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Synthesis of a silver/TiO_2 nanotube nanocomposite by gamma irradiation for enhanced photocatalytic activity under sunlight

Pham Van Viet[a,*], Truong Tan Sang[b], Nguyen Quoc Hien[c,*], Cao Minh Thi[b], Le Van Hieu[a,*]

[a] Nanomaterials for Environmental Applications Laboratory, Faculty of Materials Science and Technology, University of Science, VNU-HCMC, Ho Chi Minh City 700000, Viet Nam

[b] CM Thi Laboratory, Ho Chi Minh City University of Technology (HUTECH), Ho Chi Minh City 700000, Viet Nam

[c] Research and Development Center for Radiation Technology (VINATOM), Ho Chi Minh City 700000, Viet Nam

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ABSTRACT

In this study, a nanocomposite of silver loaded on TiO_2 nanotubes (Ag/TNTs) was synthesized by a gamma irradiation method with a 92.42% yield. The optimized scale for Ag/TNT synthesis was 1.29 g of precursors per 100 mL solvent. The morphology and crystal structure of the Ag/TNTs were determined by transmission electron microscopy and X-ray diffraction, respectively. The Ag weight percentage in Ag/TNTs was analyzed by inductively coupled plasma atomic emission spectrometry. The results showed that the size of silver nanoparticles on the TNTs decreased when the precursor weight decreased. The Ag/TNT nanocomposite removed 95.45% of methylene blue under simulated sunlight irradiation and could be reused five times with an almost unchanged activity. The formation mechanism of silver nanoparticles on TNTs is also discussed.

1. Introduction

TiO_2 is an important semiconductor because it is low in cost, nontoxic and has high chemical stability. This material is applied in many fields, such as photocatalysis [1], sensors [2,3], antibacterial applications [4,5] and so on. The use of its large specific surface area and photochemical reaction to treat polluted water is currently receiving significant attention [6,7]. Consequently, to increase the specific surface area of TiO_2, many researchers have tried to fabricate TiO_2 nanomaterials (i.e., nanoplumes [8], nanospheres [9], nanorods [10,11], nanowires [6,7,12,13], nanotubes [14,15] and so on). In addition, more than one thousand studies have been published on TiO_2 nanotubes (TNTs), because in this structure, the size of the tubes and the properties can be easily controlled, as well as it being synthesized by a simple process [15]. However, reducing the size of TiO_2 significantly increases the band gap of the material (from 3.2 eV in bulk TiO_2 to 3.8 eV in TNTs [16,17]), due to the quantum confinement effect. Therefore, UV irradiation ($\lambda \leq 326$ nm) of TNTs is required to trigger the photocatalytic activity, which limits the applications of TNTs under sunlight [18].

Recently, many studies have been focused on improving the photocatalytic activity of TNTs by doping, loading noble metals at the nanoscale (such as Au [19], Pt [20,21], Ag [22,23] and so on) or adding oxide semiconductor materials (such as SnO_2 [24], ZnO [25] and so on) into/onto TNTs. The noble metal nanoparticles can act as electron traps [26] and enhance the light absorption in the visible range by the surface plasmon resonance effect [27]. Among the noble metals, Ag is an attractive candidate for enhancing the photocatalytic activity of TNTs under visible light because Ag is chemically stable, low in cost and nontoxic for humans in low concentrations.

Although many methods have been developed to synthesize Ag/TNTs, there is no report regarding the synthesis of Ag/TNTs by gamma irradiation. Compared with other methods, such as microwave-assisted techniques [28], UV irradiation [23] and photochemical reduction [29], gamma irradiation has many advantages [30–33]. These advantages include synthesizing Ag NPs directly on TNTs in very short period of time, an easy to control reaction rate, as well as the size and shape of the Ag NPs, which can be carried out at room temperature by simply using the reducing agent in a one pot reaction, having no further treatment requirement for the product and gamma irradiation has been also considered as a green method for noble metal nanoparticle synthesis. Therefore, synthesizing Ag/TNTs by gamma irradiation is a potential method for application on an industrial scale.

Because of the above reasons, this study focused on the loading of Ag NPs on TNTs using gamma irradiation. The Ag/TNT synthesis scale (precursor weight/solvent volume) was optimized. The formation mechanism, the photocatalytic activity under simulated sunlight irradiation and the reusability of Ag/TNTs are also discussed.

* Corresponding authors.
E-mail addresses: pvviet@hcmus.edu.vn (P.V. Viet), hien7240238@yahoo.com (N.Q. Hien), lvhieu@hcmus.edu.vn (L.V. Hieu).

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Table 1
Prepared parameters of Ag/TNT samples.

Sample	Precursor weight, g	Dose, kGy	Irradiation time, min	Maximum %Ag weight
Ag/TNTs–1	m_{AgNO_3} = 0.1700 m_{TNTs} = 5.0000 $m_{precursor(total)}$ = 5.1700	20	500	2.11% (if the yield of Ag^+ reduction process reached 100%)
Ag/TNTs–2	m_{AgNO_3} = 0.0850 m_{TNTs} = 2.5000 $m_{precursor(total)}$ = 2.5850	10	250	
Ag/TNTs–3	m_{AgNO_3} = 0.0425 m_{TNTs} = 1.2500 $m_{precursor(total)}$ = 1.2925	5	125	

2. Experimental

2.1. Chemicals

TNTs were synthesized by a hydrothermal method from a commercial TiO_2 powder (Pham Van Viet research group [15]). $AgNO_3$ (Alpha Chemika, India, 99.9%), ethanol (Scharlau, Spain, 99.99%), methylene blue (JHD Fine Chemicals, China, 99%) and deionized (DI) water (Puris–Evo water system) were used without any further treatment.

2.2. Preparation of Ag/TNTs

Previous publications on Ag/TiO_2 indicate that 2.0 wt% of Ag exhibited the highest photocatalytic activity [23,34–36]. Therefore, Ag/TNTs were synthesized with 2.0 wt% Ag. First, a mixture of 80 mL of DI water and 20 mL of ethanol was used as the solvent for every synthesis. Different total weights of precursors (TNTs and $AgNO_3$, m_{AgNO_3}: m_{TNTs} were kept constant) were used to fabricate different amounts of Ag/TNTs (Table 1). Second, TNT powder was magnetically stirred with $AgNO_3$ and irradiated under a Gamma Chamber 5000, BRIT (India) (dose rate: 2.4 kGy/h, dose range: 2–20 kGy, measured by a dichromate dosimetry system [37]) at room temperature and under atmospheric pressure. The gamma irradiation dose was proportional to the precursor weight. Finally, the powder was filtered, washed with DI water five times and dried at 100 °C for 2 h.

2.3. Materials characterization

The phase composition and crystal structure of the TNTs and Ag/TNTs were determined by XRD using a Bruker D8–Advance 5005 with Cu Kα radiation (λ = 0.154064 nm). The morphologies of the TNTs and Ag/TNTs were recorded by TEM on a JEM 1400. The weight percentage of Ag in Ag/TNTs was analyzed by inductively coupled plasma atomic emission spectrometry (ICP–AES) on a Perkin–Elmer, Optima 5300 DV.

2.4. Photocatalytic activity of Ag/TNTs

MB dye is widely used as the indicator of organic pollution in water. The photocatalytic activity of the Ag/TNTs and TNTs was evaluated by measuring the degradation rate of MB under simulated sunlight irradiation. First, 30 mL of MB 10 ppm was magnetically stirred with 0.03 g of catalyst in the dark for 1 h (for the equilibrium of the absorption and desorption process of MB). Next, the mixture was irradiated with a simulated solar spectrum lamp (Philips Lampe, PAR 38EC, 230 V, and 120 W). Lux and power meters (10^5 lux = 10^3 W/m^2) were used for measuring the irradiance. After every 5-min irradiation, the MB concentration was recorded by an ultra violet–visible (UV–VIS) spectrophotometer (U2910, Hitachi, Japan).

In addition, the used catalyst was filtered, washed, dried at 90 °C for 30 min and the photocatalytic ability was tested again to determine its reusability, which is important for practical applications. All experiments to determine the photocatalytic activity were repeated three times and the values of the measurement of the photocatalytic activity were used by mean values.

3. Results and discussion

3.1. Morphology of material

The TEM images of TNTs (Fig. 1) showed that the morphology of the TNTs was uniform in diameter, and the average diameter of TNTs was ~8–10 nm. The morphology of TNTs did not change after the

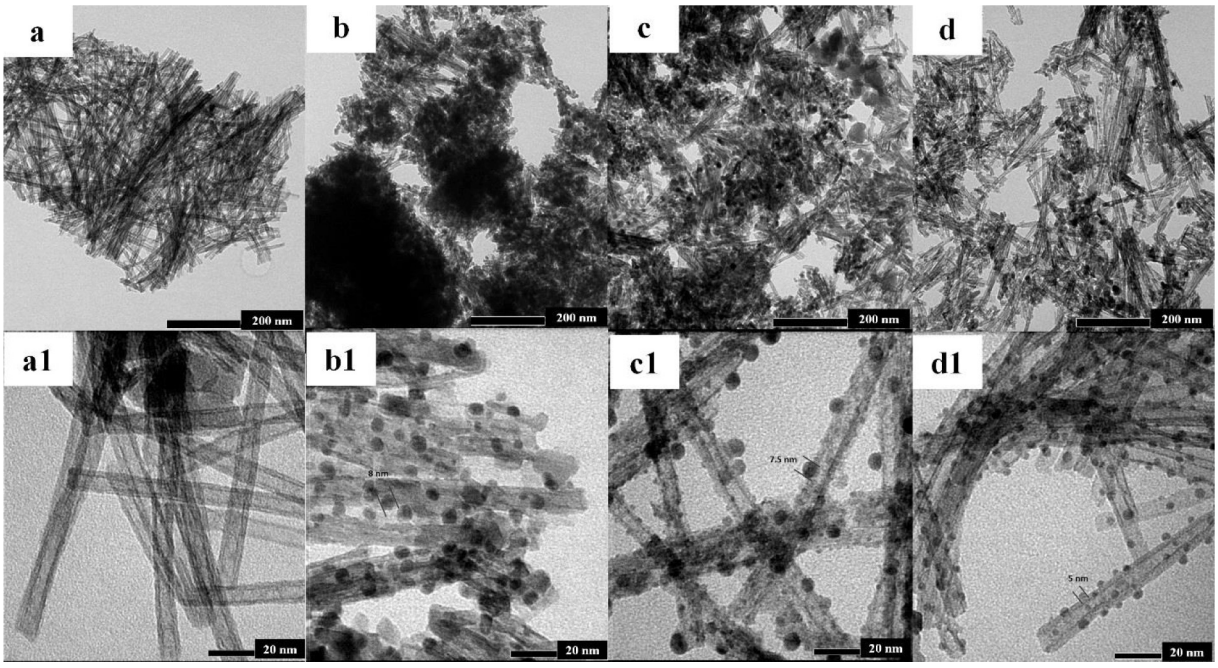

Fig. 1. TEM images of TNTs (a, a1) and Ag/TNTs–1 (b, b1), Ag/TNTs–2 (c, c1) and Ag/TNTs–3 (d, d1); (a–d: 100 nm of scale bar; a1–d1: 20 nm of scale bar).