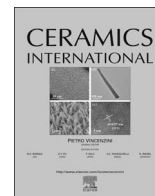




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Short communication

Fabrication of TiO₂–Ag nanocomposite thin films via one-step gas-phase deposition

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ABSTRACT

In this work, TiO₂–Ag nanocomposite thin films were fabricated for the first time via simultaneous plasma-enhanced chemical vapor deposition and physical vapor deposition of TiO₂ and Ag nanoparticles in the gas-phase, respectively. The presence of Ag nanoparticles in the prepared nanocomposites has been confirmed using transmission electron microscopy and energy dispersive X-ray spectrometry techniques. The obtained electron microscopy images showed that the average size of TiO₂–Ag nanoparticles was larger than that of pristine TiO₂. Moreover, the temperature of the anatase transformation into the rutile phase was decreased due to the presence of Ag nanoparticles in the TiO₂ matrix, while the photocatalytic activity of the produced nanocomposite (estimated by studying the degradation of methylene blue aqueous solution under UV irradiation) was 35% greater than that of pristine TiO₂. Therefore, the addition of Ag nanoparticles into the TiO₂ matrix significantly affected the morphology, phase transformation temperature, and photocatalytic performance of the fabricated material.

1. Introduction

It is well known that the addition of noble metals (such as Ag) to TiO₂ particles enhances the photocatalytic performance of the particles [1–15] because of the ability of Ag species to inhibit the electron-hole recombination, which can be explained by the electron acceptor properties of Ag atoms as well as by the plasmon resonance effect [1,2,11,16]. On the other hand, the presence of Ag particles improves the quantum yield of the resulting TiO₂-based material by accelerating the removal and transfer of electrons from the catalyst particles to molecular oxygen species [16]. TiO₂–Ag nanocomposites can be produced using various liquid-phase and gas-phase fabrication methods or their combinations. For example, spin coating, dip coating, sol-gel synthesis, precipitation, chemical reduction, liquid-phase deposition, and microwave-assisted hydrothermal reaction are commonly used liquid-phase preparation methods [1–10,17]. They allow fabrication of TiO₂–Ag nanocomposites at moderate temperatures and atmospheric pressure; however, the corresponding preparation procedures generally involve a large number of processing steps. Moreover, it is difficult to completely remove residues or impurities from the resulting product during liquid-phase synthesis, which requires additional handling of the produced liquid wastes.

Various two-step deposition methods, corresponding to either liquid/gas-phase or gas/gas-phase synthesis were also utilized for manufacturing TiO₂–Ag nanocomposites [11–13]. Furthermore, TiO₂–Ag nanocomposites have been successfully fabricated via one-step deposition by using ultrasonic spray pyrolysis [15], flame spray pyrolysis [18], and combined spray pyrolysis and physical vapor deposition (PVD) techniques [19]. Unfortunately, these methods require heating to relatively high temperatures (up to 550 °C) to ensure decomposition of the precursor solution, which leads to particle agglomeration. The latter decreases the surface area of the produced nanocomposite and reduces the number of active sites, thus lowering its photocatalytic activity. On the other hand, the spray and flame pyrolysis techniques require the use of a solvent for precursor dissolution. Moreover, radio frequency reactive magnetron sputtering [14] and chemical vapor deposition (CVD) methods [20] can also be utilized as one-step processes; however, the corresponding procedures must be conducted at high temperatures under vacuum conditions, using a limited number precursors. In addition, the described techniques of nanocomposite fabrication are based on the properties of molecules and not particles, thus making structural control of the produced nanocomposites very difficult.

Owing to the limitations of the previously developed methods, the

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purpose of this work was to fabricate TiO₂-Ag nanocomposite materials via a simple solventless process characterized by a low degree of particle agglomeration and relatively high deposition rates. To our knowledge, no studies describing the fabrication of TiO₂-Ag nanocomposites via a deposition process that utilized two different particle sources without significant agglomeration in the gas-phase have been reported yet. The use of two different particle sources of starting materials enables easy tuning of some parameters of the produced nanocomposites (such as particle diameter and content), which allows control of the nanocomposite structure. In our previous studies, we successfully synthesized TiO₂ porous films with a low degree of particle agglomeration by using a plasma-enhanced chemical vapor deposition (PECVD) method [21,22]. As a result, non-agglomerated TiO₂ nanoparticles were formed due to electrostatic repulsion between the negatively charged particles generated by a plasma reactor [23]. The formation of porous (particulate) layers, as well as in columnar film, enhances the photocatalytic activity of the produced films since it accelerates the mass transfer of probe dye molecules, thus allowing deeper penetration through the catalyst surface [24]. On the other hand, high-energy species (such as ions, radicals, and atoms) can be generated by PECVD at relatively low temperatures under appropriate operating conditions [25,26], which lower the deposition temperature and increase the deposition rate [21,22,25,26]. While, high-purity Ag nanoparticles can be produced during the evaporation and condensation steps of the PVD process.

In this study, we hypothesized that highly pure Ag nanoparticles incorporated into TiO₂ species with a low degree of agglomeration might cause significant electron transfer from the TiO₂ to the Ag phase, which would enhance their photocatalytic performance. Hence, TiO₂-Ag nanocomposite thin films have been fabricated for the first time via one-step gas-phase deposition using two different particle generators. After that, the produced films were subjected to photocatalytic testing to evaluate their photocatalytic performance and compare it to that of pristine TiO₂. We believe that the obtained results will provide valuable information and new insights into possible fabrication methods of other nanocomposite materials, which can be used in photocatalytic and antibacterial applications as well as in gas sensors and dye-sensitized solar cells.

2. Materials and methods

A schematic of the experimental setup used for the fabrication of nanocomposite thin films is shown in Fig. 1. The utilized system was composed of the following three parts: a plasma reactor for generating TiO₂ nanoparticles, a PVD apparatus for generating Ag nanoparticles, and a deposition chamber. Initially, titanium tetraisopropoxide (TTIP,

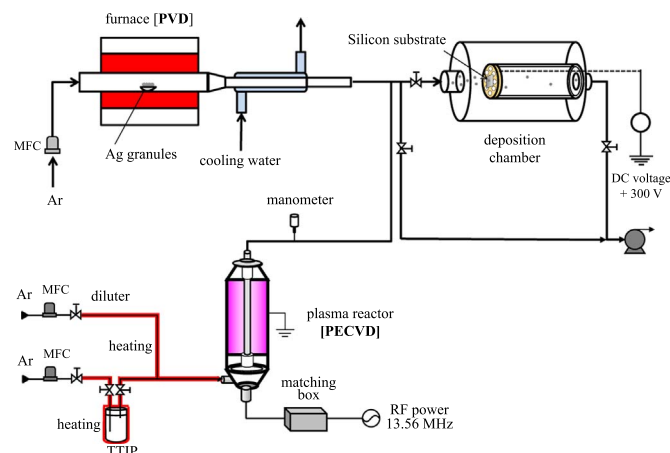


Fig. 1. Schematic describing the fabrication of TiO₂-Ag nanocomposite thin films via the simultaneous use of the PECVD and PVD techniques in the gas phase.

Kanto Chemical) was stored inside a heated bubbler at a temperature of 45 °C and vaporized by bubbling Ar gas through the TTIP precursor. The produced TTIP vapor was transported by Ar gas at a flow rate of 40 sccm inside the plasma reactor (both the TTIP vapor and Ar gas line were heated to temperatures greater than 45 °C to avoid condensation). Subsequently, TiO₂ nanoparticles were generated by the plasma bombardment of the supplied TTIP species (the obtained particles were negatively charged because of the excess of electrons produced during plasma operation [25]). The detailed procedure of TiO₂ nanoparticle generation via PECVD is described elsewhere [21,22]. The utilized plasma reactor had a coaxial bicylindrical structure and consisted of a stainless steel outer cylinder (covered with an electrically grounded Cu sleeve) and a stainless steel inner rod coupled through a matching network to a radio frequency power supply (AX-1000IIP, Adtec Plasma Technology Co., Ltd.), which was operated at a power of 100 W and frequency of 13.56 MHz.

Ag nanoparticles were generated via PVD, during which Ag granules (Kanto Chemical) placed in ceramic boats were evaporated inside a tubular furnace at a temperature of 1100 °C followed by condensation of Ag vapor using a water cooling system. The synthesized TiO₂ and Ag nanoparticles were then continuously fed into the deposition chamber using Ar as the carrier gas. A Si plate with dimensions of 1×1 cm², which was connected to a 300 V voltage source to ensure uniform nanoparticle deposition, was used as a substrate. A nanocomposite thin film was produced after 30 min of nanoparticle deposition onto the Si substrate (the total pressure inside the reactor was maintained in the range of 2–4 kPa). After that, the fabricated film was annealed in air at a temperature of 600 °C for 12 h and heating/cooling rates of 5 °C/min (the detailed illustration of the utilized fabrication procedure is shown in Fig. S1).

The obtained products were characterized using scanning electron microscopy (SEM, S-5200, Hitachi High Technologies), transmission electron microscopy (TEM, JEM-2010, JEOL), energy dispersive X-ray spectrometry (EDS), X-ray diffraction (XRD, MiniFlex 600, Rigaku), and photocatalytic testing techniques. The photocatalytic activity of the produced nanocomposites was evaluated by measuring the photocatalytic degradation of methylene blue (MB, Kanto Chemical) aqueous solution under UV light irradiation in the dark. The concentration of MB was determined by measuring the UV absorbance at a wavelength of 664 nm with a UV-visible spectrometer (V-650, Jasco).

3. Results and discussion

Fig. 2 shows the SEM images depicting the top views of the pristine TiO₂ and TiO₂-Ag nanocomposite thin films before and after annealing at 600 °C. The average particle size was estimated as the geometric mean diameter (GMD) calculated using the equation $\log(\text{GMD}) = (\sum_i^n \log d_{pi})/n$; where n and d_{pi} are the total number of particles and diameter of i -th particle, respectively. The GMD of pristine TiO₂ before annealing (15 nm) was not significantly different from that of TiO₂-Ag nanocomposites (13 nm; see Fig. 2(a) and (c)), indicating that the nanocomposite morphology was not affected by the presence of Ag nanoparticles in the as-deposited films.

In contrast, the GMD of TiO₂-Ag nanocomposites increased significantly after annealing, reaching the magnitude of 41 nm, which was larger than that of pristine TiO₂ (20 nm; see Fig. 2(b) and (d)). The observed phenomenon can be attributed to the increase of particle mobility at higher temperatures (which corresponds to the particle coalescence process induced by thermal treatment), suggesting that the presence of Ag nanoparticles may accelerate the heat transfer between various TiO₂ particles. Dehimi et al. [27] also reported the increase in the size of ZnO particles after addition of Ag dopant during annealing at a temperature of 500 °C. In addition, the average particle size of the produced TiO₂-Ag nanocomposites was larger than that of pristine TiO₂ [5,14]. The obtained data were consistent with the results of XRD

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