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TiO_2/ZnO hierarchical heteronanostructures: Synthesis, characterization and application as photocatalysts

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ABSTRACT

TiO_2/ZnO hierarchical heteronanostructures were produced following a two-step procedure in which the hydrothermal growth of nanorods takes place on the surface of decorated electrospun fibers. The reaction product was a 3D-nanorod arrangement of a single-phase hexagonal wurtzite deposited onto the surface of a TiO_2-decorated 1D-polymer nanoporous structure. The resulting composite was characterized as a potential candidate for photocatalytic applications, due to the available surface area and the high concentration of charge carriers, which minimizes the recombination of electrons and holes during photocatalytic processes. Photodegradation tests using rhodamine B (under visible-light irradiation) were performed to explore the photocatalytic activity of the nanostructures. Dye photodegradation ratio was determined to be 90% after 70 min, which indicates that TiO_2/ZnO hierarchical heteronanostructures are potential photocatalysts.

1. Introduction

Zinc oxide is a wide-band-gap II–VI semiconductor and a promising material due to its favorable piezoelectric and pyroelectric properties, which are applied in optoelectronics [1,2], thin-film transistors [3], biosensors [4], gas sensors [5], bactericidal agents [6] and photocatalysis [7]. These applications are favored by the chemical stability, low toxicity and oxidation strength of ZnO [8]. The morphology, crystal size and orientation of ZnO nanocrystals play a pivotal role to achieve a desired response [5]. As a consequence, a variety of hierarchical ZnO architectures, such as nanowire arrays and flower- and tower-like nanocolumns, have been progressively reported in the literature [5]. Thus, achieving precise control of the growth parameters represents a critical aspect in the production of ZnO nanostructures of desired morphologies [9]. In addition, titanium dioxide (another semiconductor with a wide band gap of 3.2 eV) has been considered an important candidate for photocatalytic applications, as previously reported in recent work [10,11].

Photocatalytic activity of pristine semiconductors (such as ZnO and TiO_2) is reduced due to the one-electron reduction applied in the oxygen reduction. In this direction, multi-electron transfer processes (provided by co-catalysts action) are preferred [12]. The typical limitation for application of semiconductors as photocatalysts (reduced absorption of light in the visible region and low quantum yield) has been circumvented by different strategies with the aim of activating the visible light absorption of corresponding material, which combine photo-synergistic materials such as anatase/rutile heterojunction and metal oxide/TiO_2 heterostructures. These strategies are focused on surface modification of semiconductor by addition of dopants for TiO_2, such as iron, nickel, copper and so on.

On the other side, the nucleation and growth of inorganic heterojunctions introduces the advantage of improvement in the charge separation in association with lower pair recombination rate such as from association of heterogeneous growth of rutile nanowires on electrospun fibers of anatase [13]. Alternatively, Wang et al. [14] reported the action of brookite/anatase phase as an effective photocatalyst.

The production of TiO_2-decorated electrospun fibers based on anatase/rutile dispersion of nanoparticles introduces the advantage of high efficiency in electron-hole pair separation.

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In addition to this advantage, 1D electrospun fibers can be applied as a substrate for growth of secondary hierarchical structures. Zhang et al. [15] reported the photo-synergistic effect of SnS_2 nanosheets on TiO_2 nanofibers. Yang et al. [16] reported the hydrothermal assembly of SnO_2 cubes on electrospun fibers of TiO_2 for application as humidity sensors.

In both applications, the adequate level of interaction of semiconductors and low level of aggregation of secondary structure represent important parameters applied in the synergistic effect of components.

The interaction of TiO_2 and ZnO into nanostructures improves the physical and chemical properties (such as electrical conductivity and concentration of charge carriers) of devices [17] used in lithium batteries, photocatalysis, supercapacitors and fuel cells [18–21]. In spite of these noted advantages, the preparation of heterostructures has been considered a complex process (involving two different materials) due to the conditions required for crystal growth nearby the interfaces.

To circumvent this limitation, a two-step procedure that combines electrospinning and a hydrothermal method offers an interesting alternative for the low-cost production of hierarchical heterostructures.

Free-standing mats of polymeric micro- and nano-fibers are produced by electrospinning a polymeric solution, which incorporates semiconductor nanoparticles in the resulting 1D nanostructure. This results in flexible organic matrices that are decorated with non-spinnable metal-oxide nanoparticles along the surface.

The adhesion of photocatalysts on support materials has been considered an important step for photocatalyst immobilization. A simple and low cost methodology is based on dispersion of nanoparticles in solution for electrospinning. Cossich et al. [22] reported that TiO_2 nanoparticles are homogenously dispersed on bulk and surface of electrospun fibers while a combination of different fillers (as reported by Krupa et al.) [23] favors the charge accumulation on surface of fibers.

The second step, the hydrothermal growth of zinc nanostructures on polymer electrospun fibers, forms radial-oriented ZnO nanorods around TiO_2-decorated electrospun fibers, thus producing the new hierarchical heterostructure.

This hydrothermal synthesis represents a low-temperature and environmentally friendly method that demonstrates promising results for the production of radial-oriented ZnO nanowires. The process takes place in an environment of polar and nonpolar surfaces, with nonpolar surfaces being favored for the subsequent growth of a single-phase hexagonal wurtzite [9].

The uniform distribution of 3D nanostructures on decorated-electrospun polymer fibers typifies a hierarchical structure with promising photocatalytic applications. This property is due to the available surface area of metal oxides and the surface modification that is induced by nanorods on nanoparticle seeds, which enables efficient electron-hole pair-generation with a minimal recombination rate.

With this aim, we have developed a simple methodology for production of surface modified metal oxide nanoparticles with photocatalytic efficiency under both UV and visible light irradiation, due to the nanostructured growth of zinc structures on decorated 1-D nanofibers. Electrospun polymeric fibers that are decorated with titanium dioxide nanoparticles were prepared and applied as a support for the growth of hexagonal ZnO nanorods. The distribution of radial nanostructures on TiO_2 seeds (which are dispersed on the surface of electrospun fibers) contributes to the production of 3D nanostructures that are oriented along 1D fibers. The resulting material was applied as a photocatalyst to rhodamine B to explore the photodegradation of the organic dye.

2. Materials and methods

Poly(methacrylic acid-*co*-methyl methacrylate) 1:1 (Eudragit® L 100 (EDGT), Evonik Industries, Germany), titanium dioxide P25 (TiO_2 nanopowder; anatase: rutile ratio 3:1, with medium particle size of 21 nm, purity of 99.5%; Sigma Aldrich, USA), dihydrated zinc acetate ($C_4H_6O_4Zn{\cdot}2H_2O$; Sigma Aldrich, USA), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$; Sigma Aldrich, USA), hexametilenetetramine (hexamine; Sigma Aldrich, USA), triethylamine (TEA; Sigma Aldrich, USA) and rhodamine B (Vetec, Brazil) were used in the form in which they were received.

The morphology of the hierarchical composite was analyzed using scanning electron microscopy (Vega 3XM Tescan at accelerating voltage of 20 kV) equipped with an EDS (Energy Dispersed Spectroscopy) detector. An XRD diffraction pattern was performed by means of X-Ray Diffraction (Philips X'Pert, PW3040/00) using Cu-Kα radiation (Kα = 1.54056 Å) in an interval from 2θ = 20°–70° with a step of 0.04° and a scanning time of 0.5 s per point. The identification of the crystalline phases was performed using the software X-Pert HighScore (Panalytical), and the crystallography data for all phases were obtained using the Inorganic Crystal Structure Database (ICSD).

Fourier Infrared Transform Spectroscopy – (FTIR) analysis of nanostructures was performed using IR Prestige-21 Shimadzu equipment. Absorbance of the resulting aqueous dye solution was measured using a Hach DR5000 spectrophotometer. Photoluminescence experiments were performed in a PC1 spectrofluorimeter (ISS). Brunauer- Emmett- Teller (BET) surface area and BJH average pore diameter were performed on a Micrometrics ASAP using nitrogen gas.

2.1. Synthesis of radial-oriented TiO_2-ZnO-nanorod (ROTiZn) nanostructures and EDGT-loaded radial-oriented TiO_2-ZnO nanorods (ROTiZnEDGT)

RoTiZn nanostructures were synthesized using a standard hydrothermal reaction, which makes use of two different solutions:

Solution 1 – seed solution

Dehydrated zinc acetate (0.55 g) is added to a mixture of 25 mL of ethylic alcohol and 25 mL of milli-Q water and the solution is maintained under stirring for 15 min at 85 °C. After this step, 350 μL of triethylamine is slowly added, dropwise, into the solution, and then the solution is incubated for 3 h in a volumetric flask.

Solution 2 – growth solution of ZnO

Hexamine (2.8 g) in 400 mL of milli-Q water is vigorously stirred for 10 min. Hexahydrated zinc nitrate (5.95 g) is added to the previous solution and continually stirred for an additional 24 h at 25 °C.

2.1.1. Growth of ROTiZn nanostructures

Titanium dioxide nanoparticles (0.36 g) were dispersed into 12 mL of solution 1 over the course of 2 min. The filtered solution was kept in a pre-heated oven at 120 °C for 1 h and then cooled to room temperature over a 12-h period. The resulting material was introduced into 80 mL of solution 2, which was kept at 85 °C for fixed intervals of time (3, 6, 12, 18, 24, and 36 h).

2.1.2. Synthesis of ROTiZnEDGT nanostructures

The synthesis of *ROTiZnEDGT* nanostructures was performed in a two-step procedure, which is comprised of the synthesis of electrospun fibers and the growth of nanorods on the surface of fibers.