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Synthesis, Characterization, and Regeneration of Ag/TiO_2 Nanoparticles: Photocatalytic Removal of Mixed Dye Pollutants †

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Abstract: Titanium dioxide nanoparticles were prepared via the hydrothermal method, and silver was supported on TiO_2 nanoparticles to form Ag/TiO_2 using the photoreduction method. The prepared samples were dried overnight at 60 °C and then calcined at 500 °C for 2 h. Structural and morphological characterization were carried out using X-ray diffraction, field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). The adsorption performance and photocatalytic activity of the Ag/TiO_2 were investigated using malachite green dye (MG) as a model organic pollutant in water. Along the way, the effects of various parameters were examined, such as regeneration experiments and removal of a laboratory sample (a mixture of several dyes) from aqueous solutions. The photocatalytic degradation efficiency reached 83.9%, 78.8%, and 68.5% during three cycles, compared to the standard solution (fresh), which reached 90.9%. These results underscore the potential application of Ag/TiO_2 in environmental remediation, particularly in the degradation of organic dyes.

Keywords: nanoparticles; photocatalytic; malachite green dye (MG); silver; titanium dioxide

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1. Introduction

The textile dyes, along with a large number of industrial pollutants, are highly toxic and potentially carcinogenic. Consequently, they are associated with environmental degradation and various diseases in animals and humans [1–5]. There has been a growing focus on dye degradation in industrial wastewaters, and several remediation strategies have been proposed. Pollutants have been eliminated using conventional physical techniques such as adsorption on activated carbon, ultrafiltration, and reverse osmosis [6–8]. However, these methods only succeed in transferring organic compounds from water to another phase, thus creating secondary pollution. Chemical methods such as chlorination generate carcinogenic and mutagenic byproducts that threaten human health [6]. An almost ideal solution to this problem is photocatalytic degradation. Specifically, dyes can degrade when exposed to visible light in the presence of a photocatalyst, due to their absorption in this spectrum. Because metal oxides are widely used in organic synthesis and have numerous environmental applications, there has been substantial interest in heterogeneous photodegradation by metal oxide in recent years [9,10]. Among the metal oxide semiconductors, titanium dioxide (TiO_2) is one of the most effective photocatalysts currently in use. Its strong oxidizing power, nontoxicity, and long-term physical and chemical stability contribute to its effectiveness [11–14]. TiO_2 has a wide band gap of 3.2 eV and requires only UV light for excitation to form photoactive species of holes (h+) and electrons (e−) . The (h+) acts as a strong oxidizing agent, while the (e−) works as a reducing agent [15,16]. The recombination of h+ and e− in the TiO_2 photocatalyst is rapid, resulting in an inefficient photocatalytic process. To overcome this limitation, TiO_2 is often loaded with noble metals such as Au, Pd, Pt, and Ag.

Among these, Ag is the most used in doping TiO_2, enhancing electron–hole separation, interfacial charge transfer ability, and increasing the visible light excitation of TiO_2 nanoparticles (NPs) [17,18]. In this work, titanium dioxide is prepared by the hydrothermal method and silver-modified TiO_2 (Ag/TiO_2) is prepared by photoreduction. The obtained photocatalysts are characterized by means of X-ray diffraction, field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDX). Malachite green (MG) is used as a model pollutant to study the photocatalytic activity of Ag/TiO_2 under UV light irradiation.

2. Materials and Methods

2.1. Materials

The chemicals used in this study include titanium(IV) bis(ammonium lactato) dihydroxide (TALH, 50% aqueous solution), aqueous ammonia solution (25% NH_3), ethanol 99.9%, and Malachite green dye (MG). All chemicals were used directly without further purification.

2.2. Preparation of Titanium Dioxide by Hydrothermal Method

Titanium dioxide (TiO_2) nanoparticles (NPs) were prepared via the hydrothermal method using TALH. A mixture of 10 mL of an aqueous titanium(IV) bis(ammonium lactato) dihydroxide solution, 15 mL of an aqueous ammonia solution, and 40 mL ethanol was prepared, followed by the addition of distilled water to reach a final volume of 115 mL. This solution was mixed well using magnetic stirring for 30 min, then transferred into a Teflon cup, sealed in an autoclave, and placed into an electric furnace held at 180 °C for 24 h. The autoclave was then naturally cooled in air, washed several times with distilled water, and dried overnight at 60 °C. The product powder was calcined at a temperature of 500 °C for 2 h in a furnace, resulting in TiO_2 nanoparticles.

2.3. Preparation of Silver Ag-Doped TiO_2 Nanoparticles

Silver (Ag)-doped TiO_2 nanoparticles were prepared by suspending 1 g of TiO_2 NPs powder in 100 mL of distilled water and 2.5 mL of $AgNO_3$ (0.01 M). This mixture was sonicated for 5 min and exposed to nitrogen gas for 10 min. Subsequently, 1.5 mL of methanol was added, and the mixture was irradiated with a light intensity of 1.71 mW/cm^2 (using a UVA LED lamp) overnight, with continuous stirring. The resulting powder was washed several times with distilled water and dried for 24 h at 60 °C to obtain the Ag/TiO_2 nanocomposite.

2.4. Preparation of Standard Solution of Malachite Green (MG) Dye

A stock solution (1000 mg/L) of aqueous MG dye was prepared by dissolving 1 g of MG in distilled water and then making up the solution to 1000 mL with distilled water. The solution's maximum wavelength was found at λ_{max} MG = 625 nm. Additionally, 200 mL laboratory samples of dye pollutants containing multi-mixtures of various dyes were prepared for application in real samples.

2.5. Photo Catalysis Experiment

An established concentration of Malachite green (MG) solution (50 mg/L) was used to study the photocatalytic degradation. This solution was supplemented with 0.3 g of the nanocomposite and then transferred into the photoreaction vessel. It was continuously stirred while being exposed to UV light at 365 nm with an intensity of 1.27 MW/cm^2. The solution was removed and centrifuged for 10 min at 3500 rpm after every interval of 10 min. The degradation of the centrifuged solution was measured using a UV–Vis spectrophotometer at its maximum absorbance wavelength of MG dye = 625 nm, and the result was studied.

3. Result and Discussion

3.1. XRD Diffraction of TiO_2 and Ag/TiO_2 Nanocomposite

In Figure 1 the XRD patterns of prepared TiO_2 show no other peaks that might indicate the presence of impurities, due to the effects of calcination at 500 °C. The diffraction peaks were observed at 25.3°, 37.9°, 48.2°, 54.5°, 55.3°, 62.02°, and 68.7°, which correspond to the (101), (108), (004), (112), (211), (200), (106) and (212) lattice planes of anatase TiO_2 (JCPDS card no. 21-1272). The crystal shape of the diffraction peaks appears clear and sharp [19,20].

Also we can notice in Figure 1, no crystalline phase involving Ag could be observed, indicating that the Ag is either too dispersed in the TiO_2 lattice for clear crystal formation or that the Ag content is below the detection limit. Interestingly, no Ag crystal phase was detected; thus, at low Ag content, higher dispersion of smaller Ag nanoparticles on the surface and pores is clearly achieved [21].

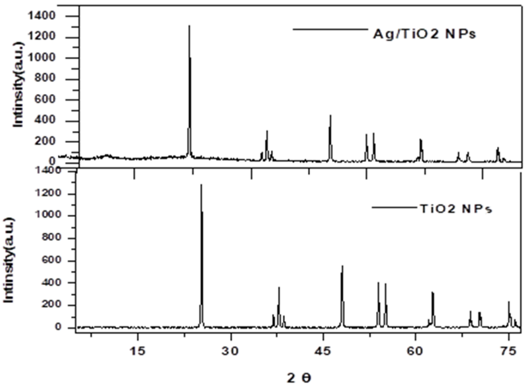

Figure 1. XRD diffraction TiO_2 and Ag/TiO_2 nanocomposite.

3.2. FE-SEM Image of TiO_2 and Ag/TiO_2 Nanocomposite

The surface morphology of pure TiO_2 nanoparticles was studied using SEM, focusing on the size, shape of particles, and clusters among them, in addition to the distribution of these particles. Figure 2A,B show an SEM image of TiO_2, where the nanoparticles exhibit an anatase shape with a mean size of between 29.34–41.34 nm, with a high degree of agglomeration. Ag/TiO2 Figure 2C,D were found to overlap with TiO_2 NPs, exhibiting cubic-like morphology with particle sizes ranging from around 48.34–120 nm [22,23].

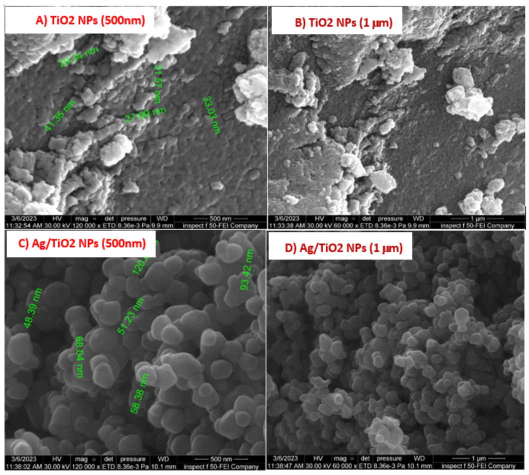

Figure 2. FE-SEM images (**A**,**B**) TiO_2 NPs in different magnitude, (**C**,**D**) Ag/TiO_2 nanocomposite in different magnitude.

3.3. TEM and EDX of TiO_2 and Ag/TiO_2 Nanocomposite

Transmission electron microscopy provides a more accurate view of the structure of prepared samples, such as crystallinity, distribution, and particle size. Figure 3 reveals that silver nanoparticles were clearly observed as the most intense dark spots on the TiO_2 surface. The Ag nanoparticles deposited on the TiO_2 are small and well deposited on the TiO_2 NPs [24].

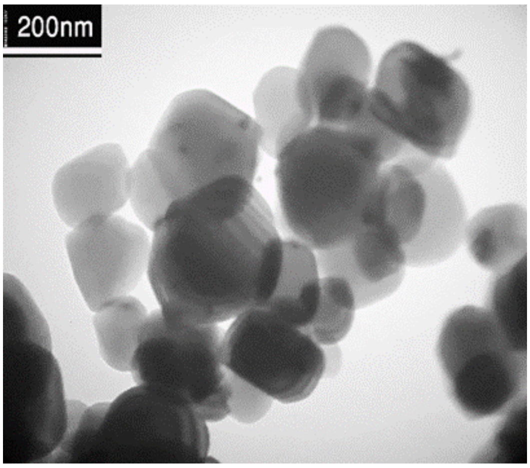

Figure 3. TEM of image Ag/TiO_2.

3.4. Application of Prepared Nanocomposite

3.4.1. Recycling of the Photocatalyst Ag/TiO_2 Nanocomposite

Recycling the catalyst is crucial in assessing the practical application of photocatalysts and developing heterogeneous photocatalysis technology for wastewater treatment. An examination of the photocatalytic activity of the recycled Ag/TiO_2 nanocomposite catalyst on Malachite green dye shows degradation efficiencies of 83.9%, 78.8%, and 68.5% during three cycles as shown Figure 4, compared to a standard solution (fresh) of 90.9%. The photocatalysts exhibit self-cleaning surface properties and reusability, making them effective and promising for environmental remediation [25,26].

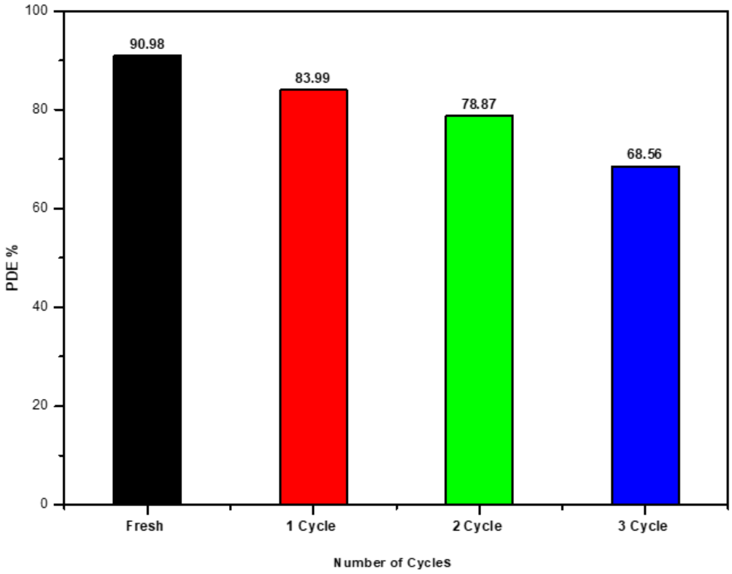

Figure 4. Reusability of the photocatalyst for photocatalytic degradation MG dye.

3.4.2. Removal of Pollutants (Mixture of Dyes) by Using Ag/TiO_2 Nanoparticles

A laboratory sample (200 mL) containing various dye pollutants was treated with 0.3 g of prepared Ag/TiO_2 nanoparticles. The mixture was exposed to ultraviolet light for 2 h while maintaining a controlled distance from the light source, followed by centrifugation to separate the supernatant (shown in Figure 5). The remaining concentration was determined using UV–visible spectrophotometry. As time increased, absorption decreased, resulting in higher percentage removal [23].

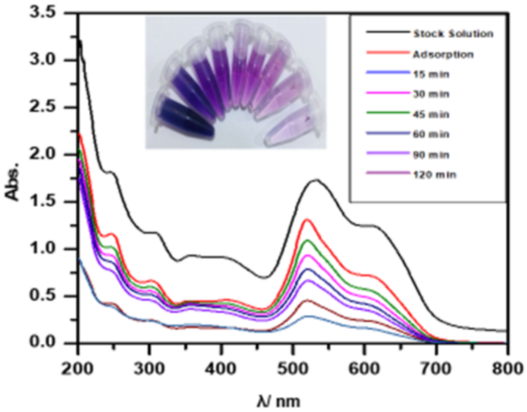

Figure 5. Effect of removal of real sample (mixture of dyes) by using Ag/TiO_2 NPs. Experimental conditions: mass amount 0.3 g/L, initial concentration 50 mg/L, temperature 25 °C, and light intensity 2.1 mW·cm^{-2}.

4. Conclusions

Titanium dioxide nanoparticles were prepared by the hydrothermal method, and further Ag/TiO_2 was prepared by the photoreduction of silver on prepared TiO_2 nanoparticles. These materials were characterized using XRD, FE-SEM, and TEM techniques. The XRD analysis concluded that the prepared TiO_2 is a pure anatase phase. The study encompasses an investigation into various parameters such as regeneration experiments and removal of a laboratory sample, including a mixture of several dyes, from an aqueous solution. The results reveal that the photocatalysts have self-cleaning surface properties and reusability, making them effective. The photocatalyst is fundamentally stable and shows promise for environmental remediation.

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