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Fabrication of PdS/ZnS NPs doped PVAc hybrid electrospun nanofibers: Effective and reusable catalyst for dye photodegradation

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ABSTRACT

Effective PdS/ZnS NPs doped PVAc hybrid electrospun nanofiber mat is introduced as an efficient and reusable photocatalyst. The NPs were synthesized in situ by addition of $(NH_4)_2S$ to PVAc/ZnAc/PdAc solution. Fabrication of good morphology nanofibers containing PdS/ZnS NPs was achieved by simple, effective, low cost and high yield technology; electrospinning of PVAc/PdS/ZnS colloid. Besides the effective photocatalytic activity, the introduced immobilization strategy of NPs is considered an acceptable methodology to solve the problems of secondary pollution of nanostructural photocatalyst. Overall, the introduced mat can be used as low cost, efficient, and reusable healthily safe photocatalyst to overcome the aforementioned problem.

1. Introduction

Environmental problems such as organic pollutants and toxic water pollutants produced by different industries are harmful to human health and general well-being of man. Various physical, chemical, and biological techniques of alleviating the negative environmental impact of hazardous wastes and toxic water pollutants have been developed. Traditional treatments such as coagulation, flocculation, absorption, and membrane technologies merely concentrate or otherwise transport wastes [1]. Destructive techniques such as chemical oxidation and advanced oxidation processes may overcome these problems [2], but still lead to high costs and incomplete degradation. Meanwhile, semiconductor photocatalysts offer the potential for conversion of solar energy into chemical energy and treatment of pollutants [3,4]. It is one of the key technologies to solve both energy and environmental problems using solar energy, in which an efficient photocatalyst is necessary. Currently, different metal sulfides have been intensively studied in photocatalysis because of their suitable band gap and catalytic functions. In particular, zinc sulfide (ZnS) with band gap of approximately 3.7 eV is one of the most well-known semiconductor photocatalysts due to its broad applicability and high efficiency in water remediation [5–7]. It can show high photocatalytic activity due to the rapid generation of electron–hole pairs by photoexcitation and the highly negative potentials of excited electrons without any assistance of noble metal cocatalysts [8–10]. But the band gap of ZnS is too large for visible light response [9], and many methods such as doping with metal ions (i.e., Ni^{2+}, Cu^{2+}, Pb^{2+}, and Pd^{2+}) [11–15] have been applied to make ZnS have visible light activity [16,17]. In this regard, the second sulfide; palladium sulfide (PdS) was adapted to the system. As we know that the nanosized PdS is an interesting photocatalyst material with narrow band gap energy (1.6 eV) and a suitable conduction band potential for the effective photodegradation of dye pollutants [18].

Most of the semiconductor catalytic powders are difficult to recycle, easy to aggregate and lose their activity due to photo corrosion. That is why many methods such as coating of particles and immobilization of nanopowders have been used to overcome the problems [19]. Immobilizations not only prevent semiconductor nanocrystals from agglomeration but also improve the reuse rate and photocatalytic activity. Semiconductor nanocrystals normally immobilized on inorganic porous carriers including metal, clinoptilolite, zeolite [20–22] etc. have made great achievement. Similarly, polymer carriers also have a lot of advantages such as diversified shape, simplest procedure, convenient operation at a large scale and convenient recycle. However,

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many polymers are difficult to mix with inorganic powders, and tend to degrade in the photocatalytic process.

The electrospinning is a simple and versatile process offering unique capability for making fibers from polymer solutions from nano-to micro scale [23] which offer high specific area [24] and good enrichment ability for organic compounds [25], leading to the improvement of the photocatalytic efficiency, stability and recyclability. It has attracted great interest among academic and industrial scientists due to its simple and effective approach to produce nanofibers, which have been found to be attractive for various applications in biomedical engineering, filtration, protective clothing, catalysis reactions, and sensors [26–32]. In an electrospinning process, a polymer solution, held by its surface tension at the end of a capillary tube, is subjected to an electric field. Charge is induced on the liquid surface by an electric field. Mutual charge repulsion causes a force directly opposite to the surface tension. As the intensity of the electric field is increased, the hemispherical surface of the solution at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone [30]. When the electric field reaches a critical value at which the repulsive electric force overcomes the surface tension force, a charged jet of the solution is ejected from the tip of the Taylor cone. Because this jet is charged, its trajectory can be controlled by an electric field. As the jet travels in air, the solvent evaporates, leaving behind a charged polymer fiber on the collector.

In this work, for the first time we have introduced the incorporation of active ZnS and PdS/ZnS NPs inside the polyvinyl acetate (PVAc) electrospun nanofibers. In situ synthesis of the solid NPs has been achieved by addition of ammonium sulfide solution to polymer/metal salt sol–gel. The resulting PdS/ZnS–PVAc hybrid electrospun nanofiber mat showed effective photocatalytic activity in the photodegradation of MB dye under solar light irradiation. Complete sheathing of the active NPs did not affect their catalytic activity as the prepared mat successfully catalyzed the photodegradation of MB dye. Hence, this cost effective hybrid electrospun nanofiber mat can be a potential candidate for the people of developing countries to solve their problems concerning water pollution.

2. Experimental

2.1. Materials

The materials used for this study were zinc acetate dihydrate (ZnAc, Showa, Japan), palladium acetate (PdAc, reagent grade, 98%, Sigma–Aldrich), N,N dimethylformamide (DMF, 99.5 assay, Showa Chemical Ltd., Japan), poly(vinyl acetate) (PVAc, MW 5,500,000 g/mol, Sigma–Aldrich), ammonium sulfide (40–48 wt% solution in water, Sigma–Aldrich), high voltage power supply (CPS-60 K02V1, Chungpa EMT, South Korea), methylene blue (MB) (Showa Chemical Ltd., Japan).

2.2. Preparation of PdS/ZnS–PVAc hybrid electrospun nanofiber mat

ZnAc (0.5 g) and PdAc (0.125 g) were dissolved in 2 ml of DMF. Then the prepared solution was mixed with 5 ml of 18 wt% PVAc in DMF. The resulted solution was kept under stirring for 2 h to ensure the proper mixing. Then 0.5 ml of ammonium sulfide was added carefully in a drop wise manner to the solution with vigorous stirring to make the fine dispersion of PdS doped ZnS NPs. The solution was kept under vigorous stirring for 5 h and electrospinning of the formed colloid was carried out using a high voltage power supply at an applied voltage of 15 kV. In this process the solution was fed to the 5 ml syringe with plastic micro-tip. The tip-to-collector distance was kept at 15 cm. During the electrospinning process, the drum was rotated at a constant speed by a DC motor to collect the developing nanofibers. Environmental conditions under which electrospinning was carried out contain temperature 25 °C and relative humidity about 60%. After vacuum drying for 24 h, the fiber mat (PdS/ZnS–PVAc hybrid electrospun nanofiber mat) was used for further analysis. For the comparison of photocatalytic activity, PVAc nanofiber containing ZnS NPs alone (ZnS–PVAc hybrid electrospun nanofiber mat) was also prepared by the same method without adding PdAc.

2.3. Characterization

The surface morphology and the elemental mapping of the nanofibers were studied by field emission scanning electron microscopy (FE-SEM, S-7400, Hitachi, Japan). The samples were coated with platinum (Pt) for 180 s using a Pt coater (E-1030, Hitachi) before characterization. In addition FE-SEM EDX spectrum of the hybrid nanofiber mats was also recorded. Images of nanofibers containing ZnS and Pd doped ZnS NPs were obtained via transmission electron microscopy (TEM, A JEM-2011F, JEOL, Co.) with a 200 kV accelerating voltage. The samples were prepared by directly collecting the nanofibers on the TEM grid during electrospinning. Information about the phase and crystallinity was obtained with a Bruker X-ray diffractometer (XRD, BRUCKER D2 PHASER, Germany) with Cu Kα (λ = 1.540 °A) radiation over Bragg angles ranging from 10° to 80°. The bonding configuration of the polymer with ZnS NPs was characterized by means of Fourier-transform infrared (FTIR, FT/IR-4200, Jasco international Co., Ltd.). UV absorbance was measured by UV–vis spectrophotometer (HP 8453 UV-vis spectroscopy system, Germany).

2.4. Photocatalytic activity investigation

The photocatalytic activity of ZnS–PVAc and PdS/ZnS–PVAc hybrid electrospun nanofiber mats was evaluated by observing the photodegradation of MB dye solution in a simple photochemical reactor. Prior to irradiation, the mat and the dye solution were magnetically stirred for 10 min under dark condition to establish an adsorption/desorption equilibrium between dyes and photocatalyst surface. In the present investigation, the reactions were carried out in inverted glass bottles under solar light. The experiment was conducted in a natural atmospheric environment on a sunny day between 11 a.m. and 2 p.m. For the photodegradation experiments, 50 ml of the MB dye solution (10 ppm concentration) was treated with a weighed amount of different mats (150 mg) in the glass bottles. In addition, a control experiment with 150 mg of pristine PVAc mat and catalyst free were also carried out to monitor photocatalytic activity of PVAc mat and self degradation of dye, respectively. At regular intervals of time, 2 ml of aliquots were taken out and the concentration of the dye was measured by recording the UV absorbance in the range of 200–900 nm, using a UV–vis spectrophotometer. In this experiment, the ability test of reused PdS/ZnS–PVAc mat was also performed after full treatment. For this purpose, the used mat was washed many times with distilled water and then photodegradation of MB dye was carried out under same conditions as before.

3. Result and discussion

3.1. Morphology study

Fig. 1 shows the typical field emission scanning electron microscopy (FE-SEM) images of the pristine PVAc electrospun nanofiber, ZnS–PVAc, and PdS/ZnS–PVAc hybrid electrospun nanofiber mats along with their FESEM–EDX analysis. When