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Visible light response of Ag^+/TiO_2–Ti_2O_3 prepared by photodeposition under foam fractionation

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ABSTRACT

An Ag^+/TiO_2–Ti_2O_3 nanocomposite was synthesized by a novel foam fractionation method: the foam traveled to a fixed vertical column and was fractionated. Silver was deposited (0–0.02 mol%) on titania photocatalytic nanoparticles by the foam fractionation method under UV irradiation. By TEM, the Ag particles were found to be highly dispersed on TiO_2 without any aggregation. XPS studies revealed the presence of both the Ti^{3+} and Ti^{4+} forms, and with an increase in Ag content, Ti^{3+} increased. Ag was found mainly in the Ag^+ state. The obtained Ag–Ti oxides were investigated for photocatalytic activity by the degradation of methylene blue under visible light and sunlight, and the catalytic activity was better under sunlight than under visible light. The activity was found to increase with an increase in Ag loading. The Ag^+/TiO_2–Ti_2O_3 obtained by the foam fractionation method was further investigated for bactericidal activity under visible light. Using 0.05 mol% Ag/Ti, the bacterial growth of *Escherichia coli* was completely inhibited under visible light.

1. Introduction

Heterogeneous photocatalysis is an attractive technique for the complete destruction of organic pollutants. An extensive variety of organic compounds, such as chlorinated alkanes and alkenes, polychlorinated phenols, aromatics, aldehydes, organic acids and amines, can be degraded by heterogeneous photocatalysis to CO_2, H_2O and mineral acids [1]. TiO_2 is a widely studied semi-conducting photocatalyst and has the advantages of visible light activity at room temperature and ambient pressure when doped with metal ions [2]. Various organisms have been photocatalytically inactivated by TiO_2, including bacteria, bacterial and fungal spores, and algae [3,4].

The principles and mechanism of photocatalysis have been discussed in several articles [1,5]. The production of electron–hole pairs in the semiconductor by light energy (UV or sunlight) plays an important role in the degradation of environmental pollutants. The production of electron–holes in TiO_2 is dependent on the crystal structure, surface area, porosity, size distribution and the adsorbates present on the surface (Ag, Au, Pd, Pt), etc., which are dependent on the synthesis conditions. The properties of the nanomaterial are greatly affected by its size and morphology. The preparation method plays a key role in the successful synthesis of catalysts. To increase the quantum yield in photocatalysis, the TiO_2 matrix is often modified by selective metal-ion doping. The function of the transition metal is to increase the electron–hole recombination time (electrons migrate from TiO_2 to metal particles, facilitating charge separation, which inhibits the recombination of electron–hole pairs) and increase the photocatalysis activity. Ag serves as good dopant for TiO_2 to increase the yields of several photocatalytic reactions; in addition, it is more suitable for industrial applications as compared with other metals.

Usual methods of semiconductor modification are thermal impregnation [6] and photodeposition [7]. In this work, we report a novel method of producing silver-loaded titanate by simultaneous photo deposition (UV) and foam fractionation, which showed high photocatalytic efficiency under visible and solar light. The characteristics of the prepared Ag/TiO_2 were determined. To evaluate the photocatalytic efficiency, the degradation of methylene blue

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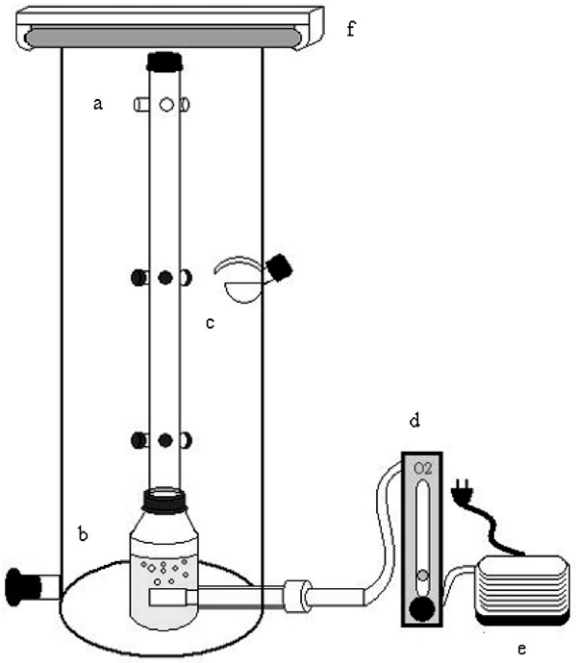

Fig. 1. Foam fractionation apparatus (a) Column height* 33 cm, (b) the feed solution containing (200 ml) (13 cm), (c) small container holding $NH_3{\cdot}H_2O$, (d) manometer held at 0.15 (Nl/min), (e) air pump, (f) UV lamps; The total height of the vessel was 51 cm, with an internal diameter of 15.5 cm, The internal diameter of the bubble column was 2.7 cm, * The height of the column was measured from above the feed solution.

under visible and sunlight was studied. The antibacterial activity of the composites against gram-negative bacteria, i.e. *Escherichia coli* (*E. coli*), was also studied.

2. Experimental

2.1. Materials

Tetrabutyl orthotitanate $Ti(OBu)_4$ (Merk), silver nitrate $AgNO_3$ (99.8%, Panreac), 2,4-Pentandion (AcAc) (99+%, Acros Organics), ethanol C_2H_5OH (99.5%), Tween 80 SigmaUltra (Sigma), ammonia (25%, Panreac), methylene blue (96%, Fluka), Difco^{tw} Agar Noble (Becton, Dickinson), Bacto^{tw}, Tryptone (Becton, Dickinson), Bacto^{tw}, Yeast Extract (Becton, Dickinson), sodium chloride NaCl (99.6%, J.T. Baker) and Milli-Q water were used in all experiments.

2.2. Preparation of the photocatalyst

The photocatalytic deposition of Ag/TiO_2 was carried out using a homemade foam fractionation apparatus, as shown in Fig. 1. The foam fraction conditions are shown in Table 1. The feed solution was prepared by mixing appropriate amounts of the reagents. Two different solutions were made, one consisting of $Ti(OBu)_4$, acac (chelating agent to slower the hydrolysis of $Ti(OBu)_4$ [6]), and ethanol and the other containing Tween 80 and $AgNO_3$. The first solution was added dropwise to the second solution to form a homogeneous mixture under vigorous stirring. Different molar percentages of Ag (0, 0.025, 0.5, 0.1, and 0.2) containing Ti were synthesized by foam fractionation under photodeposition. The feed solution containing the surfactant molecules and titanate enters the vertical column a significant distance above the base of the vessel, when air is sparged through the base of the column to create a dispersion of rising bubbles. The air was injected at a rate of 0.15 (NL/min) through a cylindrical ceramic sparger. Six ml of 25% ammonia was introduced into a small chamber (Fig. 1) in the jacketed vessel when the foam began to exit the column. This was considered the start of the reaction. The foam was then irradiated with UV light (30 W) for 6 h and white precipitates were seen in the bubbles. The flow of air was stopped when the liquid level in the bulk solution just reached the level of the air sparged. The bubbles containing the precipitate were left as such for 24 h. The pH of the initial feed solution was 4, and after exiting from the vertical column the final pH was found to be 9. The precipitate was washed thrice with Milli-Q water followed by ethanol for the complete removal of the surfactant. The obtained precipitate was dried in an air oven for 6 h at 50 °C. Finally, the precipitates were further calcined at a temperature of 600 °C for 5 h.

Table 1
Parameters for photodeposition in foam fraction.

Tween	6.158 g
$Ti(OBu)_4$	4 ml
$AgNO_3$	0–0.2 mol%
Acac	3 ml
Air flow	0.15 N/l
Ethanol	3 ml
25% Ammonia	6 ml
Milli-Q	190 ml
Height	33 cm
UV irradiation	10 W, 6 h

2.3. Photocatalysis experiments

In a typical experiment, 50 ml methylene blue (MB) solution (0.05 g/50 ml) was placed in a glass cylindrical reactor (of 100-ml capacity) and 0.05 g of Ag/TiO_2 was then added. The resulting reaction mixture was stirred magnetically in order to obtain a uniform suspension in the glass tube. All glass reactors containing the different photocatalysts were then placed in the photochemical reactor and exposed to visible light and sunlight. Aliquots were taken at regular intervals from the reactor using a pipette, centrifuged, and analyzed for the decolorization percentage of methylene blue using a Jasco UV-vis spectrophotometer (Thermospectronic, Heλiosβ, 390 nm) with a calibration curve.

A UV-cut filter was used to cut off the light under 400 nm from the lamp in the experiment for the visible light MB degradation. The suspension was irradiated with light using a Q-sun solar test chamber. The suspension was stirred during irradiation. The photocatalytic activities of the materials were studied by the degradation of methylene blue, and the antibacterial activities were also analyzed.

2.4. Photocatalyst recycling experiments

After photocatalytic degradation, the solution was centrifuged to remove the solid catalyst. The obtained particles were washed with ethanol and oven-dried at 50 °C for 5 h. The material was then used again for the photocatalytic degradation of methylene blue to ascertain its catalytic activity.

2.5. Characteristics of photocatalyst

X-ray photoelectron spectroscopy (XPS) measurements were performed in Kratos Axis Ultra DLD. Powder X-ray diffraction (XRD) was recorded on a Shimadzu X-ray diffractometer (model LabX XRD-6000) equipped with Ni-filtered CuKα (λ = 0.1541 nm, 4 kVA, 30 mA, scanning rate of 3 degree per minute (from $2\theta = 20^\circ$ to 80°)) radiation and a graphite crystal monochromator. TEM were obtained using a JEOL 3000F transmission electron microscope operated at an accelerating voltage of 300 kV. The sizes of the nano particles were measured using sigma scanpro software.