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Photocatalytic behavior of TiO₂ and TiO₂/CS nanoparticles under UV irradiation

Comportamiento fotocatalítico de nanopartículas de TiO₂ y TiO₂/CS bajo irradiación UV

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Abstract

TiO₂ nanoparticles and TiO₂/CS nanocomposites have been synthesized using the sol-gel method. Characterization by XRD, FTIR, and UV-vis was carried out to determine the structure, size, functional groups, and energy band gap of the synthesized samples. Moreover, the methyl orange (MO) degradation capability of nanoparticles and nanocomposites under ultraviolet light was studied, and the results are described in detail.

Keywords: semiconducting nanoparticles; properties; photocatalysis.

Resumen

Nanopartículas de TiO₂ y nanocompuestos de TiO₂/CS se han sintetizado mediante el método sol-gel. Se llevó a cabo la caracterización por XRD, FTIR y UV-vis para determinar la estructura, el tamaño, los grupos funcionales y la banda prohibida de energía de los sistemas de muestra. Además, se estudió la capacidad de degradación del anaranjado de metilo (AM) de las nanopartículas y los nanocompuestos bajo luz ultravioleta, y los resultados son descritos en detalle.

Palabras clave: nanopartículas semiconductoras; propiedades; fotocatalisis.

1. Introduction

During the last decades, metal oxides semiconductors such as titanium dioxide (TiO₂) has been received attention due to their attractive physical and chemical properties, as well as their interesting properties in optoelectronic devices, sensing, and photocatalytic and photovoltaic applications [1], [2], [3]. Concerning environmental applications (such as photocatalysts), this material depends on its structure and crystalline phase (anatase, rutile, and brookite), dimensions (1D, 2D, and

3D), morphology, and composition (mixed phases) [1], [4]. However, various studies show that many factors influence the photocatalytic activity of TiO₂ under UV-visible illumination, such as particle size, specific surface area, and structure, to name a someone [1], [4].

Furthermore, TiO₂ is inactive material in the visible region due to its wide energy band gap of 3.2 eV, limiting the use of this material in solar photocatalysis. However, Saravanan et. al., [5] reported that mixed TiO₂ will be used in the photodegradation of organics pollutants under

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visible light by lowering their energy band gap. Also, the use of chitosan (CS) is the safest route to carry out visible light degradation due to that contains hydroxyl and amino groups [5]. In addition, the synthesis methods have an important effect on the photocatalytic activity of metal oxide semiconductors [6]. Furthermore, TiO₂ is active under ultraviolet light.

Thus, this work aims is to study the photocatalytic behavior of TiO₂ and CS composites under UV light considering the study reported by Saravanan et. at., [5] of TiO₂/CS under visible light. Here, TiO₂ nanoparticles and two percentages of TiO₂/CS nanocomposites have been synthesized and their properties studied. Additionally, the synthesized nanocatalysts were used to degrade methyl orange (MO) dye under UV light.

2. Methodology

2.1. Materials

For the synthesis of TiO₂ and TiO₂/CS samples, titanium tetra isopropoxide (TTIP, Purity 97 %, Sigma-Aldrich), Chitosan (CS, medium molecular weight 75 – 85 % deacetylated, Sigma-Aldrich), sodium hydroxide (NaOH, Purity > 99 %, Sigma Aldrich) and acetic acid (CH₃COOH, Purity > 99 %, J.T. Baker) were used without further purification. Methyl orange (MO, Purity ≥ 97.0 %) was purchased from PanReac AppliChem and used for evaluating the photocatalytic capabilities of the samples. All solutions used in the experiments were prepared with deionized water.

2.2. Synthesis of TiO₂ nanoparticles

A sol-gel method was employed to synthesize TiO₂ nanocatalyst. The synthesis was made by the hydrolysis-condensation of TTIP using acetic acid as a solvent agent. First, a solution of acetic acid and deionized water (2% v/v) was prepared. Then, TTIP (at 5 % v/v) as a precursor agent was added until obtaining a homogeneous solution. The homogeneous solution was sonicated for 3 h and then dried on a stirrer hot plate until obtaining the gel formation. After that, the sol-gel product was ground in a mortar to obtain fine powder for analysis. The powder was calcined in a muffle at different temperatures (400, 450, and 500 °C) for 3 h to obtain the TiO₂ anatase phase. A yellow-white fine powder was obtained.

2.3. Synthesis of TiO₂/CS nanocomposites

For the preparation of TiO₂/CS nanocomposite, the sample calcined at 450 °C was used. This sample exhibit an absorption peak in the UV-vis spectrum closer to the visible range in comparison to the other powders. The

proportions TiO₂/CS (w/w) of 95/5 and 80/20 were studied. After that, with these two proportions, two solutions of 2 % w/v were prepared using acetic acid as solvent. Then, the samples were placed on a magnetic hot plate stirring for 30 min. Sodium hydroxide solved in water at a 50 % concentration was gradually added to the previous solution to control the pH level until it is precipitated. This pH has a value of approximately 6 and 10 for each TiO₂/CS proportion. Both solutions were taken to the centrifuge for 10 min to separate the liquid phase from the solid. Later, the samples were dryers in an oven at 55 °C for 12 h. The product obtained is macerated to a fine powder.

2.4. Characterization

The structural phase and crystallinity of the samples were determined using an X'Pert-PRO of the PANalytical brand, with a CuK_α radiation ($\lambda = 0.154$ nm) at room temperature (RT). The XRD was operated at 45 kV. The measurements were done with a step of 0.002°, in 2 θ angle of 10° to 90°. An FTIR spectrophotometer (model IRAffinity-1 from Shimadzu) in transmittance mode was used to obtain the IR spectra of the samples. UV-vis spectra were recorded at room temperature in the range of 200-800 nm by employing a Double Beam UV-vis spectrophotometer (E-Chrom Tech) with a step of 0.5 nm, respectively. The optical energy band gap (E_g) was determined using the Tau plot method through UV-vis measurements. Thermal analyses were carried out using a calorimeter DSC, Q-100, from TA Instrument Brand. The measurement was done in an aluminum capsule (mass: 5 mg) with a ramp of 10 °C/min.

2.5. Photocatalysis measurements

Photocatalytic activity experiments were conducted in a homemade photoreactor with a UV lamp. Methyl orange (MO, purity ≥ 97 % from Sigma-Aldrich) was selected to evaluate the photocatalytic capabilities of the samples. This was selected because, unlike methylene blue, it does not degrade under UV irradiation in the absence of a photocatalyst material. A calibration curve was made using MO in deionized water in a concentration between 1 ppm and 10 ppm, using the Double Beam UV-vis spectrophotometer (E-Chrom Tech). Measurements were made using two quartz cell (10 mm x 10 mm). The first one is filled with deionized water as a reference and the second is filled with the sample. All measurements were made with a fixed initial concentration of 5 ppm for the MO in deionized water and the photocatalyst material (TiO₂ nanoparticles and TiO₂/CS nanocomposites) was added at a concentration of 1 g/L in a beaker. This mixture was placed in the photoreactor under magnetic

stirring for 30 min without light to ensure adsorption/desorption equilibrium, and then under UV irradiation for 4 h. Absorbance measurements were made in this time frame, removing a part of the sample (~ 3 ml) and putting it to centrifuge for 4 min at 3000 rpm to separate the dye solution from photocatalyst material. This procedure was made for each sample. In addition, a calibration plot based on the Beer-Lambert law was established by relating the absorbance to the concentration, and the percentage of MO degradation was calculated using the expression $\% \eta = \frac{(C_0 - C)}{C_0} \times 100 \%$ [7], where C_0 is the initial concentration and C is the concentration of MO under UV light.

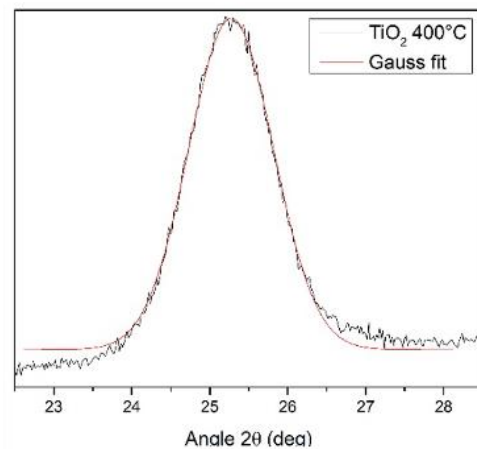
3. Results and discussions

Figure 1 shows the principal (101) plane of XRD patterns of the synthesized TiO₂ nanoparticles (NPs) treated at 400, 450, and 500 °C. The patterns have been indexed for the JCPDS 89-4921 reported in Ref [4], with crystal structure corresponding to the tetragonal anatase phase. The crystallite size estimation was determined using Scherrer's formula reported in Ref [7]. Here, the (101) plane was fitted by a Gaussian function to determine the 2θ peak and the line broadening β (FWHM) of the NPs. The results are reported in Table 1. As can be seen, the crystallite size increase with increasing the temperature of synthesis.

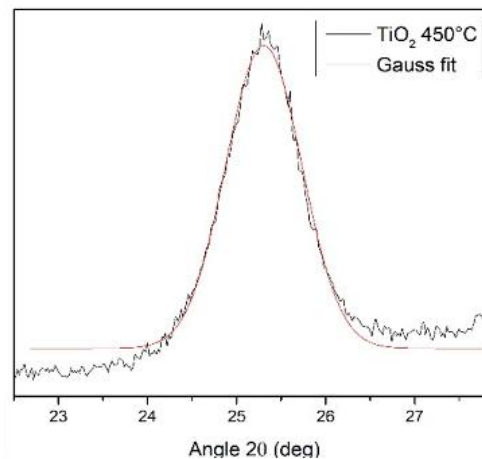
On the other hand, CS shows two principal peaks at around 11° and 21°, which is in agreement with previous reports [5], [8], while TiO₂ NPs exhibit peaks at 2θ values 25.5°, 38.2°, 48.2°, 54°, 55.2°, 62.8°, 69°, 70.6°, and 75.5° and Miller's indexes (101), (004), (200), (105), (211), (204), (116), (220), and (215), respectively. However, the XRD pattern of the anatase phase in the TiO₂/CS nanocomposite was identical to that of TiO₂ NPs without alteration of its structure (see Figure 2) and confirm the formation of the nanocomposite. Similar results were obtained for the nanocomposites with TiO₂ treated at 400 and 500 °C (not shown).

Table 1. Crystallite size of TiO₂ NPs

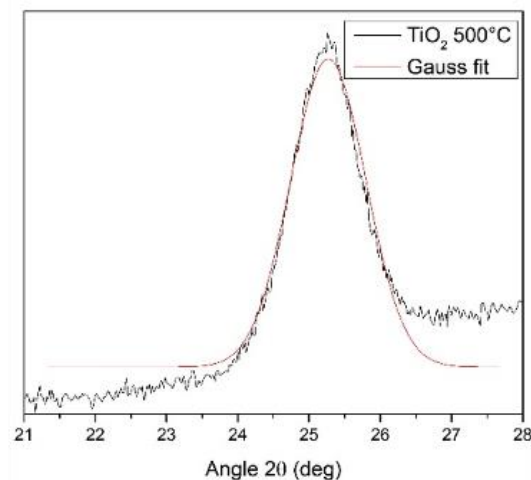
Sample	θ_B (deg)	B (rad)	Crystallite size, D (nm)
TiO ₂ at 400 °C	25.2	0.021	7.3
TiO ₂ at 450 °C	25.3	0.017	8.7
TiO ₂ at 500 °C	25.2	0.017	8.8



(a)



(b)



(c)

Figure 1. (101) Gauss fit of anatase phase for TiO₂ NPs treated at a) 400 °C, b) 450 °C, and c) 500 °C.

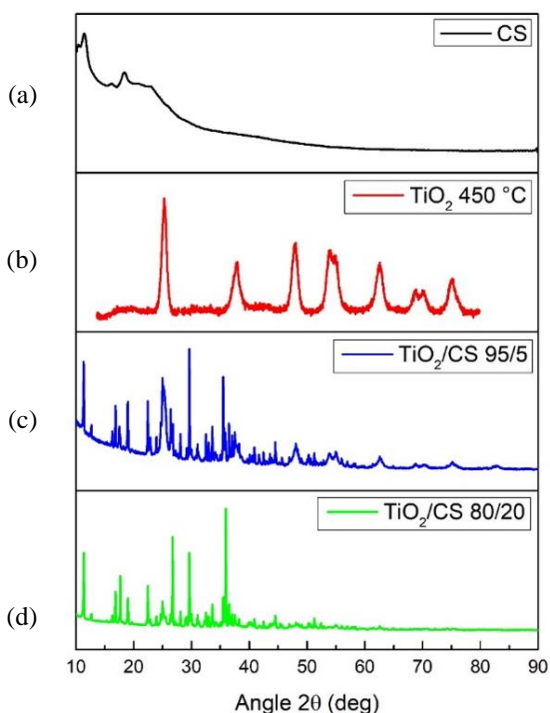


Figure 2. XRD pattern of samples a) CS, b) TiO_2 NPs, c) TiO_2/CS 95/5, and d) TiO_2/CS 80/20 treated at 450°C

Figure 3 shows the FTIR spectra for the TiO_2 NPs treated at 450°C , chitosan (CS), and nanocomposites. It is clearly observed in all of them that the characteristic stretching mode between 600 and 700 cm^{-1} corresponds to Ti-O-Ti bonds [5]. In the case of the pure CS spectrum, the OH bond is found around 3342 cm^{-1} . Another functional group is around 1028 cm^{-1} which is associated with C-O group [8], [9]. Moreover, chitosan contains an amino group that was presented around 1650 cm^{-1} . The C-H groups may be associated with the band around 2857 cm^{-1} [9], [10]. After the addition of the TiO_2 NPs to the chitosan, the stretching vibration of C-O, amino, and hydroxyl groups are modified due to the presence of TiO_2 NPs. This observation is evidence of the formation of TiO_2/CS system and agrees with XRD results.

Absorbance measurements as a function of radiation's wavelength were carried out to determine the optical energy bandgap (E_g) of the samples (not shown) and reported in Table 2. However, the direct and indirect transitions were calculated through Tauc's plot method [4], based on the dependence of the absorption coefficient, α ($\alpha = 0$), and the photon energy, $h\nu$. Here, it was observed that TiO_2 NPs show an absorbance peak in the UV range. For the TiO_2/CS (80/20 and 95/5) nanocomposites compared with pure TiO_2 , the E_g increases for TiO_2/CS 95/5 but decreases for TiO_2/CS 80/20, see Table 2. In addition, we observed that the

optical absorption edge for direct transition in the anatase phase of TiO_2 NPs is $E_g \sim 3.2\text{ eV}$ (387 nm), however, the synthesized NPs exhibit blue shift concerning the bulk reported [4]. Given these results and under UV light, the photocatalytic activity was carried out.

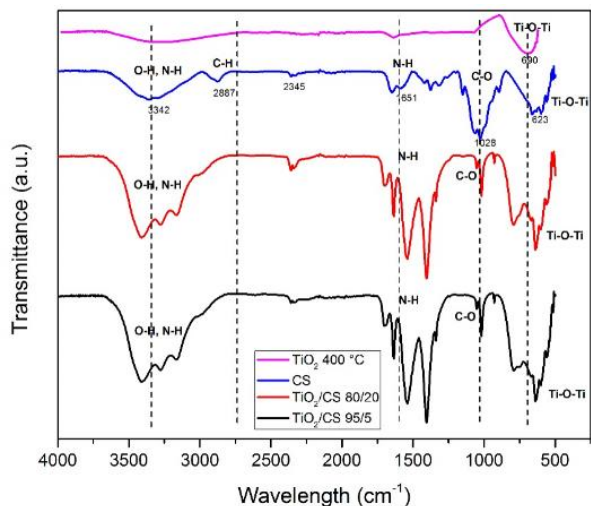


Figure 3. FTIR spectra of samples studied

Table 2. Optical energy bandgap of synthesized samples

Sample	Optical E_g (eV) indirect transition	Optical E_g (eV) direct transition
TiO_2 at 400°C	4.11	3.75
TiO_2 at 450°C	4.13	3.74
TiO_2 at 500°C	4.11	3.75
TiO_2/CS 95/5	4.19	3.89
TiO_2/CS 80/20	3.37	2.62

A differential scanning calorimetry (DSC) study was carried out to determine thermal events associated with phase transition in the samples. All NPs, do not show any thermal phase transition in the range from -50 to 550°C . however, for the TiO_2/CS nanocomposites (See Figure 4), several endothermic and exothermic transitions are observed. One of them, at about 450°C , which is an exothermic transition is associated with the CS decomposition of the amine group, which for pure CS occurs at around 300°C . therefore, the results indicate that the addition of TiO_2 NPs to CS stabilizes the CS polymer matrix.

On the other hand, the nanocomposite sample, TiO_2/CS 95/5, shows an exothermic peak at about -50°C that may be associated with a spontaneous recrystallization process followed by its melting point at $\sim 60^\circ\text{C}$. There is another endothermic peak at around 150°C that may be

attributed to the evaporation of water molecules trapped in the TiO₂ NPs. These phenomena, which are not frequently observed, were not exhibited by the 80/20 concentration sample, probably due to a different thermal history or amorphous character. Finally, an endothermic peak around 330 °C is observed in both TiO₂/CS samples, which can be attributed to melting of a crystalline phase in the nanocomposites due to the presence of TiO₂ in CS.

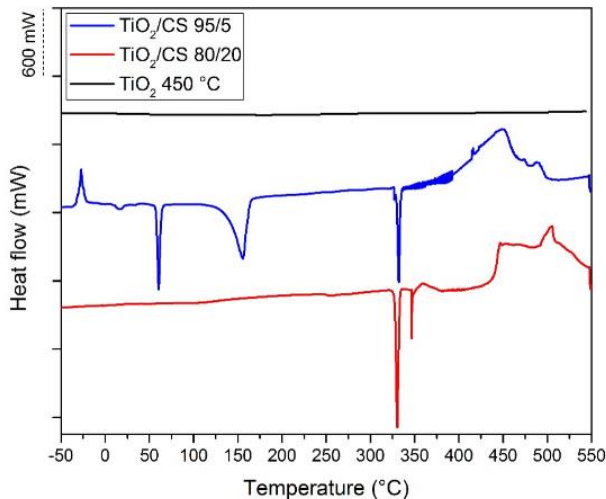
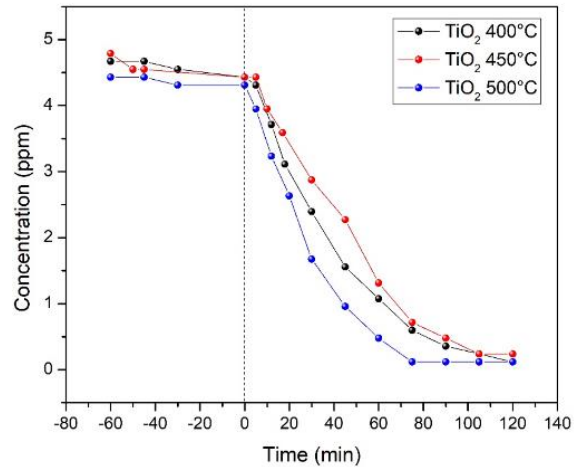


Figure 4. DSC of samples studied

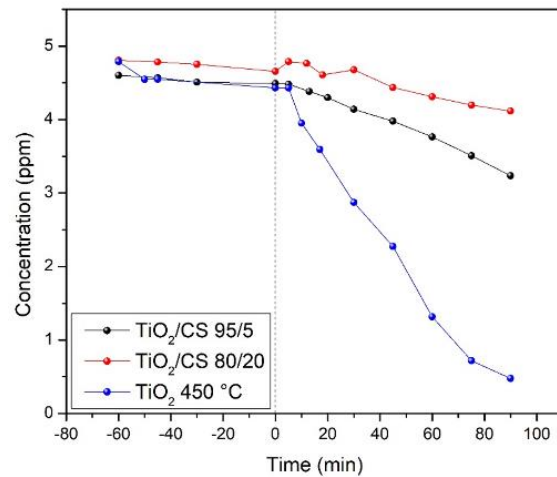
The main objective of this work is to evaluate the degradation capacity of the synthesized nanocomposite system under ultraviolet light. As mentioned in the experimental section, methyl orange (MO) dye was used as the contaminating organic molecule. Making use of a photoreactor, the radiation inside the sample was controlled. Initially, a photolysis investigation (without catalyst) was performed, and its results showed that the MO dye had good stability under ultraviolet illumination. First without illumination and then with light, the irradiated dye solutions were collected in a vial at different periods. The absorption value of the solutions was measured using a UV-Vis spectrophotometer. However, qualitatively is observed that the TiO₂ NPs are the best photocatalyst under UV light with a degradation time of between 75 to 90 min. Instead, in the nanocomposites, the degradation process was slower than in TiO₂ NPs.

To obtain a quantitative analysis of the photocatalytic activity of the samples, degradation kinetics studies were carried out. First, a calibration curve of MO was done to know the concentration as a function of absorbance.

Then, the photodegradation was made for each sample. It was observed that TiO₂ NPs acts as a good catalyst for MO degradation under UV light. The results are shown in Figure 5.



(a)

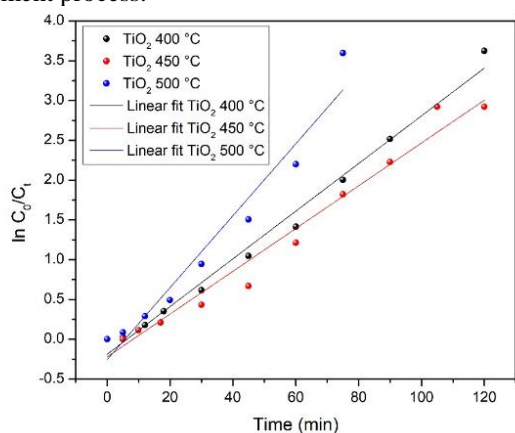


(b)

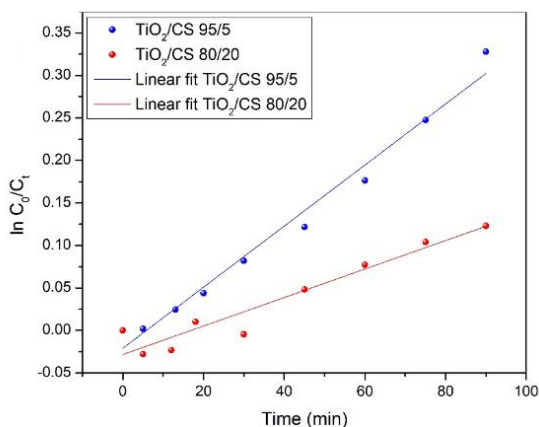
Figure 5. Degradation Kinetic for samples studied. a) nanoparticles, and b) nanocomposites

Additionally, a plot $\ln\left(\frac{C_0}{C}\right)$ as a function of the time of UV light exposure was made to obtain the rate constant k of degradation. This constant determines how fast the reaction occurs, such that, higher values of k correspond to faster reactions. By fitting the linear part of the curves, the corresponding slopes (or k values) are determined and reported in Figure 6 and Table 3. Here, the TiO₂/CS system was less efficient than TiO₂ NPs where the worse photocatalytic material under UV radiation was TiO₂/CS 80/20.

Here, there is low recombination of the reactive hole (h^+) and electron (e^-) pair in the nanocomposite systems, which is required for the photocatalytic reactions under UV-visible illumination. In addition, during the adsorption and degradation process MO adsorbed on the surface of the catalyst affects the recombination process during the photocatalytic activity under UV light. The results of this study can contribute to the dye wastewater treatment process.



(a)



(b)

Figure 6. Linear fit of $\ln\left(\frac{C_0}{C_t}\right)$ as a function of exposure time of the samples studied. a) nanoparticles, and b) nanocomposites

Table 3. Degradation rate constant for each sample of a MO dye solution

Sample	Rate constant k (min^{-1})
TiO ₂ at 400 °C	0.0299
TiO ₂ at 450 °C	0.0268
TiO ₂ at 500 °C	0.0451
TiO ₂ /CS 95/5	0.0036
TiO ₂ /CS 80/20	0.0017

4. Conclusions

TiO₂ nanoparticles and TiO₂/CS nanocomposites were synthesized by the sol-gel method to perform adsorption-photocatalytic decolorization of MO dye under UV irradiation. XRD and FTIR results confirm the structure of the nanoparticles and nanocomposite using chitosan as the induced matrix. The crystallite size and optical energy bandgap of the samples were determined. All nanoparticles were photoactive for MO degradation after 75 min of being irradiated with UV light. Instead, the nanocomposites present lower photocatalytic activity due to poor recombination of hole-electron pairs under UV light. The results of this study may be useful in the dye wastewater treatment process.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reports in this manuscript.

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