Preparation and Characterization of Ag@TiO₂/α-Fe₂O₃ Ternary Nanocomposite for enhanced visible light photocatalytic performance

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Research Article

Keywords: solvothermal, hydrothermal, silver, titanium dioxide, iron oxide, photocatalyst

Posted Date: August 19th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-814762/v1>

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Abstract

In this work, ternary $\text{Ag@TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ nanocomposite were synthesized via solvothermal chemical reduction method using N,N-dimethylformamide (DMF) as solvent and reducing agent. The chemical procedure involves the use of only metals precursors without the need to use any other surfactants or capping agents. Physicochemical properties of the designed photocatalyst are found by means of various modern techniques. XRD data confirmed the high crystallinity of the obtained ternary nanocomposite. On the other hand, using TEM and HRTEM instruments, the shape and morphology of the $\text{Ag@TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ nanocomposite were found to be spherical with an average particle size of 150 nm. The UV-Vis measurement shows that $\text{Ag@TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ as photocatalyst exhibited good photo response in the visible region. The effect of preparation method and the performance of the designed photocatalyst were evaluated by photodegradation measurements of MB under visible light irradiation. We observed that the combination of metallic silver nanoparticles (AgNPs) and hematite iron oxide ($\alpha\text{-Fe}_2\text{O}_3$) with titanium dioxide (TiO_2) enhance the photocatalytic activity of the ternary $\text{Ag@TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ photocatalyst compared to bare TiO_2 suggesting its potential for many purification applications.

1. Introduction

Environmental pollution resulting from numerous artificial and industrial events is essentially constituted of inorganic, organic and harmful pollutants such as antibiotic, pesticides and dyes [1]. Generally, the most adopted methods to decompose pollutions such as chemical, heating, or biological process are found to be very expensive and ineffective mostly for the degradation of antibiotic. In recent years, nanomaterials are found to be very useful for different applications [2–4]. On the other side, photocatalytic reactions have been widely suggested as green solution to decompose many categories of pollutants under mild conditions and under solar light source [5–11]. However, the photodegradation mechanism involves the presence of only a photocatalyst and a light as exciting source. This process can mineralize pollutants to harmless products such as carbon dioxide and water and therefore produces useful products. Among the semiconductor photocatalyst, titanium dioxide (TiO_2) can be considered as the most promising photocatalyst in recent years due to its high stability and easy to prepare in different shape and size [12–20]. On the other hand, unfortunately, TiO_2 nanoparticles suffer from its large energy gap (3.2 eV), which limits its usage under visible light source [14]. The second inconvenient which inhibits the photocatalytic efficiency of TiO_2 is related to the high charge carrier recombination rate during the photodegradation reaction [15]. To resolve this problem, the synthesis of hybrid nanocomposite was found to be very efficient for decreasing the energy gap and the separation of charge carrier recombination. Using a simple two-step hydrothermal and photo-reduction method, Zhang *et al.* prepared ternary $\text{BiVO}_4/\text{NiS}/\text{Au}$ nanocomposites with efficient charge separations for enhanced visible light photocatalytic performance [11]. They found that the photodegradation activity was enhanced 4.25 times compared to pure BiVO_4 . Using the sol-gel method, Khasawnhem *et al.* [1] designed hybrid $\text{Fe}_2\text{O}_3\text{-TiO}_2$ heterogenous photocatalyst for the removal of acetaminophen (ACT) pharmaceutical compound. The obtained results revealed that photodegradation rate of ACT was observed at pH = 11 and the

photocatalytic activity was further optimized compared to bare TiO_2 . Sahu *et al.* developed for the first time a combined sol–gel-assisted hydrothermal method to prepare Copper/ TiO_2 /graphene oxide ternary nanocomposites (CuTGR) [2]. This photocatalyst exhibited high photocatalytic activity. Indeed, preliminary results show that an optimal loading of Cu and graphene in TiO_2 matrix can significantly enhance the surface and optical response of the designed nanocomposites and thereby allowing it to be an efficient ternary photocatalyst for many applications.

In this context, the main purpose of this work is to prepare a ternary system based on titanium dioxide (TiO_2) nanoparticles with excellent light absorption and high photocatalytic efficiency. In recent years, iron oxide more precisely the hematite phase ($\alpha\text{-Fe}_2\text{O}_3$) was found to be an ideal metal oxide to expand the photo response of TiO_2 and therefore enhance its photocatalytic performance [16–19]. On the other side, silver nanoparticles (AgNPs) are a plasmonic metal nanoparticles with their intrinsic plasmonic properties can increase the electrons activity over the surface of TiO_2 NPs and slows down the recombination of e^-/h^+ pairs. Consequently, the loading of both hematite iron oxide ($\alpha\text{-Fe}_2\text{O}_3$) and silver nanoparticles (AgNPs) at the TiO_2 surface can subsequently boost the photocatalytic activity of the final nanocomposite. The present paper develop a simple one pot solvothermal protocol to synthesize ternary $\text{Ag@TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ nanocomposite using N,N-dimethylformamide (DMF) as solvent and reducing agent without recourse to use any capping agent or surfactant. The photodegradation reaction against MB dyes prove the efficiency of this ternary system compared to bare TiO_2 or $\alpha\text{-Fe}_2\text{O}_3$ NPs.

2. Materials And Methods

2.1. Measurement and Characterizations

Powder X-ray diffraction (D8 Advance Bruker, USA) technique was performed to study the obtained crystalline phase. Shape and size of the photocatalyst was examined using transmission electron microscope (Philips Tecnai F-20 SACTEM working at 200 kV). X-ray photoelectron spectrometry (XPS, Kratos Axis Ultra DLD) was recorded for further elemental analysis. Optical response was investigated via UV–Visible Perkin-Elmer Lambda 11 spectrophotometer. To study the charge recombination process, Photoluminescence (PL) measurements were adopted using Jobin Yvon Fluorolog-3-11 instrument equipped with 450 W xenon lamp. Photocatalytic test were evaluated at room temperature for removal of MB molecules dyes under visible light illumination (lamp of 400 W Metal Halide. The solution pH was fixed at 7. The photocatalyst amoun was fixed to 7 mg during the photocatalytic test. The initial MB concentration solution was $3.0 \cdot 10^{-5}$ mol/L.

2.2. Synthesis of $\text{Ag@TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ Photocatalyst

Iron oxide was first synthesized using the hydrothermal process [21] by mixing iron chloride and ammonium dihydrogen phosphate. After that, the mixture was transferred into a Teflon-lined autoclave and heated at 220°C for 48 h. $\text{Ag@TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ photocatalyst was prepared as follows: Titanium(IV)

butoxide (5 ml) and silver nitrate (100 mg) were first dissolved in 50 ml of N,N-dimethylformamide (DMF) at room temperature. The resulting mixture was magnetically stirred, and an adequate amount of as-prepared iron oxide nanoparticles (10 mg) was added. Then the obtained final mixture was heated at 153 °C for 2 h. The recuperated powder was then calcinated in air at 400°C for 2 h to produce the desired ternary Ag@TiO₂/α-Fe₂O₃ nanocomposite.

3. Results And Discussion

Powder X-ray diffraction patterns of TiO₂, α-Fe₂O₃ and ternary Ag@TiO₂/α-Fe₂O₃ photocatalyst are shown in Fig. 1. As can be observed, in the diffractogram of the ternary nanocomposite, all diffractions peaks characteristic of titanium dioxide, silver and iron oxide are detected. No other peaks or impurities can be detected which prove the purity of the obtained sample. Based on the XRD data, we can assume the successful fabrication of the ternary Ag@TiO₂/α-Fe₂O₃ heterojunction. Figure 2 displays the morphology of the ternary photocatalyst. As shown, we can detect the deposition of both AgNPs and α-Fe₂O₃ NPs on the TiO₂ surface. Furthermore, the HRTEM image confirms the ternary heterojunction by the presence of (111), (003) and (101) lattice spacing characteristic of Ag, α-Fe₂O₃ and TiO₂ NPs, respectively. The SAED pattern further confirms the presence of the three system by the detection of all characteristic electron diffraction responses. To further confirm the successful synthesis of Ag@TiO₂/α-Fe₂O₃ nanocomposites, XPS measurement was performed to study the chemical composition and their corresponding valence states (Fig. 3). The XPS spectra of the asprepared sample are shown in Fig. 3. In the Ti 2p spectrum, two peaks at 458 eV, and 465 eV were assigned to Ti 2p_{3/2} et Ti 2p_{1/2}, respectively. Values agree well with the Ti⁴⁺ state in TiO₂. The spectrum of Fe which exhibites also two peaks at 711 eV and 725 eV can be ascribed to the Fe 2p element of hematite α-Fe₂O₃. In the case of O 1s, it can be detected the presence of asymmetrical peak located at 529.9 eV which can be attributed to lattice oxygen and surface oxygen. For Ag element, two characteristic peaks are located at 273.6 and 367.8 eV which can be assigned to Ag 3d_{3/2} et Ag 3d_{5/2} respectively. Values agree well with Ag⁰ metal. The deconvolution of the XPS peaks of Ag (Figure S1) revealed the presence of peaks characteristic of Ag-O bonds. As mentioned above, HRTEM results showed the deposotion of AgNPs on both TiO₂ and α-Fe₂O₃ surfaces. The XPS data agree well with the HRTEM observation. However, the presence of XPS peaks characteristic of Ag-O bonds confirmed the the adsorption processes of AgNPs on TiO₂ and α-Fe₂O₃ surfaces, through chemical oxygen bonds. This chemisorption between AgNPs and metals oxide ensures the formation of .he ternary heterojunction and avoiding metal desorption [12, 13]. The optical properties of Ag@TiO₂/α-Fe₂O₃ nanocomposite, hybrid Ag@TiO₂ and as well as bare TiO₂ and α-Fe₂O₃ were investigated using UV-visible absorption spectroscopy (Fig. 4-a). Regarding the TiO₂, Ag@TiO₂ and Ag@TiO₂/α-Fe₂O₃ spectra, each spectrum shows an absorption edge at 346 nm that corresponds to a band gab energy of 3.85 eV. Result agree well agreement with the band gap energy reported in the literature. On the other hand, for Ag@TiO₂ and Ag@TiO₂/α-Fe₂O₃, an additional absorption band located between 435 and 480 nm which can be attributed to the surface plasmon resonance of silver nanoparticles. On the other side, iron oxide is generally reported to absorb strongly in the ultraviolet (UV)

region. However, regarding the $\alpha\text{-Fe}_2\text{O}_3$ and $\text{Ag@TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ spectra, effectively an absorption edge located at 245 nm can clearly be detected and can be assigned to the electronic transition in the hematite $\alpha\text{-Fe}_2\text{O}_3$ structure. The change of the absorption behaviour of $\text{Ag@TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ compared to bare TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$, implies that the charge-transfer transition between the three materials occurs while loading Ag to TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$. This observation was further supported by PL measurements (Fig. 4-b). Indeed, as can be seen, the PL spectrum of all samples exhibited blue emission located at 445 nm. It has been reported that the visible luminescence, related to deep level emissions, mainly results from defects such as interstitials and oxygen vacancies. On the other hand, as can be seen in Fig. 4-b, a considerable PL emission quenching of $\text{Ag@TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ nanocomposite was observed which indicated that a lower recombination rate of the photogenerated carrier could be efficiently achieved resulting from the synergistic effects between Ag, TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$. This result implying that the intimate contact between Ag, TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$ could make for the vectorial migrate of charge carriers among the nanocomposite, enhancing the photogenerated carrier's separation and therefore improving the photocatalytic efficiency.

The photocatalytic efficiencies of $\text{Ag@TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ nanocomposites were evaluated using MB dyes as a model pollutant. Photocatalytic activities of hybrid Ag@TiO_2 , bare TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$ were also measured for comparison. As shown in Fig. 5-a, the photodegradation rate of MB was found to be the highest using the ternary $\text{Ag@TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ photocatalyst. On the other side, the photodegradation rate using pristine $\alpha\text{-Fe}_2\text{O}_3$ photocatalyst is the lowest. However, the photocatalytic performance of hematite $\alpha\text{-Fe}_2\text{O}_3$ is limited due to the charge carrier recombination. On the other hand, the hybrid Ag@TiO_2 photocatalyst exhibited interesting photodegradation rate due to the presence of plasmonic AgNPs which can generate more electrons and therefore boost the photocatalytic activity of TiO_2 . It can be seen that ternary $\text{Ag@TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ photocatalyst exhibits much higher photodegradation activities than that of hybrid Ag@TiO_2 may be due to the support given by $\alpha\text{-Fe}_2\text{O}_3$ NPs which increases the surface area of the photocatalyst and also increases the light absorption which generates more electron-hole pairs for dye photodegradation and consequently enhances the photocatalytic activity of the ternary nanocomposite. To examine the reaction kinetics of photocatalysts, experimental data were fitted by a first-order kinetic equation ($\ln(C_0/C) = k_{\text{ap}}t$) using the Langmuir–Hinshelwood model. It can be seen from the curves displayed in Fig. 5-b that the photodegradation process followed first order kinetics. A proposed possible photocatalytic mechanism is illustrated in Fig. 5-c. After excitation the VB electrons of both TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$ were excited to the CB, creating holes in the VB. These photogenerated electrons-holes recombined rapidly, leading to a low photocatalytic performance of the photocatalyst. However, after loading the AgNPs, the photogenerated electrons could be continuously transported from TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$ to AgNPs. Those vector transfers led to spatial separation of the photogenerated carries with an electron transferred to AgNPs while the holes remain trapped at the TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$ surface. Subsequently, the adsorbed oxygen molecule (O_2) can after that react with electrons produce therefore reactive oxygen species (such as $\text{O}_2^{\cdot-}$, $\cdot\text{O}^{2-}$) that could oxidize and destruct MB dyes.

4. Conclusion

In summary, the synthesis of ternary Ag@TiO₂/α-Fe₂O₃ nanocomposite using modified solvothermal protocol was reported. Physicochemical properties of the designed photocatalyst are found by means of various modern techniques such as XRD, TEM/HRTEM, XPS and UV-visible. The designed photocatalyst exhibited the highest photocatalytic activity. The performance of the ternary nanocomposite could be attributed to the synergistic effects of co-loading α-Fe₂O₃ and Au cocatalyst with TiO₂ which expand the separation efficiency of photogenerated electron-hole carriers and consequently boost the photodegradation rate.

Declarations

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Taif University Researchers Supporting Project number (TURSP-2020/28), Taif University, Taif, Saudi Arabia.

References

1. S. Omar Fawzi, P. Khasawneh, M. Palaniandy, H. Ahmadipour, Mohammadi, Mohammad Razak Bin Hamdan, Removal of acetaminophen using Fe₂O₃-TiO₂ nanocomposites by photocatalysis under simulated solar irradiation: Optimization study. *Journal of Environmental Chemical Engineering* Volume 9(1), 104921 (February 2021)
2. K. Sahu, M. Dhonde, V.V.S. Murty, Preparation of copper/TiO₂/ graphene oxide ternary nanocomposites and their structural, surface morphology, and optical properties. *J. Mater. Sci.: Mater. Electron.* **32**, 15971–15980 (2021)
3. Y.-C. Zhang, Y. You, Sen Xin, Ya-Xia Yin, J. Zhang, P. Wang, X. Zheng, F.-F. Cao, Yu-GuoGuo. Rice husk-derived hierarchical silicon/nitrogen-doped carbon/carbon nanotube spheres as low-cost and high-capacity anodes for lithium-ion batteries. *Nano Energy* Volume 25, July 2016, Pages 120–127
4. Z. Fang, M. Xu, Q. Li, M. Qi, T. Xu, Z. Niu, N. Qu, J. Gu, J. Wang, D. Wang. Over-Reduction-Controlled Mixed-Valent Manganese Oxide with Tunable Mn²⁺/Mn³⁺ Ratio for High-Performance Asymmetric Supercapacitor with Enhanced Cycling Stability. *Langmuir* 2021, 37, 8, 2816–2825
5. Y. Ge, H. Luo, Juanru Huang, Z. Zhang. Visible-light-active TiO₂ photocatalyst for efficient photodegradation of organic dyes. *Optical Materials* Volume 115, May 2021, 111058 [6] A. Temir, K. Sh Zhumadilov, M.V. Zdorovets, A. Kozlovskiy, A.V. Trukhanov. Study of the effect of doping CeO₂ in TeO₂–MoO–Bi₂O₃ ceramics on the phase composition, optical properties and shielding efficiency of gamma radiation. *Optical Materials*, Volume 115, 2021, 111037

6. Y. Zhang, S.M. Zhao, Q.W. Su et al., Visible light response ZnO–C₃N₄ thin film photocatalyst. *Rare Met.* **40**, 96–104 (2021)
7. X. He Wang, P.N. Liu, Porous Two-Dimensional Materials for Photocatalytic and Electrocatalytic Applications. *June 2020 Matter* 2(6):1377–1413
8. T. Xu, X. Liu, S. Wang et al., Ferroelectric Oxide Nanocomposites with Trimodal Pore Structure for High Photocatalytic Performance. *Nano-Micro Lett* **11**, 37 (2019)
9. K.S. Mahesh Dhonde, V.V.S. Dhonde, Murty, Novel sol–gel synthesis of Al/N co-doped TiO₂ nanoparticles and their structural, optical and photocatalytic properties *Journal of Materials Science: Materials in Electronics* <https://doi.org/10.1007/s10854-018-9962-7>
10. G.C. Zhang, J. Zhong, M. Xu, Y. Yang, Yu Li, Z. Fang, S. Tang, D. Yuan, B. Wen, Jianmin Gu. Ternary BiVO₄/NiS/Au nanocomposites with efficient charge separations for enhanced visible light photocatalytic performance. *Chem. Eng. J.* **375**, 122093 (2019)
11. O. Todorka Vladkova, D. Angelov, D. Stoyanova, L. Gospodinova, A. Gomese, Soarese, Filipe Mergulhae, Iliana Ivanovac. Magnetron co-sputtered TiO₂/SiO₂/Ag nanocomposite thin coatings inhibiting bacterial adhesion and biofilm formation. *Surf. Coat. Technol.* **384**, 125322 (2020)
12. M.Jayapriy and M.Arulmozhi. *Beta vulgaris* peel extract mediated synthesis of Ag/TiO₂ nanocomposite: Characterization, evaluation of antibacterial and catalytic degradation of textile dyes-an electron relay effect
13. *Inorganic Chemistry Communications Volume 128*, June 2021, 108529
14. A. Mezni, M.M. Ibrahim, M. El-Kemary, A.A. Shaltout, N.Y. Mostafa, J. Ryl et al., Cathodically activated Au/TiO₂ nanocomposite synthesized by a new facile solvothermal method: an efficient electrocatalyst with Pt-like activity for hydrogen generation. *Electrochim. Acta* **290**, 404–418 (2018)
15. A. Mezni, N. Ben Saber, M.M. Ibrahim, N. Hamdaoui, A. Alrooqi, A. Mlayah et al., Photocatalytic activity of hybrid gold-titania nanocomposites. *Mater Chem Phys* **221**, 118e24 (2019)
16. A. Mezni, N. Ben Saber, A. Bukhari, M.M. Ibrahim, H. Al-Talhi, N.A. Alshehri et al.. Plasmonic hybrid platinumtitaniananocomposites as highly active photocatalysts:selfcleaning of cotton fiber, under solar light. *J Mater Res Technol* **9**, 1447e56 (2020)
17. A. Mezni, N. Ben Saber, M.M. Ibrahim, M. El-Kemary, A. Aldalbahi, P. Feng et al., Facile synthesis of highly thermally stable TiO₂ photocatalysts. *J Chem* **41**, 5021 (2017)
18. Omar Fawzi Suleiman Khasawneh, Puganeshwary Palaniandy, *Removal of organic pollutants from water by Fe₂O₃/TiO₂ based photocatalytic degradation.*, vol. 21 (A review *Environmental Technology & Innovation*, February 2021), p. 101230
19. Y. Li, B. Yang, B. Liu, MOF assisted synthesis of TiO₂/Au/Fe₂O₃ hybrids with enhanced photocatalytic hydrogen production and simultaneous removal of toxic phenolic compounds. *Journal of Molecular Liquids Volume 322*, 15 January 2021, 114815
20. C.-L. Yanming Fu, Wu Dong, Y.-R. Zhou, Y.-C. Lu, Y. Huang, P. Liu, L. Guo, W.-C. Zhao, Chou, Shaohua Shen. A ternary nanostructured Fe₂O₃/Au/TiO₂ photoanode with reconstructed interfaces for

efficient photoelectrocatalytic water splitting. Applied Catalysis B: Environmental Volume **260**, 118206 (January 2020)

21. Yudong Xue and Yunting Wang. A review of the α -Fe₂O₃ (hematite) nanotube structure: recent advances in synthesis, characterization, and applications Nanoscale, 2020,12, 10912–10932

Figures

Figure 1

XRD diffractograms of bare α -Fe₂O₃, TiO₂ and Ag@TiO₂/ α -Fe₂O₃ nanocomposite.

Figure 2

TEM images of (a) bare α -Fe₂O₃ and (b) Ag@TiO₂/α-Fe₂O₃. (c) HRTEM image of Ag@TiO₂/α-Fe₂O₃ with (d) SAED pattern.

Figure 3

XPS spectra of Ag@TiO₂/α-Fe₂O₃

Figure 4

Optical absorption property and PL response of Ag@TiO₂/α-Fe₂O₃ nanocomposite

Figure 5

(a,b) Photocatalytic activity of $\text{Ag@TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ Nanocomposite. (c) proposed photocatalytic mechanism

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