO_3$ alone.

Keywords: A. Electrospinning; B. Nanocomposite; E. Photocatalyst; E. H_2 release

1. Introduction

Energy crisis and environmental pollution are the biggest challenge in the 21st century at a global level. Many photocatalysts have been reported for the splitting of water in the presence or absence of sacrificial agents, producing Hydrogen as a clean energy source, and for the degradation of organic pollutants [1–6]. Semiconductor photocatalysts have attracted much attention in recent years because of their potential in solving global energy and environmental problems. Among them, composite systems made of more than two semiconductor components are considered a promising method to develop a high efficiency photocatalyst working under visible light because they can compensate for the disadvantages of the individual component, and induce a synergistic effect, such as an efficient charge separation and improvement of photostability [7,8].

Since the discovery of the photocatalytic activity of TiO_2 for hydrogen production and organic dye degradation, photocatalysis has been considered to be a promising technique for solving energy and environmental issues using abundant sunlight [9]. Titanium based oxides are of great interest due to their high refractive index, direct wide energy band gap and low absorption properties [10,11]. Although TiO_2 has been extensively studied and widely used for water splitting and environment treatment, it has practical limitations in its use due to the requirement of near ultraviolet (UV) irradiation for effective photocatalysis. Therefore, the development of efficient visible-light-responsive photocatalysts is a highly

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http://dx.doi.org/10.1016/j.ceramint.2013.07.042

challenging but desirable goal for renewable energy resource and environment remediation which can effectively use a maximum of the solar spectrum.

Due to the excellent activity under visible-light and suitable negative conduction band (CB) edge compared to the reduction potential of hydrogen, CdS (2.4 eV) is most extensively used as a photocatalyst [12,13]. However, the low surface area and high recombination rate of photo induced charge carriers owing to its band energies lower the photocatalytic activity of CdS [14,15]. The photocatalytic efficiency of CdS can be enhanced by reducing the recombination rate of photo induced charge carriers. For this strategy, coupling with wide band gap semiconductors such as TiO_2, ZnO, NiO has been carried out [16–18]. One of these oxides, cadmium titanate ($CdTiO_3$), has excellent dielectric, sensing and optical properties [19,20]. By incorporation of CdS nanoparticles to the system the application of cadmium titanate can be broadened as a photocatalyst. Secondary pollution is one of the problems limiting the widespread applications of nanostructured photocatalysts. In other words, most of the reported nanostructured photocatalysts can effectively eliminate the organic pollutants; however, they create a serious issue due to the difficulty of separating the utilized nanostructured photocatalysts from treated water, especially in the case of large-scale processes [21]. Therefore, here, prior formed CdS NPs are incorporated into $CdTiO_3$ nanofibers to achieve better stability. By doping the CdS nanoparticles inside the $CdTiO_3$ nanofibers, we were simultaneously able to solve the problem of photo corrosion and toxicity of CdS nanoparticles. The introduced materials overcame the toxicity problem of CdS as it is well incorporated on the nanofibers.

Hydrogen energy is one of the most important kinds of energy; it is pollution-free compared with petroleum products. Storage of hydrogen in large quantities for on-board applications remains a major constraint for its widespread usage. The low density of H_2 makes it difficult to store it in compressed or liquefied form. In recent years, hydrogen was stored in solid materials; they were considered a reservoir for hydrogen. Among these materials, the ammonia–borane complex (AB, H_6BN) has been identified as one of the leading candidates as a hydrogen reservoir owing to its high hydrogen content (19.6 wt%) which exceeds that of gasoline [22], solubility/stability in aqueous solution and stability toward hydrolysis in aqueous solutions for at least 4 days [23,24]. It can release hydrogen by two main routes; pyrolysis or a hydrolysis route. Recently, the hydrolysis of AB was accomplished by the use of noble and non-noble metallic, bimetallic, and tri metallic nanoparticles (NPs) due to their good catalytic activity and large surface area to volume ratios. The development of efficient, low cost and stable catalysts is very important for practical application to overcome the high cost of the reported precious metals [25].

Electrospinning has attracted much attention as a simple and versatile technique capable of generating continuous nanofibers not only from polymers [26,27], but also from inorganic [28] and hybrid (organic–inorganic) compounds [29–31] which have different applications in a wide range of areas, e.g., filtration, protective clothing, catalysis, sensors, energy storage, biomaterials [31–33]. Here, we report the synthesis of ilmenite rhombohedral phase $CdTiO_3$ nanofibers with simultaneous formation of CdS NPs throughout the surface of nanofibers via the electrospinning technique followed by calcination in air. This is a simple and efficient approach to synthesize the composite of cadmium titanate decorated with CdS nanoparticles. Imran et al. reported a humidity sensor based on electrospun $CdTiO_3$ nanofibers [34,35]. Similarly, bulk $CdTiO_3$ and its thin films have been investigated widely [36–38]. However, the synthesis of $CdTiO_3$ nanofibers containing CdS NPs has not been reported yet. To explore a new application, the CdS/$CdTiO_3$ nanocomposite is primarily employed as a photocatalyst for release of hydrogen by the hydrolysis of ammonia–borane and the degradation of methylene blue under visible light irradiation to our knowledge.

2. Experimental procedure

2.1. Materials

Polyvinylpyrrolidone (PVP), titanium tetraisopropoxide (Ti (Iso), 97%), cadmium acetate dihydrate 98%, ammonium sulfide (40–48 wt%), and the ammonia–borane complex (AB, 97.0%) were obtained from Sigma-Aldrich. Acetic acid was obtained from Showa Chemicals Co. Ltd., Japan. All the chemicals were analytic grade and used without further purification.

2.2. Preparation of CdS/$CdTiO_3$ nanocomposite

At first, 1.5 g of titanium tetraisopropoxide was mixed with 3 g acetic acid. After 10 min of stirring, 0.45 g of PVP and 4 g of ethanol were added to the solution followed by the addition of 1 g of cadmium acetate and 0.5 g of ammonium sulfide (drop-wise). After stirring for 12 h at room temperature, the resulted mixture solution was subjected to the electrospinning process in a plastic syringe fitted with a pointed nozzle, which was clamped at about a 20° angle relative to the horizontal axis. The positive pole copper electrode was secured inside the solution. An electric voltage was applied at 20 kV. A rotating steel drum covered with alumina foil used as a collector of the electrospun nanofibers and was positioned 15 cm from the tip of the syringe. The collected nanofibers were dried at room temperature for 12 h and vacuum dried for further 12 h. After calcination in air at 600 °C for 3 h, the sample was used for further analyses.

2.3. Characterization

The surface morphology of nanofibers was studied by using a JEOL JSM-5900 scanning electron microscope, JEOL Ltd., Japan, and a field-emission scanning electron microscope equipped with EDX (FE-SEM, Hitachi S-7400, Japan). The phase and crystallinity were characterized by using a Rigaku X-ray diffractometer (Rigaku Co., Japan) with Cu Kα (λ=1.54056 Å) radiation over 2θ range of angles, from 10°