Biomaterial (Garlic and Chitosan)-Doped WO₃-TiO₂ Hybrid Nanocomposites: Their Solar Light Photocatalytic and Antibacterial Activities

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ABSTRACT: In this work, WO₃-TiO₂, chitosan-blended WO₃-TiO₂, and garlic-loaded WO₃-TiO₂ nanocomposites were synthesized by the sol–gel and precipitation technique. The synthesized nanocomposites were characterized by XRD, FE-SEM, HR-TEM, EDX, UV-DRS, FT-IR, and TG-DTA analysis. The photocatalytic efficiency of the three synthesized nanocomposites on the degradation of dyes such as rhodamine B (Rh-B), methylene blue (MB), and methyl orange (MO) as organic pollutants was evaluated under solar light irradiation. The results show that garlic-loaded WO₃-TiO₂ nanocomposites act as an excellent photocatalyst than chitosan-blended WO₃-TiO₂ and WO₃-TiO₂ nanocomposites. Further, the antimicrobial activity of the synthesized nanocomposites was examined against Gram-negative bacteria (Escherichia coli) by the well diffusion method. Garlic-loaded WO₃-doped TiO₂ nanocomposites have demonstrated good antibacterial activity over chitosan-blended WO₃-TiO₂ nanocomposites and WO₃-TiO₂ nanocomposites. The possible reason may be the presence of organic sulfur compounds in garlic.

1. INTRODUCTION

Over the past decades, the catalytic degradation method is one of the best ways to prevent water pollution from dyes. The catalytic degradation technique contains a photocatalytic material that acts as a catalyst by absorbing light (ultraviolet or visible) and enhances the photochemical reaction. TiO₂, ZnO, CuO, ZrO₂, etc., are some of the metal oxides used as photocatalysts. Out of these metal oxides, TiO₂ and ZnO have been used extensively as photocatalysts. The photocatalyst generates electrons and holes when it absorbs light energy. The electrons of the valence band (VB) get excited and move to the conduction band (CB) through the band gap, creating e⁻ (negative) and h⁺ (positive) pairs, and the phenomenon is named as the “photoexcitation” state. The positive holes of the photocatalyst cleave the H₂O molecules to produce H₂ gas and hydroxyl radicals. The electrons react with the O₂ molecule to create a superoxide anion and this cyclic process continues until light is available. In most cases, the electrons and positive holes recombine and decrease the photocatalytic efficiency. To overcome these shortcomings, certain metal oxides are added as dopants. To increase the photocatalytic efficiency further, hybrid photocatalysts are prepared to employ biomaterials. This hybrid photocatalyst not only increases photocatalytic activity but also acts as good antimicrobial agents. The hybrid materials are potentially applied in many biomedical fields and they could also enhance the mechanical properties of the materials.

The WO₃-TiO₂ nanocomposite has been used as an energy storage photocatalyst, which could store the electrons produced under the illumination of light and release these electrons in the absence of light, which takes place in electron-mediated reactions. The band gap of WO₃ is 2.8 eV (wavelength of ~440 nm), which is lower than that of anatase (3.2 eV) so that WO₃ shows significant photocatalytic activity due to the enhancement of the ability of visible-light photons. Sun et al. designed spindle-like WO₃-TiO₂, which proves better photocatalytic activity compared to the single TiO₂ and WO₃. Crystallinity played a significant role in the photocatalyst activity.

Currently, chitosan-based hybrid materials are applied for various applications. Chitosan is a biomaterial, which is basically a polysaccharide prepared from the deacetylation of chitin. It is the second-most abundant biopolymer widely present in crustaceans and...
The chitosan structure is similar to that of cellulose. It has an excellent adsorbing capacity, which is around 1100 g kg$^{-1}$, and is more superior to activated carbon, which is usually used as an adsorbent.$^{17}$ The adsorption capacity of chitosan with the contaminants may be due to the presence of amino and hydroxyl groups on the surface. The hybrid photocatalyst prepared by using chitosan and TiO$_2$ has a potential significance in catalytic activity and antimicrobial property. The chitosan adsorbed the organic substrates as a result of electrostatic attraction between the $-$NH$_2$ groups and solutes. The presence of chelating groups ($-$NH$_2$ and $-$OH groups) on the chitosan also increases the chitosan binding ability for metal ions.$^{18}$

A TiO$_2$-garlic hybrid material was used as a photocatalyst, which revealed significant improvement in the photocatalytic activity in the visible region compared to commercially available catalysts like Degussa P25.$^{19}$ Garlic (Allium sativum) is a herb containing 33 sulfur compounds, 17 amino acids, glycosides, aginine, selenium, and certain enzymes like alliinase, peroxidases, myrosinase, etc.$^{20}$ It is used as a flavoring agent for cooking foods and also serves as a medicine to cure certain diseases. When garlic is cut, it is influenced by the presence of an alliinase enzyme, a cysteine sulfoxidelyase, and converts into allicin. Allicin is responsible for the strong smell of garlic, which falls between 20 and 40 nm. It was observed that the morphology of the formed nanocomposites was strongly influenced by the hydrolysis agent. The moist air, both at 50 and 100% relative humidity levels, used as the hydrolysis agent, allowed the occurrence of the precursor’s thermal decomposition, resulting in the formation of micrometer-size agglomerates.

The elements present in the nanocomposites are confirmed due to the presence of corresponding peaks and the atomic and weight percentages are tabulated.

The X-ray diffraction (XRD) patterns of WO$_3$-TiO$_2$, chitosan-blended WO$_3$-TiO$_2$, and garlic-loaded WO$_3$-TiO$_2$ hybrid nanocomposites are presented in Figure 1, respectively, which show the TiO$_2$ anatase phase and WO$_3$-TiO$_2$. The XRD patterns of (a) WO$_3$-TiO$_2$, (b) chitosan-blended WO$_3$-TiO$_2$, and (c) garlic-loaded WO$_3$-TiO$_2$ hybrid nanocomposites are presented in Figure 2a–c, respectively. The synthesized nanocomposites indicate that the particles have a nonuniform form with a high degree of agglomeration. The agglomerated spherical size of the particle falls between 20 and 40 nm. It was observed that the morphology of the formed nanocomposites was strongly influenced by the hydrolysis agent. The moist air, both at 50 and 100% relative humidity levels, used as the hydrolysis agent, allowed the occurrence of the precursor’s thermal decomposition, resulting in the formation of micrometer-size agglomerates.

The elementary composition of the nanocomposites was confirmed due to the presence of corresponding peaks and the atomic and weight percentages are tabulated.

### 2. RESULTS AND DISCUSSION

#### 2.1. XRD Analysis

The X-ray diffraction (XRD) patterns of WO$_3$-TiO$_2$, chitosan-blended WO$_3$-TiO$_2$, and garlic-loaded WO$_3$-TiO$_2$ hybrid nanocomposites are presented in Figure 1, respectively, which show the TiO$_2$ anatase phase and WO$_3$-TiO$_2$ tetragonal phase. For the TiO$_2$ anatase phase, the 2θ values are 25.356°, 37.847°, 48.145°, 53.974°, 55.186°, 62.812°, 68.879°, and 70.812°, which correspond to the (101), (004), (200), (105), (211), (204), (116), and (220) planes, respectively, which are in good agreement with the standard JCPDS pattern (89-4921). The presence of peaks at 2θ = 24.06, 28.12, 33.61, 34.13, 44.73, and 50.15° corresponding to the (001), (111), (201), (220), (221), and (112) planes, respectively, indicates the tetragonal WO$_3$ (89-1287) and their crystal parameters are tetragonal, primitive, $a = 7.39$ Å, $b = 7.39$ Å, $c = 3.88$ Å, $\alpha = 90°$, $\beta = 90°$, and $\gamma = 90°$.

The average crystallite sizes of the nanocomposites have been deduced from the full width at half maximum (FWHM) of the 101 anatase peak of TiO$_2$ using the Scherrer equation (eq 1)

$$
t = \frac{K\lambda}{\beta \cos \theta}
$$

where $t$ is the crystallite size, $K$ is the shape factor of a value of 0.9, $\lambda$ is the wavelength of the X-ray used, $\theta$ is Bragg’s diffraction angle, and $\beta$ is the corrected line broadening, $\beta = \beta_h - \beta_s$, where $\beta_h$ is the broadened profile width of the experimental sample and $\beta_s$ is the standard profile width of the reference (high-purity silica) sample. According to eq 1, the average crystallite sizes of WO$_3$-TiO$_2$, chitosan-blended WO$_3$-TiO$_2$, and garlic-loaded WO$_3$-TiO$_2$ are 13, 11, and 9 nm, respectively. It is essential to indicate that the crystallite size decreased gradually by the influence of biomaterials in the synthesized nanocomposites.

The SEM investigations show that the nanocomposites reveal a composite network with sizes in the range of 10–40 nm. It was observed that the morphology of the formed nanocomposites was strongly influenced by the hydrolysis agent. The moist air, both at 50 and 100% relative humidity levels, used as the hydrolysis agent, allowed the occurrence of the precursor’s thermal decomposition, resulting in the formation of micrometer-size agglomerates.

### 2.2. Electron Microscopic Studies

Figure 2a–c shows the field emission scanning electron microscopy (FE-SEM) images of WO$_3$-TiO$_2$, chitosan-blended WO$_3$-TiO$_2$, and garlic-loaded WO$_3$-TiO$_2$ hybrid nanocomposites, respectively. The SEM micrographs of the synthesized nanocomposites indicate that the particles have a nonuniform size with a high degree of agglomeration. The agglomerated spherical size of the particle falls between 20 and 40 nm. It was observed that the morphology of the formed nanocomposites was strongly influenced by the hydrolysis agent. The moist air, both at 50 and 100% relative humidity levels, used as the hydrolysis agent, allowed the occurrence of the precursor’s thermal decomposition, resulting in the formation of micrometer-size agglomerates.

Figure 3a–c illustrates the high-resolution transmission electron microscopy (HR-TEM) images of WO$_3$-TiO$_2$, chitosan-blended WO$_3$-TiO$_2$, and garlic-loaded WO$_3$-TiO$_2$ hybrid nanocomposites, respectively. The HR-TEM images of the nanocomposites reveal a composite network with sizes in the range of 10–50 nm having a mean average particle distribution of 35 nm. ImageJ software is used to measure the average particle size distribution diameter. TEM investigations show that the nanocomposites are randomly distributed with a nonuniform particle size.

### 2.3. EDX Analysis

Energy-dispersive X-ray (EDX) spectroscopy images of the WO$_3$-TiO$_2$, chitosan-blended WO$_3$-TiO$_2$, and garlic-loaded WO$_3$-TiO$_2$ hybrid nanocomposites are shown in Figure 4a–c, respectively. EDX analysis of the nanocomposites in a TiO$_2$-based matrix reveals peaks corresponding to carbon, oxygen, titanium, and doped metals. The elements present in the nanocomposites are confirmed due to the presence of corresponding peaks and the atomic and weight percentages are tabulated.

### 2.4. UV-DRS Analysis

Diffuse reflectance spectroscopy (DRS) spectra of WO$_3$-TiO$_2$, chitosan-blended WO$_3$-TiO$_2$, and...
Figure 2. FE-SEM images of (a) WO$_3$-TiO$_2$, (b) chitosan-blended WO$_3$-TiO$_2$, and (c) garlic-loaded WO$_3$-TiO$_2$ nanocomposites.

Figure 3. HR-TEM images of (a) WO$_3$-TiO$_2$, (b) chitosan-blended WO$_3$-TiO$_2$, and (c) garlic-loaded WO$_3$-TiO$_2$ nanocomposites.
garlic-loaded WO₃-TiO₂ hybrid nanocomposites are displayed in Figure 5a−c, respectively, which indicates that the absorption appeared mostly in the visible region. DRS of the garlic-loaded WO₃-TiO₂ nanocomposite shows intense absorption in the visible region. Chitosan-blended WO₃-TiO₂ and WO₃-TiO₂ nanocomposites also absorb visible light significantly, which may be due to the implantation of nanocrystalline WO₃ in TiO₂ nanocomposites. As it can be seen, in the case of garlic-loaded TiO₂ calcinated at 450 and 700 °C, the absorption edge was observed in the visible region of the solar spectrum, representing that the catalyst excitation efficiently exploits more photons. Such absorption mentioned the substitution of lattice titanium by S⁶⁺ and the formation of a newly isolated band above the TiO₂ valence band and consequently narrowed a band gap. ²⁶ Furthermore, the results suggest that loading greatly promotes the band gap to red-shift, which eases the electron excitation from the VB to the CB that results in higher photocatalytic activity.

2.5. FT-IR Analysis. Figure 6a−c displays the Fourier transform infrared (FT-IR) spectra of WO₃-TiO₂, chitosan-blended WO₃-TiO₂, and garlic-loaded WO₃-TiO₂ nanocomposites.
blended WO₃-TiO₂, and garlic-loaded WO₃-TiO₂ nanocomposites, respectively. Figure 6a shows that the strong band that appeared around 3400 cm⁻¹ represents O–H. The band at 2300 cm⁻¹ corresponding to vibrations of atmospheric CO₂ and the band around 1630 cm⁻¹ represent the deformation of water δH–OH. The different vibrational modes of TiO₂ appeared between 650 and 800 cm⁻¹. Chitosan-blended WO₃-TiO₂ hybrid nanocomposites (Figure 6b) show peaks around 3400 and 1630 cm⁻¹, which indicate amine (−NH₂) and hydroxyl (−OH) functional groups that act as coordination and reaction sites for the adsorption of the organic species. The existence of a peak around 700 cm⁻¹ represents TiO₂. The vibrations of atmospheric CO₂ appeared around 2300 cm⁻¹. Garlic-loaded WO₃-TiO₂ hybrid nanocomposites (Figure 6c) show a strong band around 3400 cm⁻¹, indicating O–H group stretching vibrations. The presence of a peak around 460 cm⁻¹ is attributed to the S–S stretching of sulfur. The band at 1130 cm⁻¹ may be corresponding to the C–O–H bending of the carboxylic group found in garlic extract compounds. A weak band at 2300 cm⁻¹ corresponds to atmospheric CO₂. The presence of bands between 650 and 800 cm⁻¹ are attributed to

Figure 5. DRS of (a) WO₃-TiO₂, (b) chitosan-blended WO₃-TiO₂, and (c) garlic-loaded WO₃-TiO₂ nanocomposites.

Figure 6. FT-IR spectra of (a) WO₃-TiO₂, (b) chitosan-blended WO₃-TiO₂, and (c) garlic-loaded WO₃-TiO₂ nanocomposites.
the different vibrational modes of TiO$_2$. The FT-IR results supported the formation of hybrid nanocomposites.

2.6. TG-DTA Analysis. Thermal stability of the synthesized nanomaterials was analyzed by thermogravimetry−differential thermal analysis (TG-DTA) between 50 and 800 °C under a N$_2$ atmosphere, as shown in Figure 7a−c. The TGA analysis of the WO$_3$-TiO$_2$ nanocomposite (Figure 7a) indicates two weight losses. The first major weight loss occurs at 283 °C and the second weight loss occurs at 523 °C. The first and second weight losses may be attributed to the decomposition of the residual −OH groups and the condensation of nonbonded oxygen and crystallization of TiO$_2$, respectively. In DTA, a strong intense exothermic peak is obtained at 298 °C, which corresponds to the decomposition of the residual −OH groups.

In the TGA analysis of the chitosan-blended WO$_3$-TiO$_2$ nanocomposite (Figure 7b), there was no change up to 341 °C. After 341 °C, a significant decrease was observed and then a steady state was reached. The weight loss between 300 and 400 °C was allocated to the complex dehydration of the saccharide rings, depolymerization, and decomposition of the acetylated and deacetylated units of the polymer.$^{30−32}$

TGA analysis of the garlic-loaded WO$_3$-TiO$_2$ nanocomposite (Figure 7c) shows the observance of a sharp decrease from 250 to 280 °C and 420 to 580 °C. The first and second weight losses can be attributed to the decomposition of the residual −OH groups and the condensation of nonbonded oxygen and crystallization of TiO$_2$, respectively. DTA analysis reveals two peaks that correspond to the condensation of nonbonded oxygen and crystallization of TiO$_2$.

2.7. Photocatalytic Activities. Figure 8a−c shows the photocatalytic activities of TiO$_2$, WO$_3$-TiO$_2$, chitosan-blended WO$_3$-TiO$_2$, and garlic-loaded WO$_3$-TiO$_2$ nanocomposites with visible light, which have been evaluated using rhodamine B (Rh-B), methylene blue (MB), and methyl orange (MO). The degradation studies of Rh-B under visible light are found to be good for the three synthesized nanocomposites such as garlic-loaded WO$_3$-TiO$_2$, chitosan-blended WO$_3$-TiO$_2$, and WO$_3$-TiO$_2$ but feeble for TiO$_2$. The orders of photocatalytic degradation of Rh-B, MB, and MO by the catalysts are as follows: garlic-loaded WO$_3$-TiO$_2$ > chitosan-blended WO$_3$-TiO$_2$ > WO$_3$-TiO$_2$ > TiO$_2$.
The higher photocatalytic efficacy of the garlic-loaded WO₃-TiO₂ nanocomposite may be due to the presence of organic sulfur, which does have an excellent degradation property.

The higher rate of photodegradation of the three dyes by the chitosan-blended WO₃-TiO₂ photocatalyst may be due to the fact that the surface of the positively charged chitosan matrix increased the anionic dye adsorption. The presence of amine groups in chitosan composites can undergo protonation (forming protonated amine) that adsorbs the dye molecules/metallic ions by using different types of interaction mechanisms like electrostatic attraction, chelation, etc. They can be high-capacity adsorbents for the efficient removal of contaminants from wastewater. The presence of amine groups in chitosan also creates active sites for the formation of complexes with attracted molecules, thereby enhancing the solar light photocatalytic activity.

The WO₃-doped TiO₂ nanocomposite also shows good photocatalytic activity but not like the chitosan-blended and garlic-loaded WO₃-TiO₂ nanocomposites. The good photocatalytic activity of the WO₃-TiO₂ nanocomposite is due to the dye-sensitized photocatalytic degradation.

The photocatalytic degradation of the three dyes by TiO₂ is minimal and there is no significant change in the degradation process. TiO₂ is very much inferior to the other three photocatalysts.

The reason for photocatalytic activity enhancement of the hybrid nanocomposites may be (i) the high degree of crystallization of loaded/doped anatase and stability that ease the electron transfer and subsequently decrease recombination within the photogenerated holes and/or (ii) oxygen vacancies that have increased as a result of doping or deformation in the defects of the lattice, which trap the photoinduced electrons, suppressing the recombination of holes and electrons. It is usually agreed that doping materials may distort the TiO₂ lattice and the substitution of either Ti⁴⁺ or O²⁻ takes place. The crystallite size, crystallinity, the morphology of particles, and phase/chemical composition of the catalysts affect the photocatalytic degradation process. Thus, the holes present in the VB could be trapped by OH⁻ or the radicals have been produced by the adsorption of H₂O species on the surface of the catalyst, whereas the reduction of adsorbed oxygen into O₂⁻ has been caused by the photogenerated electrons present in the CB, which contribute to the enhancement of catalytic activity. Additionally, the effective oxidation of the target pollutants adsorbed on the catalyst surface was achieved by the hole itself.

The degradation of all the three dyes (Rh-B, MB, and MO) progressed over the catalyst surface by the synergistic effect of produced radicals and holes and was not processed in the bulk of the solution because the lifetime of the photogenerated radicals was short and leaned to the recombination. In addition, the enhancement of degradation of all the dyes in the liquid phase...
has occurred by the introduction of dopants of the slightly distorted lattice and the occurrence of the anatase phase with a high degree of crystallinity.41,42

2.8. Antimicrobial Activities. The antimicrobial activities of WO_{3}-TiO_{2}, chitosan-blended WO_{3}-TiO_{2}, and garlic-loaded WO_{3}-TiO_{2} were determined by using a well diffusion method employing Gram-negative bacteria (Escherichia coli) with four different concentrations (250, 500, 750, and 1000 μg). The inhibition zones of all the nanocomposites are shown in Figure 9 with the corresponding bar diagram (Figure 10).

The WO_{3}-TiO_{2} nanocomposite is inert to the antibacterial activity. Chitosan-blended WO_{3}-TiO_{2} has no activity for 250 and 500 μg but shows significantly less activity for 750 and 1000 μg. Garlic-loaded WO_{3}-TiO_{2} exhibited good activity for all the four concentrations. In garlic-loaded, metal oxide-doped TiO_{2} nanocomposites, the inhibitory effect of garlic on the growth of E. coli is due to the presence of the allicin compound in the extract of garlic. It is a volatile compound that decomposes into other sulfurous compounds such as diallyl disulfide and ajoene. Sulfurous compounds interact with the cell wall of bacteria by rupturing their layer and change their total metabolic activity, thereby inhibiting the activity of bacteria.

2.9. Recyclability and Reusability. The recyclability experiments have been investigated and are displayed in Figure 11. After every experiment, the synthesized nanocatalysts were washed two to three times with absolute alcohol, filtered, dried at 70 °C, and reused. Garlic-loaded WO_{3}-TiO_{2} and chitosan-blended WO_{3}-TiO_{2} nanocomposites exhibit outstanding recyclability with no significant loss in the activity of the catalyst even after three times of recycling. After each cycle, some amount of loss in the catalytic activity was observed. The decrease in the rate of degradation (recyclability) might be weakening the ability of the absorbance or some amount of photocatalyst lost at the time of the collection of the catalysts.

3. CONCLUSIONS

Novel garlic-loaded WO_{3}-TiO_{2}, chitosan-blended WO_{3}-TiO_{2}, and WO_{3}-TiO_{2} nanocomposites were synthesized by a simple sol–gel and precipitation method. The FT-IR results supported the formation of the hybrid nanocomposites. The thermal behavior and crystallinity of the nanocomposites were analyzed.
by TG-DTA and XRD. The surface morphology and the evidence for the immobilization of the samples were examined by FE-SEM and HR-TEM techniques. The garlic-loaded \( \text{WO}_3 \)-\( \text{TiO}_2 \) catalyst showed higher photocatalytic activity for the photodegradation of the Rh-B, MO, and MB dyes under the illumination of solar light for 120 min. The result displayed that recycling the use of nanocomposites for three times did not eminently affect their photocatalytic activity. The antibacterial effect of the nanomaterials against \( E. \) coli was determined by CFU. It was evidenced that garlic-loaded \( \text{WO}_3 \)-\( \text{TiO}_2 \) nanocomposites exhibited superior antibacterial activity than chitosan-blended \( \text{WO}_3 \)-\( \text{TiO}_2 \) and \( \text{WO}_3 \)-\( \text{TiO}_2 \) nanocomposites. Novel hybrid nanocomposites could be used as an eco-friendly, economical, and considerable material for removal of dyes with excellent photocatalytic and antimicrobial activities.

4. EXPERIMENTAL SECTION

4.1. Reagents. Titanium tetraisopropoxide (TTIP) was purchased from Sigma Aldrich Chemicals. Tween-80 (templat- ing agent) was purchased from Loba Chemie Pvt. Ltd., India. Tungstic oxide \( (\text{WO}_3) \), isopropyl alcohol, glacial acetic acid, methyl orange powder, methylene blue powder, and rhodamine B powder were obtained from SD Fine Chemicals, India. Hydrochloric acid and sodium hydroxide were purchased from SRL Chemicals, India. Crab shells were obtained from a seafood market (Chennai). During the synthesis, Milli-Q water was used.

4.2. Synthesis of Undoped \( \text{TiO}_2 \) Nanocomposite. The sol–gel method was used to synthesize the \( \text{TiO}_2 \) nanocomposite using titanium tetraisopropoxide (TTIP) as the precursor and Tween-80 as the templating agent. TTIP was mixed with isopropyl alcohol and then blended with Tween-80 and stirred for 30 min. The gel formed was subjected to aging for 24 h undisturbed. The gel was then separated and calcinated at 3 h for 500 °C to get \( \text{TiO}_2 \) nanocomposites.

4.3. Synthesis of \( \text{WO}_3 \)-Doped \( \text{TiO}_2 \) Nanocomposite. In the synthesis of the \( \text{WO}_3 \)-doped \( \text{TiO}_2 \) nanocomposite, 0.070 g of \( \text{WO}_3 \) was added in distilled ethanol (20 mL) for attaining homogeneous dispersion, which was allowed to stir for 30 min. Tween-80 (3.0 mL) was added to this homogeneous dispersion and stirring was continued for further 30 min. To this suspension, a mixture of TTIP (3.0 mL) in isopropyl alcohol (10 mL) was added dropwise and stirred continuously for 2 h to get a gel. The resulting gel was isolated and thoroughly washed with aqueous ethanol, filtered, and kept in an oven at 6 h for 120 °C. The obtained solid material was calcined at 3 h for 500 °C using an electrical muffle furnace.

4.4. Synthesis of Chitosan. The synthetic procedure for the preparation of chitosan from a crab shell was followed from the previously reported literature.\(^{23}\)

4.5. Synthesis of Chitosan-Blended \( \text{WO}_3 \)-\( \text{TiO}_2 \) Nanocomposite. \( \text{WO}_3 \) \( (0.070 \text{ g}) \) was added in distilled ethanol (20 mL) for attaining homogeneous dispersion, which was allowed to stir for 30 min. Tween-80 (3.0 mL) was added to this homogeneous dispersion and stirring was continued for further 30 min. To this suspension, a mixture of TTIP (3.0 mL) in isopropyl alcohol (10 mL) was added dropwise and stirred continuously for 2 h to get a gel. Chitosan solution \( (1 \text{ g of chitosan in } 100 \text{ mL of } 1\% \text{ (v/v) acetic acid}) \) was added to this gel and stirred for 1 h. The obtained mixture was filtered and thoroughly washed with aqueous ethanol, filtered, and kept in the oven for 6 h at 120 °C. The solid samples were calcined at 500 °C for 3 h using an electrical muffle furnace.

4.6. Synthesis of Garlic-Loaded \( \text{WO}_3 \)-\( \text{TiO}_2 \) Nanocomposite. Fresh garlic cloves were bought from a grocery shop, and they were cut into small pieces, ground well with a small quantity of water, and then filtered to get the garlic extract. \( \text{WO}_3 \) \( (0.070 \text{ g}) \) was added in absolute alcohol (20 mL) and stirred for 30 min. Tween-80 (3.0 mL) was added to this homogeneous dispersion and stirring continued for 30 min. To this suspension, a mixture of TTIP (3.0 mL) in isopropyl alcohol (10 mL) was added dropwise and stirred continuously for further 2 h. A freshly prepared garlic extract (10 mL) was added under constant stirring and the resulting mixture was kept for aging (24 h). It was then filtered, dried at 120 °C in a hot air oven for 6 h, and calcinated for 3 h at 500 °C to get the corresponding garlic-loaded \( \text{WO}_3 \)-doped \( \text{TiO}_2 \) nanocomposites.

4.7. Characterization Techniques. XRD studies were investigated using a Bruker D2 Phaser Desktop X-ray diffractometer equipped with Ni-filtered Cu Ka radiation \( (\lambda = 1.542 \text{ Å}) \) and operated at an accelerating voltage and emission current of 30 kV and 10 mA, respectively. A DXS-10 ACKT scanning electron microscope was used to analyze FE-SEM equipped with EDAX. A JEOL JEM-3010 microscope was used to take TEM images with magnification of 600k and 800k times operated at 300 kV. The DRS/UV–visible spectra for all the samples in the reported work were recorded using a Shimadzu 2100 UV–visible spectrophotometer in the range of 200–800 nm equipped with an integrating sphere and BaSO\(_4\) was used as the reference. The FT-IR spectra were recorded using a Perkin Elmer RX1 instrument within the wavenumber range of 400–4000 cm\(^{-1}\) at 25 °C using solid KBr pellets. TG-DTA analysis of the synthesized nanocomposites was done by employing a WATERS SDT Q600 TA model instrument.

4.8. Solar Light Photocatalytic Activities. 4.8.1. Dye Estimation. Solutions of Rh-B, MB, and MO of the required ppm were prepared in doubly distilled water and their UV–visible spectra were recorded. Rh-B, MB, and MO show absorption maxima in the visible region at 555, 663, and 464 nm, respectively. The calibration curve was constructed by measuring the absorbance at different ppm (Rh-B up to 5 ppm, MB up to 5 ppm, and MO up to 20 ppm). The concentrations of the dyes prior to and post illumination were determined from their measured absorbance.

4.8.2. Photocatalytic Studies. To 50 mL of freshly prepared dye solution, a calculated amount of the catalyst was added followed by passing of air through the solution at a constant rate.
After irradiation, the catalyst was separated and the dye was estimated spectrophotometrically.

4.8.3. Solar Light Intensity Measurements. The intensity of solar light was determined every 30 min and the average intensity of each experiment over the period was calculated. The solar light intensity was determined using a New 200,000 Lux Digital Meter Light Luxmeter Meter Photometer with Foot-candle FC. The intensity was 1200 × 100 ± 100 lux and it was nearly constant throughout the experiments.

4.8.4. Photocatalytic Degradation of the Dyes. All the photocatalytic studies were investigated on sunny days between 12 and 3 p.m. under identical conditions. For each experiment, 50 mL of the reaction mixture was irradiated under sunlight. A 50 mL open borosilicate glass beaker was used as the reaction vessel and the irradiation process was performed under open-air conditions. The synthesized catalyst with 50 mL of the dye solution was aired constantly through a pump for providing oxygen and also for getting a homogeneous solution. The volatility of the solvent was not observed at the time of illumination. The sample (2–3 mL) was withdrawn at specific time intervals (15 min) and its absorbance values at 555, 663, and 464 nm were measured immediately to monitor the degradation of dyes Rh-B, MB, and MO, respectively.

4.9. Antibacterial Assay. The synthesized nanocomposites were tested with Gram-negative bacteria (E. coli) by using the well diffusion method. The nutrient for the bacteria was prepared by mixing agar in distilled water, transferred into a sterile Petri dish, and allowed to solidify. Four wells were dug by employing a sterile cork borer to which 24 h-cultured Gram-negative bacteria (E. coli) were swabbed. Four different concentrations of the nanocomposites were incorporated into the four wells separately and one well was loaded with control. The plates were placed in an incubator for 24 h and maintained at 37 °C. After the incubation period, the plates were removed and the inhibition diameters of the four different concentrations of the nanocomposites were measured. Identical procedures were adopted for the other nanocomposites. The inhibition diameter was measured after the incubation and the inhibition percentage was determined by using the following equation (eq 2).

\[
\% \text{ of inhibition} = \left( \frac{I(\text{inhibited zone diameter})}{90(\text{Petri plate diameter in mm})} \right) \times 100
\]

(2)

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Notes

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**REFERENCES**

(1) Chen, Y.; Stathatos, E.; Dionysiou, D. D. Microstructure characterization and photocatalytic activity of mesoporous TiO2 films with ultrafine anatase nanocrystallites. Surf. Coat. Technol. 2008, 202, 1944–1950.

(2) Jang, Y. H.; Kochuveedu, S. T.; Cha, M.-A.; Jang, Y. J.; Lee, J. Y.; Lee, J.; Kim, J.; Byu, D. Y.; Kim, D. H. Synthesis and photocatalytic properties of hierarchical metal nanofilms/ZnO thin films heterostructures assisted by diblock copolymer inverse micellar nanotemplates. J. Colloid Interface Sci. 2010, 345, 125–130.

(3) Momeni, M. M.; Ghayeb, Y.; Mozafari, A. A. Optical and photo catalytic characteristics of Ag2S/TiO2 nanocomposite films prepared by electrochemical anodizing and SILAR approach. J. Mater. Sci.: Mater. Electron. 2016, 27, 11201–11210.

(4) Momeni, M. M.; Ghayeb, Y. Synthesis and characterization of iron-doped titania nanohoneycomb and nanoporous semiconductors by electrochemical anodizing method as good visible light active photocatalysts. J. Mater. Sci.: Mater. Electron. 2015, 26, 5509–5517.

(5) Douglas, T. E. L.; Dziadek, M.; Schietse, J.; Boone, M.; Declercq, H. A.; Coenye, T.; Vanhoorne, V.; Vervaeke, C.; Balcaen, L.; Buchweitz, M.; Vanhaecke, F.; Van Assche, F.; Cholewa-Kowalska, K.; Skirtach, A. G. P.entin-bioactive glass self-gelling, injectable composites with high antibacterial activity. Carbohydr. Polym. 2019, 205, 427–436.

(6) Saveleva, M. S.; Efekhari, K.; Abalymov, A.; Douglas, T. E. L.; Volodkin, D.; Parakhonskiy, B. V.; Skirtach, A. G. Hierarchy of Hybrid Materials—The Place of Inorganics-in-Organics in it, Their Composition and Applications. Front. Chem. 2019, 7, 179.

(7) Bali, N. R.; Salve, P. S. Impact of rasagiline nanoparticles on brain targeting efficiency via gelan gum based transdermal patch: A nanotheranostic perspective for Parkinsonism. Int. J. Biol. Macromol. 2020, 164, 1006–1024.

(8) Rial, R.; Liu, Z.; Russo, J. M. Soft actuated hybrid hydrogel with bioinspired complexity to control mechanical flexure behavior for tissue engineering. Nanomaterials 2020, 10, 1302.

(9) Momeni, M. M. Study of synergistic effect among photo-, electro-, and sonoprocesses in photocatalyst degradation of phenol on tungsten-loaded titania nanotubes composite electrode. Appl. Phys. A 2015, 119, 1413–1422.

(10) Momeni, M. M. Fabrication of copper decorated tungsten oxide—titanium oxide nanotubes by photochemical deposition technique and their photocatalytic application under visible light. Appl. Surf. Sci. 2015, 357, 160–166.

(11) Momeni, M. M.; Ghayeb, Y. Preparation of cobalt coated TiO2 and WO3—TiO2 nanotube films via photo-assisted deposition with enhanced photocatalytic activity under visible light illumination. Ceram. Int. 2016, 42, 7014–7022.

(12) Huang, D.; Wan, S.; Wang, L.; Xue, Q. Surface and electrochemical analysis for the understanding of the TiO2 doped WO3 with high conductivity ad good wettability. Surf. Interface Anal. 2011, 43, 1064–1068.
(13) Miyachi, M.; Nakajima, A.; Watanabe, T.; Hashimoto, K. Photoinduced Hydrophobic Conversion of TiO2/WO3 Layered Thin Films. Chem. Mater. 2002, 14, 4714–4721.

(14) Sun, D.; Liu, J.; Li, J.; Feng, Z.; He, L.; Zhao, B.; Wang, T.; Li, R.; Yin, S.; Sato, T. Solvothermal synthesis of spindle-like WO3-TiO2 particles with enhanced photocatalytic activity. Mater. Res. Bull. 2014, 53, 163–168.

(15) Rinaudo, M. Chitin and chitosan: Properties and applications. Prog. Polym. Sci. 2006, 31, 603–632.

(16) Rabea, E. I.; Badawy, M. E.-T.; Stevens, C. V.; Smagghe, G.; Steurbaut, W. Chitosan as antimicrobial agent: Applications and mode of action. Biomacromolecules 2003, 4, 1457–1465.

(17) Yan, W. L.; Bai, R. Adsorption of lead and humic acid on chitosan hydrogel beads. Water Res. 2005, 39, 688–698.

(18) Chieu, M.-S.; Ho, P.-Y.; Li, H.-Y. Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads. Dyes Pigments 2004, 60, 69–84.

(19) Virkutyte, J.; Varma, R. S. Synthesis and visible light photocatalysis of anatase Ag and garlic loaded TiO2 nanocrystalline catalyst. RSC Adv. 2012, 2, 2399–2407.

(20) Amagase, H.; Petesch, B. L.; Matsuura, H.; Kasuga, S.; Itakura, Y. Antibacterial effect of garlic (Allium sativum) on Streptococcus iniae, and on growth in orange-spotted grouper Epinephelus coioides. Aquaculture 2012, 364–366, 364–338.

(21) Deresse, D. Antibacterial effect of garlic (Allium sativum) on Staphylococcus aureus: An in vitro study. Asian J. Med. Sci. 2010, 2, 62–66.

(22) Guo, J.-J.; Kuo, C. M.; Chuang, Y. C.; Hong, J. W.; Chou, R. L.; Chen, T. I. The effects of garlic-supplemented diets on antibacterial activity against Streptococcus iniae and on growth in orange-spotted grouper Epinephelus coioides. Aquaculture 2012, 364-365, 364–338.

(23) Magesan, P.; Samuja, S.; Umamathy, M. J. Novel hybrid chitosan blended MoO3−TiO2 nanocomposite film: evaluation of its solar light photocatalytic and antibacterial activities. RSC Adv. 2015, 5, 42506–42515.

(24) Kruger, G.; Boltersdorf, D.; Overkempe, K. Novel Surfactants, preparations, applications and biodegradability; Surfactant Science Series; Marcel Dekker: New York, 2003, vol. 114, pp. 224–230.

(25) Periyat, P.; Pillai, S. C.; McCormack, D. E.; Colreavy, J.; Hinder, S. J. High-temperature stability and sun-light-driven photocatalytic activity of sulfur-doped anatase TiO2. J. Phys. Chem. C 2008, 112, 7644–7652.

(26) Liu, S.; Chen, X. A visible light response TiO2 photocatalyst derived from cationic S-doping and its application for phenol degradation. J. Hazard. Mater. 2008, 152, 48–55.

(27) Kumar, P. M.; Badrinarayanan, S.; Sastry, M. Nanocrystalline TiO2 studied by optical, FTIR and X-ray photoelectron spectroscopy: correlation to presence of surface states. Thin Solid Films 2000, 358, 122–130.

(28) Rastogi, L.; Arunachalam, J. Green synthesis route for the size controlled synthesis of biocompatible gold nanoparticles using aqueous extract of garlic Allium sativum. Adv. Mater. Lett. 2013, 4, 548–555.

(29) Tahir, M. B.; Farman, S.; Rafique, M.; Shakil, M.; Khan, M. I.; Ijaz, M.; Mubeen, L.; Ashraf, M.; Nadeem Riaz, K. Photocatalytic performance of hybrid WO3/TiO2 nanomaterials for the degradation of methylene blue under visible light irradiation. Int. J. Environ. Anal. Chem. 2019, 1–13.

(30) Haldorai, S.; Shim, J.-J. Novel Chitosan-TiO2 Nanohybrid: Preparation, Characterization, Antibacterial, and Photocatalytic Properties. Polym. Compos. 2014, 35, 327–333.

(31) Sirajuddeen, P.; Meneaksi, S. Facile synthesis of chitosan-La3+-graphite composite and its influence in photocatalytic degradation of methylene blue. Int. J. Biol. Macromol. 2019, 133, 253–261.

(32) Peniche-Covas, C.; Argüelles-Monal, W.; San Román, J. A kinetic study of the thermal degradation of chitosan and a mercaptan derivative of chitosan. Polym. Degrad. Stab. 1993, 39, 21.

(33) Wan Ngah, W. S.; Teong, L. C.; Hanafiah, M. A. K. M. Adsorption of dyes and heavy metal ions by chitosan composites: A review. Carbohydr. Polym. 2011, 83, 1446–1456.

(34) Periyat, P.; Pillai, S. C.; McCormack, D. E.; Colreavy, J.; Hinder, S. J. Improved high-temperature stability and sun-light-driven photocatalytic activity of sulfur-doped anatase TiO2. J. Phys. Chem. C 2008, 112, 7644–7652.