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Influence of temperature on the photodegradation process using Ag-doped TiO_2 nanostructures: Negative impact with the nanofibers

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ABSTRACT

In this study, the influence of the temperature on the photodegradation process using Ag-doped TiO_2 nanostructures was investigated. Two morphologies were used; nanoparticles and nanofibers. The nanofibers were synthesized by electrospinning of a sol–gel consisting of titanium isopropoxide, silver nitrate and poly(vinyl acetate). The silver nitrate amount was changed to produce nanofibers having different silver contents. Typically, sol–gels containing 0.5, 1.0, 1.5, 2.0 and 2.5 wt% silver nitrate were utilized. Calcination of the electrospun mats at 700 °C led to produce well morphology Ag-doped TiO_2 nanofibers for all formulations. The nanoparticles were prepared from the same sol–gels, however, instead of spinning the gels were dried, grinded and sintered at 700 °C. Photodegradation under UV irradiation for the rhodamine B at 5, 15, 25, 45 and 55 °C were performed. For the nanoparticles, increasing the temperature has positive impact as the best degradation was obtained at 55 °C. In contrast to the known influence of the temperature on the chemical reactions, in case of the nanofibrous morphology, the temperature has negative impact as the experimental work indicated that the optimum temperature is 25 °C. The observed strange effect of the temperature in case of the nanofibrous morphology indicates instant degradation of the dye molecules in the active zones surrounding the nanofibers. Therefore, the increase of temperature results in increase the kinetic energy of the dye molecules so the molecules escape from the active thin film surrounding the photocatalyst. Overall, this study shows that the nanofibrous morphology strongly enhances the surface activity of the photocatalyst which generates negative influence of the temperature.

1. Introduction

Fast electrons/holes recombination is the main dilemma facing the semiconductors photocatalysts in general and titanium oxide in particular. Incorporation of noble metal nanoparticles (NPs) into the titania dielectric matrix is a recent strategy to overcome this problem and simultaneously improve the photocatalytic activity of titanium oxide [1,2]. Doping with foreign metal nanoparticles can produce high Schottky barrier that facilitates electron capture [3]. The capture of electrons postulate to produce a longer electron–hole pair separation lifetime, and therefore hinder the recombination of electron–hole pairs and enhance the transfer of holes and possibly electrons to O_2 adsorbed on the TiO_2 surface. Afterward, excited electrons migrate to the metal, where they become trapped and the electron–hole pair recombination is suppressed. Therefore, many investigations have reported the enhancement of photoactivities in both liquid and gas phases [4,5]. Moreover, this incorporation provides an absorption feature due to the surface plasmon resonance (SPR) occurring over the visible range of the spectrum [6]. Particularly, silver and gold nanoparticles are more familiar because of their color varieties in the visible region, which is attributed to oscillations of the electrons at the surface of the nanoparticles [7]. Silver is the most common metal used to modify titania, because its *d*–*s* band gap is in the UV region and does not damp out the plasmon mode as strongly as gold [8,9]. Titania-modified-silver particles have raised extensive interest due to their applications in photocatalytic degradation [10]. The researchers have intensively studied how silver provides titania distinct photocatalytic activity, the mechanism has been well explained in previous reports [11–13]. Moreover, some researchers have concluded that incorporation of silver in titanium dioxide leads to increases in the total surface area of the prepared titanium dioxide [14,15]. This can be considered an additional benefit of

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utilizing silver-loaded titanium oxide in the field of photocatalytic degradation. Therefore, many researchers have practically demonstrated that the degradation rates of the dyes can be enhanced by the deposition of silver on titanium dioxide [16–18].

In the last decades, nanostructural materials have been intensively investigated because of their high surface area, which strongly affects their physiochemical properties. Different shapes have been introduced. Of the reported nanostructure shapes, special attention has been paid to one-dimensional forms such as nanorods, nanowires, and nanofibers. This is due to their potential applications in the nanodevices [19–21]. Nanofibers have received special consideration due to their high axial ratio, good mechanical properties, and their manageable and novel physical properties.

Compared to nanoparticles, nanofibers have small surface area which might be considered a negative impact upon using as catalyst in the chemical reactions. Therefore, if the morphology has no impact, the nanoparticles will have higher catalytic activity. Moreover, for the same surface activity, the temperature should have the same influence on both formulations. In most of the chemical reactions, positive effect of the temperature on the reaction rates is a prevailing impression. Temperature is a measure of the kinetic energy of a system, so higher temperature implies higher average kinetic energy of the molecules and more collisions per unit time. This hypothesis might be true in the normal cases, however, the nanostructures usually have unexpected behaviors compared to the bulk scales.

In this study, the aforementioned facts have been investigated for the Ag-doped TiO_2 nanophotocatalyst. Two nano-formulations have been utilized; nanofibers and nanoparticles. Silver-grafted titanium oxide nanofibers have been synthesized using the electrospinning of silver nitrate/titanium isopropoxide/poly(vinyl acetate) sol–gel. However, the nanoparticulate form has been obtained by calcination of a ground powder prepared from the same electrospun sol–gels. In contrast with the aforementioned known influences, compared to nanoparticles, the nanofibers showed better performance as a photocatalyst catalyzing the photodegradation of rhodamine B and methylene blue dyes. Moreover, negative effect of the temperature on the photocatalytic degradation of the rhodamine B dye was observed when the Ag-doped TiO_2 nanofibers were utilized as photocatalyst.

2. Experimental

2.1. Materials

Silver nitrate (99.8 assay), methylene blue dihydrate dye (95.0 assay), N,N-dimethylformamide (DMF, 99.5 assay), and rhodamine B dye were obtained from Showa, Co., Japan. Titanium (1V) isopropoxide (Ti(Iso), 98.0 assay) was purchased from Junsei Co. Ltd., Japan. Poly (vinyl acetate) (PVAc, MW = 500,000 g/mol) was obtained from Aldrich, USA. These materials were used without any further purification.

2.2. Preparation of nanofibers and nanoparticles of Ag/TiO_2 composite

2.2.1. Nanofibers (NFs)

The electrospinning process was utilized to prepare the silver-grafted titania NFs. Typically, a sol–gel was prepared by mixing titanium isopropoxide (Ti(Iso)) and poly(vinyl acetate) (PVAc, 14 wt% in DMF) with a weight ratio of 2:3, respectively, and then few drops of acetic acid were added until the solution became transparent. The mixing process was carried out at 25 °C using magnetic stirrer rotating at 150 rpm. To prepare sol–gels containing different contents of silver, silver nitrate solutions in DMF were mixed with proper quantities of the prepared Ti(Iso)/PVAc solution to prepare final solutions containing 0.5, 1.0, 1.5, 2.0 and 2.5 wt% $AgNO_3$. Afterward, these solutions were homogeneously mixed under stirring conditions for 10 min at 25 °C and moderate stirring speed. A high voltage power supply (CPS-60 K02V1, Chungpa EMT Co., Republic of Korea) was used as the source of the electric field. The sol–gel was supplied through a plastic syringe attached to a capillary tip. A copper wire originating from the positive electrode (anode) connected with a graphite pin was inserted into the sol–gel and the negative electrode (cathode) was attached to a metallic collector covered with polyethylene sheet. Briefly, the solution was electrospun at 6 kV and 15 cm working distance (the distance between the needle tip and the collector). The electrospinning process was carried out at 25 °C in 40% relative humidity atmosphere. The formed nanofiber mats were initially dried for 24 h at 80 °C in a vacuum and then calcined in air atmosphere at 700 °C for 1 h with a heating rate of 5 °C/min.

2.2.2. Nanoparticles

Silver nitrate/Ti(Iso)/PVAc solutions having the aforementioned compositions and preparation procedure were utilized to prepare nanoparticles containing different silver contents. The process parameters (temperature and stirring) were not changed. Instead of spinning, the solution was vacuously dried at 80 °C for 48 h to completely remove the solvent. The obtained solid materials were finely grinded and sintered in air at 700 °C for 1 h.

2.3. Photocatalytic degradation

The photocatalytic degradation of two selected dyes; methylene blue and rhodamine B in the presence of Ag–TiO_2 nanofibers and nanoparticles was carried out in a simple photo reactor. The reactor was made of glass (1000 ml capacity, 23 cm height and 15 cm diameter), covered with aluminum foil, and equipped with ultra-violet lamp emitting radiations at 365 nm. The initial dye solution and the photocatalyst were placed in the reactor and continuously stirred to ensure proper mixing during the photocatalytic reaction. Typically, 100 ml of dye solution (10 ppm, concentration) and 50 mg of catalyst were used. At specific time intervals, a 2 ml sample was withdrawn from the reactor and centrifuged to separate the residual catalyst, and then the absorbance intensity was measured at 664 and 554 nm for methylene blue and rhodamine B dyes, respectively.

2.4. Characterization

Surface morphology of nanofibers was studied by JEOL JSM-5900 scanning electron microscope (JEOL Ltd., Japan) and field-emission scanning electron microscope (FESEM, Hitachi S-7400, Japan). The phase and crystallinity were characterized by using Rigaku X-ray diffractometer (Rigaku Co., Japan) with Cu Kα (λ = 1.54056 Å) radiation over a range of 2θ angles from 20° to 100°. High resolution image and selected area electron diffraction pattern were observed by JEOL JEM-2200FS transmission electron microscope (TEM) (JEOL Ltd., Japan). The concentration of the dyes during the photodegradation study was investigated by spectroscopic analysis using HP 8453 UV–visible spectroscopy system (Germany). The spectra obtained were analyzed by HP ChemiStation software 5890 series.

3. Results and discussion

3.1. The photocatalyst characterization

The polymer is an essential constituent in sol–gels to achieve the electrospinning process [19,22–24]. Metal alkoxides are the best candidates to form the gel structure due to their affinity to