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Composite nanofibers/water photosplitting and photocatalytic degradation of dairy effluent

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ABSTRACT

Photocatalytic removal of Dairy effluent (DE) was studied by using TiO_2-GeO_2 and TiO_2-CdO nanofibers (NFs), produced by electrospinning method. These NFs were characterized by SEM, TEM and XRD studies. The TiO_2-GeO_2 and TiO_2-CdO NFs were smooth and continuous, with an average diameter of about 273 nm and 256 nm respectively, and held their nanofibrous morphology even after more than 9 h of photocatalytic removal of DE under visible light irradiation. TiO_2-GeO_2 and TiO_2-CdO NFs were effective materials for removal of DE, even after many runs and cycles. TiO_2-GeO_2 and TiO_2-CdO NFs showed a maximum removal of 65% and 75%, respectively, after 3 h. The TiO_2-GeO_2 and TiO_2-CdO NFs also showed excellent results in hydrogen release.

1. Introduction

Photocatalytic removal of organic/inorganic compounds in dairy effluents using semiconductors has been a promising green technology for environmental purification, as they provide an interface with an aqueous medium and prompt an advanced oxidation process [1–4].

Semiconducting materials are important in various photocatalytic induced applications, production of hydrogen gas by splitting water, decomposition of organic pollutants, production of gas sensors, electronic devices (solar cells, laser diodes, photodetectors), catalysts, coatings, and energy-harvesting devices, and conversion of CO_2 [5,6–8]. Titanium dioxide (TiO_2) is an important semiconductor with a wide band gap, tunable crystal structure (anatase, rutile, brookite), high exciton binding energy, and efficient photocatalytic activity [9–11]. The band gaps of these three TiO_2 phases are 3.2, 3.0 and 3.25 eV, respectively. The useful attributes of TiO_2 are: (i) readily available (ii) photostable, (iii) insoluble in aqueous media, (iv) chemically and biologically inert, (v) inexpensive, and (vi) nontoxic [9,12–14]. In comparison to bulk forms TiO_2 nanomaterials show extraordinary features and can be designed in various morphologies for different applications [15–18].

Precisely, nanostructured TiO_2 has been proved to be an effective photocatalyst for particular removal of environmental pollutants [9,10,19–22]. However, it responds mainly to UV light which only forms less than 5% of total solar radiation. Under the presence of visible light, the catalytic efficiency is restrained by lower electron transfer and higher electron-pair recombination rates. For economic reasons, it is extremely important that visible light driven photocatalysts with higher efficiency is developed. TiO_2 is currently synthesized as nanofibers, nanoparticles, nanotubes, core shells, nanocubes and nanorods using relatively lower temperatures and inexpensive methods [7,23–27]. To improve the poor photocatalytic performance under solar light, TiO_2 is a potential candidate for productive modifications and functionalization to elevate photocatalytic performance. For TiO_2-hybrid nanocomposites, the objective is to elevate quantum efficiency and exploit visible light to degrade organic/inorganic pollutants [28]. In our previous work, the photocatalytic properties of titanium dioxide were greatly enhanced by coupling CdO [29].

GeO_2 is a semiconductor transition metal used in electronic industry, radiation detectors, and optical devices [30]. Germanium nanostructures have high electron and hole mobilities. In comparison to silicon (4.9 nm), germanium nanostructures have higher exciton radius of 24.3 nm and, therefore, show greater quantum effects [31,32]. The use of complementary metal oxide semiconductors (CMOS) has increased interest in this material [33]. Ge is a material with a smaller energy difference between the indirect gap and the direct gap (DE = 0.12 eV) [34]. GeO_2 nanostructures have been prepared in various shapes, including nanofibers, [35], nanowires, [36], nanosheets, [37], nanorods, [38], and nanowhiskers, [39]. GeO_2 is a blue photoluminescence material with peak energies around 3.1 and 2.2 eV respectively, a dielectric oxide and it has a refractive index and a linear coefficient of thermal expansion higher than those for silicate (SiO_2). GeO_2 is a promising material for nanoconnections in optoelectronic communication and vacuum technology and optical waveguides

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[40,41].

In this study we report for the first time the fabrication of TiO_2-CdO and TiO_2-GeO nanofibers for photocatalytic removal of (DE). The prepared nanomembranes were exploited as a photocatalyst for the degradation of model DE. These NFs also showed excellent results in hydrogen release.

1.1. Materials used

Tetrahydrofuran (THF) and N,N-dimethyl formamide (DMF) (analytical grade from Showa Chemicals Ltd., Japan), titanium (IV) isopropoxide (CAS number 546-68-9), Cadmium acetate and Germanium Isopropoxide were purchased from Sigma Aldrich. All chemicals were used as such without further purification. DE was kindly donated by Purmil Ltd. 197-3Daeri-ro, Shinpyong-meum Imsil-gun, Cheollabukdo, South Korea. The solution was used without any purification and the composition is unknown. Halogen High Voltage SE (Film/Studio) (6994P 2000 W GY16 240 V 1CT) was purchased from PHILIPS, The Netherlands.

1.2. Characterizations of TiO_2-GeO_2 and TiO_2-CdO NFs

The surface morphology of the NFs was studied with a JEOL JSM-5900 scanning electron microscope (JEOL Ltd., Japan). The samples were coated with gold by sputtering before analysis. The phase identification and crystal structures were observed by the XRD technique using an X-ray diffractometer (Rigaku Co., Japan) with Cu Kα (λ = 1.54056 Å) radiation over a range of 2θ angles from 10 to 90. The TiO_2-GeO_2 and TiO_2-CdO NFs were also evaluated using a UV–visible spectrometer (Lambda 900, Perkin-Elmer, USA). High-resolution images and selected area electron diffraction patterns were observed by a JEOL JEM- 2200FS transmission electron microscope (TEM) operating at 200 kV (JEOL Ltd., Japan). The spectra obtained were analyzed by HP Chemi Station software 5890 series. The concentration of the DE during the photodegradation study was investigated by spectroscopic analysis using the HP8453UV–visible spectroscopy system (Germany).

1.3. Photocatalytic experiments

The experiments were carried out in an indigenous glass photo reactor. The reactor was made of glass (capacity of 1000 ml, height 23 cm and diameter 15 cm), covered with alumina foil and equipped with a visible light source (sunlight lamp emitting source at a 2000 watt radiation). At the start, DE and photocatalyst were placed in the reactor and continuously stirred until the photocatalyst submerged completely during the photocatalytic reaction. Typically, 500 ml of DE solution and calcined NFs weight equal to 50 mg were used as the catalyst. At specific time intervals, a 2 ml sample was withdrawn from the reactor and the absorbance intensity was then measured at the corresponding wavelength (204 nm).

1.4. Water photosplitting

The water photosplitting was estimated by measuring the rate of hydrogen produced in a typical water filled gas burette system. A burette filled with water was connected to the reaction flask to measure the volume of the hydrogen gas produced from the reaction. Next, 75 mL aqueous 0.5 M sodium sulphide (Na_2S) and 0.5 M sodium sulphite (Na_2SO_3) containing 50 mg catalyst was added into the reaction flask with 600 rpm stirring rate. The volume of hydrogen gas gradually evolved was recorded by the displacement of water level every minute. It was supposed that the evolved gases composed of oxygen and hydrogen with a mole (a consequently volume ratio) of 1:2, so the volume of hydrogen was estimated accordingly. For a control experiment, the same experiment was repeated without any catalyst. It was observed that no appreciable gas was evolved. Moreover, the same experiment was repeated using methanol instead of the inorganic scavengers in this experiment methanol: water volume ratio was kept 1:1. All the experiments were conducted under mercury lamp (2000 W) as a source of visible light.

1.4.1. The synthesis of TiO_2-GeO_2 and TiO_2-CdO NFs

Electrospinning is a wonderful technique that involves the usage of high voltage to charge the surface of polymer solution, to stimulate the ejection of a spray through a spinneret. The spray is stretched accordingly many times to form smooth, constant, very thin fibers [1,2,3,4,42].

A high voltage power supply (CPS-60 K02V1, Chungpa EMT Co., Republic of Korea), capable of generating voltages up to 60 kV, was used as a source of electric field for spinning the nanofibers. The solution to electrospun was supplied through a syringe attached to a capillary tip. The copper wire from the positive electrode (anode) was inserted into the solution, and a negative electrode (cathode) was attached to a metallic collector. The prepared solutions were electrospun onto an aluminum plate covered with aluminum foil (to produce TiO_2-GeO_2 and TiO_2-CdO nanostructures) with the following experimental parameters: current supply of 20 kV, 15 cm working distance, and 0.3 mL/h flow rate; the collection time was set to 5 h.

Fig. 1a and b shows the SEM image of the dried Ti(Iso)/PVAc/GeIsp and Ti(Iso)/PVAc/CdAc NFs. It is clear from these figures that smooth and continuous NFs were produced by the electrospinning technique. Fig. 1c and d shows the SEM image of the Ti(Iso)/PVAc/GeIsp and Ti (Iso)/PVAc/CdAc NFs after calcination at 500 °C. These NFs have smaller diameters as compared to the dried nanofibers due to elimination of the polymer content at high temperature. These NFs still maintained their one-dimensional texture, indicating that the removal of PVAc and calcination at 500 °C did not damage the one dimensional morphologies. The average diameter of TiO_2-GeO_2 and TiO_2-CdO nanofibers were about 273 and 256 nm, respectively. The detailed preparation method of TiO_2-CdO was reported in our previous study [29].

The inner structure of the TiO_2-GeO_2 NFs was studied by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analysis (Fig. 2). The low magnification image of TiO_2-GeO_2 NFs (2a) shows smooth surfaces with clear borders, and without any structural defects. The low magnification image of NFs is in agreement with the SEM image concerning the morphology and dimensions. The high-resolution TEM image indicates good crystallinity since the atomic planes could be identified in the Fig. 2b. In which the crystal planes are parallel with the same planar distance. The SAED in upper left inset of (2a) also supports the crystalline structure. The inset in Fig. 2b shows the inverse fast Fourier transformation (FFT) image, which also confirms the good crystallinity in accordance with the SAED patterns.

The XRD spectra of the TiO_2-GeO_2 NFs after calcination at 500 °C are shown in Fig. 3. The diffraction pattern revealed the existence of crystalline phases. As shown in this spectra, the existence of strong diffraction peaks at 2θ values of 25.24°, 38.12°, 48.00°, 53.86°, 54.95°, 62.71°, 70.10°, and 75.11° correspond to the crystal planes (1 0 1), (1 1 2), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (2 2 0), and (2 1 5), respectively, indicating the formation of the anatase titanium dioxide [JCPDS card no 21-1272]. In addition, clear GeO_2 crystalline peaks were detected at 20.02°, 25.91°, 37.00° and 68.58°, correspond to the crystal planes (1 0 0), (1 0 1), (1 0 2), and (3 0 1), respectively [JCPDS card no 36-1463].

Photocatalytic removal of DE in the presence of TiO_2-CdO and TiO_2-GeO_2 NFs was carried out as shown in Fig. 4. To evaluate the efficiency of electrospun fibers each formulation was utilized three times. In the case of TiO_2-CdO NFs as shown in Fig. 4a, the first run removed about 75% DE after 3 h. The efficiency of TiO_2-CdO NFs decreased to 70% in second run after 6 h and 66% DE was eliminated in run 3 after 9 h. Similarly, TiO_2-GeO_2 NFs were utilized three times as shown in Fig. 4b, the first run removed about 65% DE after 3 h. The efficiency of TiO_2-