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Proceeding Paper

Formation of Nanostructured Functional Elements in TiO_2-PVTMS-Ag-La Nanocomposites for Photocatalytic Applications †

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Abstract: The nanoparticles are composed of tens or hundreds of atoms or molecules with different sizes and morphologies (amorphous, crystalline, spherical, needle-shaped, etc.). Most commercially used nanoparticles are in the form of dry powder or liquid. Of course, nanoparticles combined in an organic or aqueous solution in the form of a suspension or paste are also of interest. Photocatalysts are a group of catalysts that act when exposed to light. Photocatalysts are usually solid semiconductor oxides in which the absorption of photons creates electron-hole pairs that can react with molecules on the surface to produce active radicals. Nowadays, nanocomposites have attracted the attention of many researchers due to their special properties, their many technological applications, their unique absorption, photocatalysis, and antimicrobial properties, and their use in the elimination of bacteria. In this research, TiO_2-PVTMS-Ag-La nanocomposites with different stoichiometric proportions were synthesized as a disrupting agent and photocatalyst using the sol-gel method. The samples were calcined at a temperature of 700 °C, and then characterizations consisting of XRD were performed. The degradation and photocatalytic effect of TiO_2-PVTMS-Ag-La nanocomposites on methylene blue dye were studied. As a result, the nanocomposites TiO_2 (80 wt.%), PVTMS (7 wt.%), Ag (2 wt.%), and La (11 wt.%) showed degradation properties.

Keywords: TiO_2-PVTMS-Ag-La; nanocomposite; photocatalyst; degradation

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1. Introduction

Nanotechnology is one of the most important technologies whose applications are associated with lower costs, longer lives, lower energy consumption, and better properties. The best way to clean contaminated sites is to use photocatalyst nanocomposites, which are suitable for a large number of pollutants [1]. Among all existing photocatalysts, titanium oxide (TiO_2) was considered for its non-toxicity and availability, high stability, high photochemical properties, and corrosion resistance. The band gap of titanium oxide is 3 eV for the rutile phase and 3.2 eV for the anatase phase in the ultraviolet region, which accounts for less than 10% of the solar energy. In addition to this obstacle, the high rate of electron-hole rearrangement limits the application of these particles [2]. Photocatalysts are a group of catalysts that act when exposed to light. Photocatalysts are usually solid semiconductor oxides in which the absorption of photons creates electron-hole pairs that can react with molecules on the surface to produce active radicals [3]. PVTMS is synthesized by polymerization of VTMS [4]. The features of the vinyl group (–CH–CH_2) in the structure of PVTMS can be used to perform free radical polymerization. Moreover, PVTMS can improve the thermal stability and physical properties of the framework [5]. Moreover, Rabiei et al. have proven the PVTMS synthesis route [4,6]. It has a functional group like silanol (Si–O–H) that can help with bonding; therefore, it is useful for preventing the decomposition of composites [5]. PVTMS is a polysiloxane-based component that is of particular interest due to its dense structure of siloxane cross-linked with polymeric groups. In addition, PVTMS improves mechanical properties by forming a stable Si–O–Si framework [7]. PVTMS is an organosilane molecule and provides a hydrophobic environment in the composite. Since water can easily diffuse into the polymer structure, it can lead to the breakdown of intermolecular forces and create voids in the polymer [8]. The sol-gel method (chemical solution deposition) is a wet chemical method widely used in engineering and materials science for the synthesis of various nanostructures. In this method, the molecular precursor is dissolved in water or alcohol and transformed into a gel by hydrolysis under heat and stirring. Now the gel needs to be dried, which can be performed by burning the alcohol in the alcoholic solution. After the gel is dried, it is powdered, and the resulting powder is heated for calcination [9]. In this study, considering the potential of La and polyvinyl trimethoxy silane (PVTMS), TiO_2-PVTMS-Ag-La nanocomposites with different weight fractions were prepared. In addition, the characterization and evaluation of the degradation performance in the presence of aqueous pollutants and the effects of the performance on the photocatalytic properties were investigated.

2. Synthesis Nanocomposites

The chemical structure of PVTMS as a reinforcement in the composition of nanocomposite is depicted in Figure 1. In addition, the synthesis route of nanocomposites is shown in Figure 2. (1) 100 mL of 2-propanol was poured into the dish, then lanthanum nitrate was added, and the sample was stirred for 1 h. After the lanthanum nitrate dissolved completely and the solution became reasonably transparent, silver nitrate was added and stirred. After the above time has elapsed and the silver nitrate has completely dissolved and the solution has become homogeneous, titanium isopropoxide is slowly added to the solution, and after 1 h, distilled water is added dropwise until a gel is formed. (2) Then the gel was heated at 120 °C for 30 min, and the gel was converted into powder. (3) Then the powder was washed with distilled water and filtered, and the product was put into the oven for 2 h at 200 °C in an air-conditioned environment for the calcination process. Two composites with different weight percentages of the TiO_2 and PVTMS components were synthesized, consisting of (**1**) [TiO_2 (82 wt.%), PVTMS (5 wt.%), Ag (2 wt.%), and La (11 wt.%)] and (**2**) [TiO_2 (80 wt.%), PVTMS (7 wt.%), Ag (2 wt.%), and La (11 wt.%)].

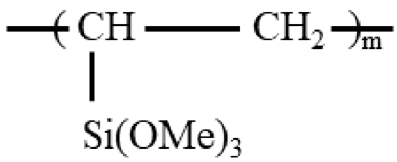

Figure 1. Chemical structure of PVTMS.

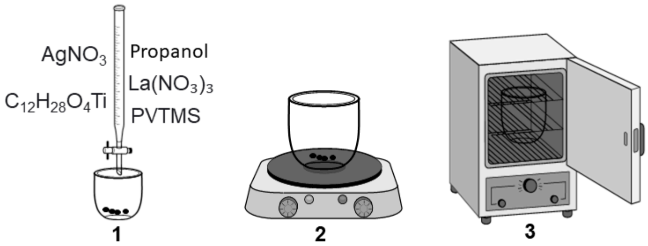

Figure 2. Synthesis route for nanocomposites.

3. Results and Discussions

3.1. X-ray Diffraction Analysis

The phase series was confirmed by X-ray diffraction (XRD) and a Philips XRD diffractometer with $Cu_{k\alpha}$ radiation at 40 KV, 30 mA, a step size of 0.05° (2θ) and a scan rate of

1°/min, and X'Pert software was used for qualitative analysis and report of width diffraction peaks (rad, β) at full width half maximum (*FWHM*) in different 2θ values according to the situation of peaks (Version 4.9.0). Figure 3 shows X-ray diffraction analyses of nanocomposite samples. As can be seen in the stoichiometry of all the synthesized nanocomposites, the desired phases are formed without additional peaks and impurities, and the intensity of the corresponding peaks decreases with the decrease in TiO_2 content. It can also be seen that due to the constant amount of lanthanum in all samples, the corresponding peaks in all diffraction patterns are almost the same [10,11]. The modified Scherrer method was used for calculating nanocrystallite size values of nanocomposites, and the values were gained in the range of 61 and 57 nm, respectively, for compounds **1** and **2**. As predicted, with increasing PVTMS, the crystalline size decreased.

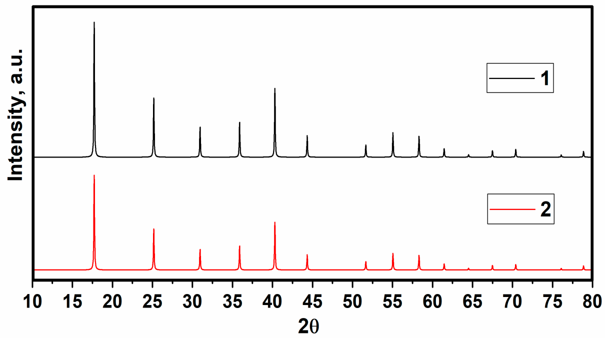

Figure 3. X-ray diffraction of nanocomposites **1** and **2**.

3.2. Investigation of FTIR

Fourier-transform infrared spectroscopy (FTIR) spectra of the compounds were attached to the potassium bromide (KBr) powders, and the instrument that was used was a Perkin-Elmer Spectrum BX FT-IR spectrometer. The FTIR spectra of nanocomposites are shown in Figure 4. As can be seen in Figure 4, the bands obtained from infrared absorption, which change as the wavenumber is monitored, are in the form of a spectrum whose width axis indicates the transmittance percentage and the longitude axis indicates the wavenumber corresponding to the confirmed infrared [12]. In the infrared spectrum, each peak represents the amount of absorption in the corresponding wavenumber and is identified by a chemical bond. Consequently, the wavenumber of each peak indicates the presence of a particular functional group in the sample. In general, the more polar a bond is, the higher the absorption rate and the higher the transmittance of the peak. Bending vibrations of Si–OH can be associated with the peaks at 1300 and 1650 cm^{-1}, and the peaks at around 800 cm^{-1} can correspond to Si–O and Ag–O. In addition, OH groups have suggested the existence of PVTMS, and the small range of wavenumber values of 956 cm^{-1} may be from La oxide and PVTMS [13,14].

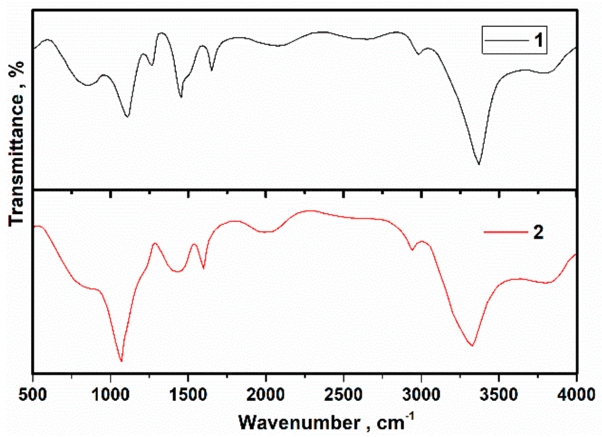

Figure 4. FTIR spectra of compounds.

3.3. Degradation Analysis

The destruction results are shown in Figure 5. These samples were added to a solution of 20 ppm methylene blue with a pH of 9 and initially stirred for 10 min in a dark room with a turned-on UV lamp. From the diagram, it can be seen that the amount of 7% PVTMS in the sample shows a better result compared to the other sample since larger amounts with agglomerated particles reduce the surface area, and thus the degree of destruction is also lower [15].

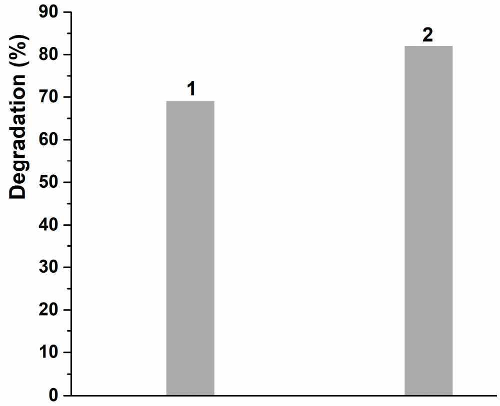

Figure 5. Degradation curve of compounds.

3.4. Investigation of the Absorption Performance of Methylene Blue by an Optimal Photocatalyst

Figure 6 shows the comparison of the optimal degradation and absorption performance of photocatalysts in the presence and absence of light. To ensure the non-absorption of methylene blue by the nanocomposites, the absorption test was performed under optimal conditions in the absence of light. The results showed that sample **1** with the nanocomposite tested in the absence of light as an absorbent had an absorbance of 68.20% under the same optimal conditions and in a period of 1 h. It can be concluded that the prepared sample was not efficient in the absorption process and can be expected to have high activity only as a photocatalyst in the degradation process.

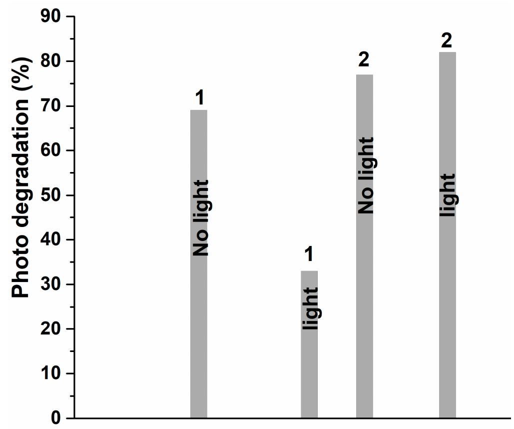

Figure 6. Comparison of the optimal degradation and absorption performance of photocatalysts in the presence and absence of light.

4. Conclusions

(1) In this study, a TiO_2-PVTMS-Ag-La nanocomposite was synthesized by the sol-gel method at the appropriate calcination temperature.

(2) The size of nanocrystallites was detected by the XRD diagram, and the amorphous phases were not observed.

(3) FTIR was used, and the group bands of the nanocomposites showed that there were no impurities in the compositions.

(4) Nanocomposite 2 showed better behavior in the degradation test.

(5) The increasing percentage of PVTMS improved the degradation efficiency of the photocatalyst nanocomposite sample.

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Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could influence the work reported in this paper.

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