Effects of the surface of solar-light photocatalytic activity of Ag-doped TiO\textsubscript{2} nanohybrid material prepared with a novel approach

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Abstract

Surface modification with a nanomaterial has been confirmed to be an effective strategy to enhance the visible-light photodegradation efficiency of titanium dioxide nanoparticles (TiO\textsubscript{2}-NPs). In this regard, we used silver as an additive into TiO\textsubscript{2}-NPs to improve their photodegradation activity under visible light irradiation. Here, a novel and eco-friendly process was developed to prepare the Ag-doped TiO\textsubscript{2} nanohybrid and named as photon-induced method (PIM). The XRD technique showed that the prepared Ag-doped TiO\textsubscript{2} has mixed phases of anatase and rutile. However, the rutile-only phase was detected for the pure TiO\textsubscript{2}-NPs at 700 °C of calcination. Ultraviolet–visible (UV–Vis) absorption spectra revealed a reduction in the energy bandgap of TiO\textsubscript{2} after Ag doping. Besides, the addition of Ag resulted in a significant improvement of TiO\textsubscript{2} morphology. Methylene blue (MB) dye was chosen to be an organic target to investigate the photocatalyst activity of the TiO\textsubscript{2}-NPs. In this regard, the degradation rate of MB was found to be 100% for the Ag-doped TiO\textsubscript{2}, which is higher than that of pure rutile TiO\textsubscript{2}. The incorporation of Ag additive plays a significant role in the improvement of TiO\textsubscript{2} stability and photodegradation performance due to the surface plasmon resonance phenomenon.

Keywords Nanoparticles · Photo-induced method · Titanium dioxide · X-ray diffraction · Silver

1 Introduction

Nowadays, nanomaterials (NMs) are an important type of advancing structure and attract great attention from research society and industries. Semiconductor NMs such as TiO\textsubscript{2}, zinc oxide, tin oxide, and so on are the most used materials for various applications due to their fascinating features [1–3]. Also, nanoparticles have been prepared and employed in last decades due to their size-hooked on chemical and physical properties [4–6]. The use of NM for biomedical applications is crucial because NMs tend to be at the lowest level and immediately permit the food chain of the ecosystem [7]. Recently, researchers draw superior interest to TiO\textsubscript{2} and silver (Ag) incorporated TiO\textsubscript{2} crystalline structure because of their excellent electrical, optical, and chemical characteristics [8–10]. The semiconducting TiO\textsubscript{2} has an incredible photodegradation performance, which is mainly used as a photocatalyst due to its high light sensitivity, low environmental impact, strong oxidizing power, chemical inertness, and relative cheapness [11]. In addition, TiO\textsubscript{2} can be employed as an antimicrobial agent to deactivate microorganisms because of its chemical and physical stability, good photocatalytic efficiency, and ease of fabrication [12]. Nevertheless, two drawbacks limit the use of TiO\textsubscript{2}, which are low absorption ability in the visible range can be absorbed only under UV light and high recombination of carrier charges [13].

A broad variety of noble metals may well be combined with the TiO\textsubscript{2}-NPs to prompt photodegradation performance of dyes under visible light [14]. To date, Ag is an inexpensive metal with unique electronic merits compared with other ones, which makes it a good candidate for employing as an additive into the TiO\textsubscript{2}-NPs [15]. Thus, Ag can impede the recombination rate of the carrier charges by receiving the TiO\textsubscript{2} photo-induced charge.
which serves as an electron accumulator [16]. Moreover, the wide energy bandgap of TiO₂ can be easily tuned by Ag modification leading to increasing the absorption of visible light [17].

To increase the photodegradation performance, several interdisciplinary studies have been conducted on TiO₂ [18–20]. As reported in the literature, photocatalytic performance of NMs depends upon their crystallinity [21], additive engineering [22], surface area, and hydroxyl group [23]. Besides, Ag incorporating on the surface of semiconductors is used to improve the photocatalytic performance by slowing down recombination rates [24]. Lin and coworkers prepared mesoporous TiO₂ doped with Ag⁺-coated graphene (MT-Ag/GR) by a sol–gel and solvothermal methods as catalyst. The as-prepared hybrid of MT-Ag/GR showed stronger photodegradation abilities of MB dye than those realized with pure MT, MT-Ag, and MT/GR [25]. Siti and coworkers reported the development of a two-dimensional and porous metals-doped TiO₂ hybrids for studying their photocatalytic activity. They revealed that the Ag additive enhances the crystalline structure and gives an external oxidation level into the system for an improved charge transport pathway and surface reaction. As a result, this hybrid structure enhanced the photocatalytic activity toward rhodamine B [26]. Recently, our group investigated the visible-light photocatalytic activity of pure TiO₂ prepared with facile and green process named as photo-induced method (PIM). Our previous findings showed that pure, highly crystalline, and good TiO₂-NPs catalysts can be achieved by suggested approach [27].

For further improvement of TiO₂ photodegradation efficiency, we used Ag additive TiO₂ and doped into TiO₂ lattice using PIM. The prepared hybrid was systematically compared with standard TiO₂ using a series of techniques. Most importantly, the photocatalyst activity of the prepared hybrid was measured using the photodegradation of MB organic under visible light irradiation.

2 Experimental procedures

2.1 Synthesis of Ag-doped TiO₂

Briefly, 0.5 gm of silver nitrate (AgNO₃, Merck) and 3 gm of titanium tetra isopropoxide (TTIP, Sigma-Aldrich) were added to 1 L of distilled water. After that, the mixed solution was carefully stirred under a halogen light for 5 days. Then, the mixture was dried at 100 °C for 12 h and sintered at 700 °C for 60 min. The standard TiO₂ (Merck) sample was purchased and sintered at 700 °C for 60 min before further characterization.

2.2 Photocatalyst activity

The photocatalytic performance of pure and Ag-doped TiO₂ nanohybrid was characterized through MB degradation experiment. An aqueous dispersion of MB (1 × 10⁻⁵ M) was mixed well with 0.05 g catalyst powder into a glass beaker containing 100 ml of distilled water. The obtained suspension was maintained under sunlight for measuring the photodegradation activity. Finally, the UV absorption spectra were measured at intervals of 5 min.

2.3 Characterization

UV–Vis spectroscopy was used to record the optical characteristics of films using Ocean Optics (CHEM2000-UV–VIS). The structural properties of films were conducted by the XRD technique with CuKα (λ = 1.54050 Å) irradiation operated at 40 kV and 30 mA and (Shimadzu XRD-6100/7000 X-ray diffractometers). The morphology of samples was investigated using field emission SEM (Mira3). The FTIR spectra of samples were obtained using a Burker (IFS-125HR) device with KBr disc.

3 Results and discussion

To characterize the crystal nature of the standard and Ag-doped TiO₂ NPs, XRD measurement was performed in the range of 10°–75° (Fig. 1). The XRD shows the patterns of TiO₂ and Ag-doped TiO₂ NPs after sintering at 700 °C for 60 min. The X-ray pattern of the Ag-TiO₂ hybrid matches with the standard TiO₂ without any X-ray peaks from the Ag dopant (JCPDS card no. 21–1272) [8], therefore implying that the Ag additives are well loaded into the TiO₂ lattice.

Fig. 1 XRD patterns of a pure TiO₂, b Ag-doped TiO₂ NPs. A and R denoted to anatase and rutile phases, respectively
The X-ray pattern of Ag-doped TiO₂ NPs shows a mixed phase of an anatase and rutile phase, while the standard TiO₂ shows rutile-only phase. The average crystallite sizes of the standard TiO₂ and Ag-doped TiO₂ were found to be 60 nm and 25 nm, respectively, as determined by the Scherrer formula [28–30]. Also, XRD clearly exhibits TiO₂ peaks without any related pattern corresponding to Ag.

The absorption spectra of pure and Ag/TiO₂ hybrid were recorded using a UV–Vis spectrophotometer and are displayed in Fig. 2a. As shown, the absorption spectrum of the hybrid sample reveals a redshift at the absorption edge, which is ascribed from Ag addition. The energy bandgap of NPs was estimated by employing Tauc plot [31]. The plots of $(\alpha h\nu)^{1/2}$ vs energy ($h\nu$) are demonstrated in Fig. 2b. The bandgap can be directly obtained by extrapolating the line to the x-axis intercept. In this content, the energy bandgap of pure TiO₂ was 2.87 eV, while Ag-doped TiO₂ decreased to 2.7 eV. For hybrid NPs, this redshifting indicates the suppression of the recombination process of carrier charge and consequently enhanced visible light absorbance [4].

To further explore the impact of Ag doping on the structural properties of the prepared TiO₂ NPs, FTIR analysis was studied. The FTIR spectra of standard and Ag-doped TiO₂ samples are illustrated in Fig. 3. As shown, the peaks observed at ~3426 cm⁻¹ are assigned to the O–H vibration of the hydroxyl oxygen group [3]. By comparing with previous studies, the intensive peaks in the range of 744–726 cm⁻¹ are corresponding to lattice vibrations of Ti–O–Ti bonds [10, 12], which further confirms that the Ag additive is dispersed well into the TiO₂ lattice.

The FESEM micrographs of standard and Ag/TiO₂ NPs are depicted in Fig. 4. In the pure TiO₂ NPs, the NPs seem to be more aggregated, as revealed in Fig. 4a. Comparing with pure TiO₂, this finding indicates that the shape and morphology of TiO₂ NPs change with Ag addition. The effect of Ag incorporating on the morphology TiO₂ is particles like structures, as shown in Fig. 4b. The average particle size of pure TiO₂ and Ag-doped TiO₂ was found to be 80–100 nm and 30–50 nm, respectively. Moreover, the FESEM observations demonstrate that the adding of Ag clearly altered in the morphology of the photocatalyst surface. The spongy and porous structure causes more surface area at high hardness that surely would be more effective for enhancing the light absorbance and photodegradation performance [32].

The photocatalyst performance was estimated using the UV–Vis measurements of MB degradation under visible light illumination. The NP precursor is mixed with organic MB to form a colloidal solution using stirring for 5 min in the dark conditions. Then, the mixed solution containing NPs and MB was irradiated using visible light illumination. Nevertheless, if the electrons and holes pass through the surface of the
TiO$_2$ without recombination, they can act a part in different oxidation and reduction reactions with adsorbed agents, such as organic species, oxygen, and water. As shown in Fig. 5, the electrons in the valence band can be energized to the conduction band, leaving a positive hole in the valence band of the photocatalyst. When a photocatalyst is illuminated by light with energy as the same to or greater than the bandgap energy, photocatalysis initiated by electron-doping with Ag does not disturb the crystal structure of anatase TiO$_2$. The small size of Ag-TiO$_2$ hybrid increased surface area as indicated by the FESEM measurements, with an increasing lifetime of photogenerated electrons and holes. This process is beneficial to enhance the photocatalytic efficiency. Through the evaluation, the rate constants among the Ag-doped TiO$_2$ have shown to be markedly enhanced compared with standard TiO$_2$ sample. This is due to the insignificant particle size of Ag-doped TiO$_2$ and reduced recombination of electron–hole pairs, and bandgap narrowing [33, 34].

The photocatalytic activities of standard TiO$_2$ and Ag-TiO$_2$ hybrid calcined at 700 °C are presented in Fig. 6. In comparison, the photodegradation curves of MB by Ag-TiO$_2$ sample are 100% achieved within 30 min, whereas the standard TiO$_2$ sample, only 10% degradation of MB is achieved within 30 min (standard TiO$_2$ rutile phase only and large
particle size so no photocatalytic activity). Thus, we find that Ag-TiO₂ sample shows enhanced degradation in this case. This may be correlated with the size of the particles, and mixed-phase and the bandgap. Table 1 reveals the results of previous studies related with TiO₂ photodegradation and compared with the results established in this work.

4 Conclusion

In summary, the novel and eco-friendly photo-induced method was used to prepare Ag-doped TiO₂ nanoparticles with improved photodegradation activity. In this regard, high-quality TiO₂ NPs were achieved with higher crystallinity and better morphology compared with pure TiO₂. Ag-doping has a significant impact on the narrowing energy bandgap of TiO₂ (decreasing from 2.87 eV to 2.7 eV), which improves the light absorption ability toward a visible light region as well as delaying the electrons-holes recombination rate. The obtained results indicate that the enhancement of photodegradation activity was acquired after Ag doping. The measurement of photodegradation of MB dye showed that the Ag-doped TiO₂ NPs had 100% photocatalytic activity, while standard TiO₂ achieved 10% after 30 min illumination. It was noted that the incorporation of Ag can effectively improve the photocatalytic activity of TiO₂ by increasing its adsorption property, inhibiting charge recombination, and reducing the energy bandgap, which was due to the synergistic influence of TiO₂ and Ag doping. This low cost and environment friendly approach can pave a new pathway for using semiconducting TiO₂ in fabricating highly active nanostructured composites for water purification under solar irradiation.

Fig. 6 a MB degradation by standard TiO₂ under solar light, b MB degradation by Ag-TiO₂ under solar light

| Study            | Material       | Method            | Degradation efficiency (%) | References |
|------------------|----------------|-------------------|----------------------------|------------|
| Harikishore et al. | Ag/TiO₂       | Sol–gel           | 88                         | [35]       |
| Siti et al.      | Ag/TiO₂       | Liquid phase deposition | 91                     | [26]       |
| Adilah et al.    | N/Ag/TiO₂     | Solvothermal method | 98.82                    | [36]       |
| Lin et al.       | GR/Ag/TiO₂    | Sol–gel           | 72.5                      | [25]       |
| Nagaraj et al.   | Ag/TiO₂       | PIM               | 100%                      | This work  |
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Author contributions GN and MKAM wrote introduction and revised version HGA wrote SEM and XRD results, PS and SK completed experimental parts, ST supervised and revised the manuscript.

Declarations

Conflict and interest The authors declare there is no conflict of interest in this research paper.

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