Solar Energy as Renewable Energy for the Degradation of Pollutants using High Active $Ag@TiO_2/\alpha\text{-}Fe_2O_3$ Ternary Nanocomposite Photocatalyst

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Research Article

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Abstract

In this work, ternary Ag@TiO_2/α-Fe_2O_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 Ag@TiO_2/α-Fe_2O_3 nanocomposite were found to be spherical with an average particle size of 150 nm. The UV-Vis measurement shows that Ag@TiO_2/α-Fe_2O_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 (α-Fe_2O_3) with titanium dioxide (TiO_2) enhance the photocatalytic activity of the ternary Ag@TiO_2/α-Fe_2O_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 $BiVO_4$/NiS/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 Fe_2O_3-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 (α-Fe_2O_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 (α-Fe_2O_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 Ag@TiO_2/α-Fe_2O_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 α-Fe_2O_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 Flurolog-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 $.10^{-5}$ mol/L.

2.2. Synthesis of Ag@TiO_2/α-Fe_2O_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. Ag@TiO_2/α-Fe_2O_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@TiO_2/α-Fe_2O_3 nanocomposite.

3. Results And Discussion

Powder X-ray diffraction patterns of TiO_2, α-Fe_2O_3 and ternary Ag@TiO_2/α-Fe_2O_3 photocatalyst are shown in Figure 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@TiO_2/α-Fe_2O_3 heterojunction. Figure 2 displays the morphology of the ternary photocatalyst. As shown, we can detect the deposition of both AgNPs and α-Fe_2O_3 NPs on the TiO_2 surface. Furthermore, the HRTEM image confirms the ternary heterojunction by the presence of (111), (003) and (101) lattice spacing characteristic of Ag, α-Fe_2O_3 and TiO_2 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@TiO_2/α-Fe_2O_3 nanocomposites, XPS mesearement was performed to study the chemical composition and their corresponding valence states (Figure 3). The XPS spectra of the asprepared sample are shown in Figure 3. In the Ti 2p spectrum, two peaks at 458 eV, and 465 eV were assigned to Ti 2p3/2 et Ti 2p1/2, respectively. Values agree well with the Ti^{4+} state in TiO_2. 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-Fe_2O_3. 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 3d3/2 et Ag 3d5/2 respectively. Values agree well with Ag^0 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 TiO_2 and α-Fe_2O_3 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 TiO_2 and α-Fe_2O_3 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@TiO_2/α-Fe_2O_3 nanocomposite, hybrid Ag@TiO_2 and as well as bare TiO_2 and α-Fe_2O_3 were investigated using UV-visible absorption spectroscopy (Figure 4-a). Regarding the TiO_2, Ag@TiO_2 and Ag@TiO_2/α-Fe_2O_3 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@TiO_2 and Ag@TiO_2/α-Fe_2O_3, 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 α-Fe_2O_3 and Ag@TiO_2/α-Fe_2O_3 spectra, effectively an absorption edge located at 245 nm can clearly detected and can be assigned to the electronic transition in the hematite α-Fe_2O_3 structure. The change of the absorption behaviour of Ag@TiO_2/α-Fe_2O_3 compared to bare TiO_2 and α-Fe_2O_3, implies that the charge-transfer transition between the three materials occurs while loading Ag to TiO_2 and α-Fe_2O_3. This observation was further supported by PL measurements (Figure 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 Figure 4-b, a considerable PL emission quenching of Ag@TiO_2/α-Fe_2O_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 α-Fe_2O_3. This result implying that the intimate contact between Ag, TiO_2 and α-Fe_2O_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 Ag@TiO_2/α-Fe_2O_3 nanocomposites were evaluated using MB dyes as a model pollutant. Photocatalytic activities of hybrid Ag@TiO_2, bare TiO_2 and α-Fe_2O_3 were also measured for comparison. As shown in Figure 5-a, the photodegradation rate of MB was found to be the highest using the ternary Ag@TiO_2/α-Fe_2O_3 photocatalyst. On the other side, the photodegradation rate using pristine α-Fe_2O_3 photocatalyst is the lowest. However, the photocatalytic performance of hematite α-Fe_2O_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 Ag@TiO_2/α-Fe_2O_3 photocatalyst exhibits much higher photodegradation activities than that of hybrid Ag@TiO_2 may be due to the support given by α-Fe_2O_3 NPs which increases the surface are 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 ($Ln(C_0/C) = k_{ap}t$) using the Langmuir–Hinshelwood model. It can be seen from the curves displayed in Figure 5-b that the photodegradation process followed first order kinetics. A proposed possible photocatalytic mechanism is illustrated in Figure 5-c. After excitation the VB electrons of both TiO_2 and α-Fe_2O_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 α-Fe_2O_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 α-Fe_2O_3 surface. Subsequently, the adsorbed oxygen molecule (O_2) can after that react with electrons produce therefore reactive oxygen species (such as$O_2.^-$, $.O^{2-}$) that could oxidize and destruct MB dyes.

4. Conclusion

In summary, the synthesis of ternary Ag@TiO_2/α-Fe_2O_3 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-Fe_2O_3 and Au cocatalyst with TiO_2 which expand the separation efficiency of photogenerated electron-hole carriers and consequently boost the photodegradation rate.

Declarations

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Notes

The authors declare no competing financial interest.

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Figures

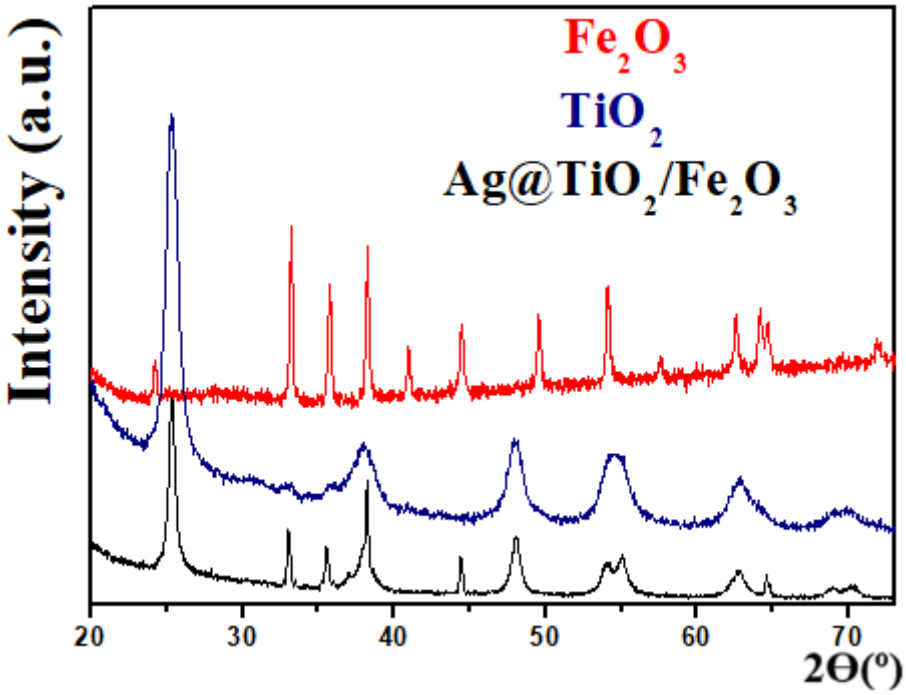

Figure 1

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

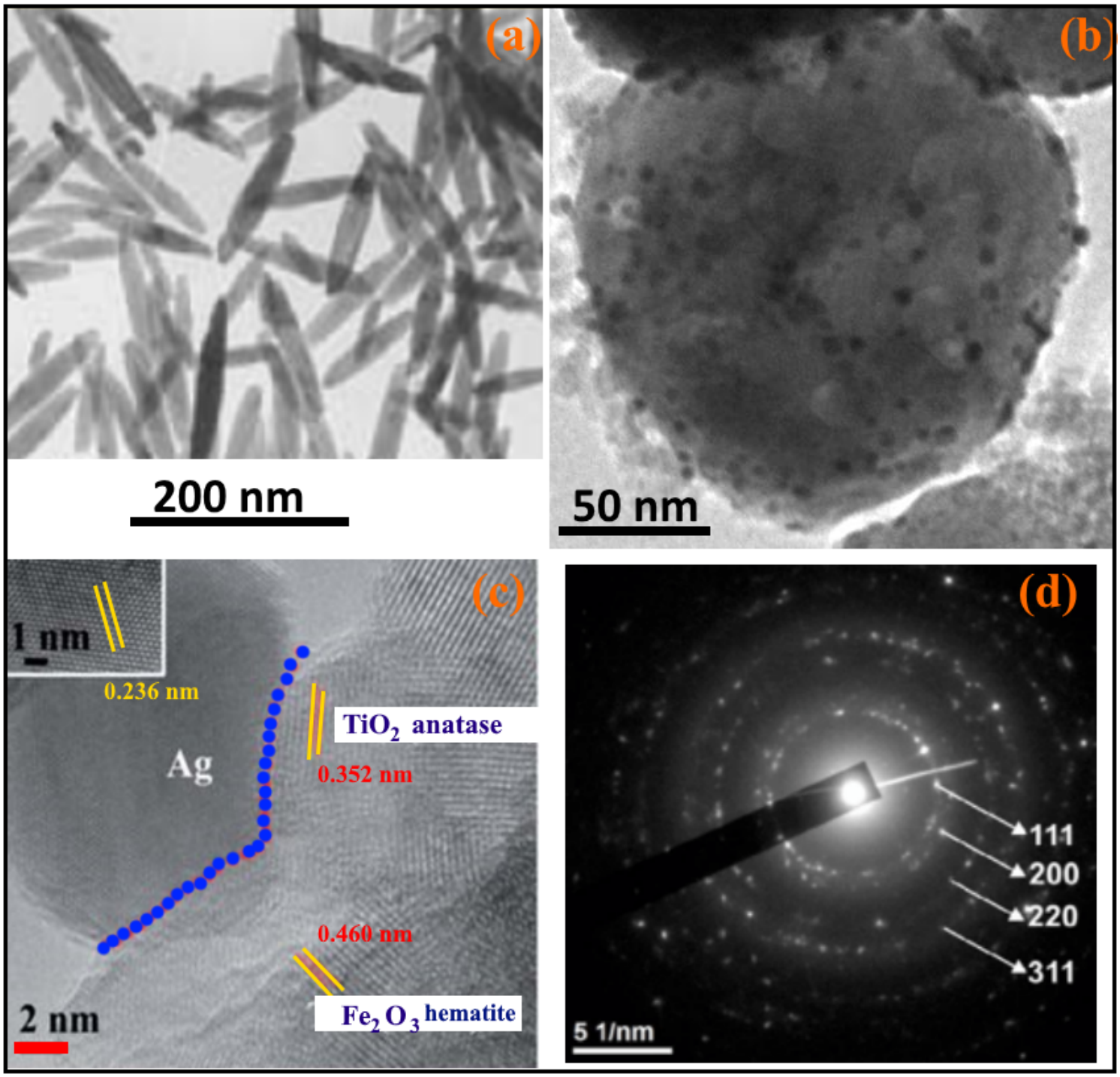

Figure 2

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.

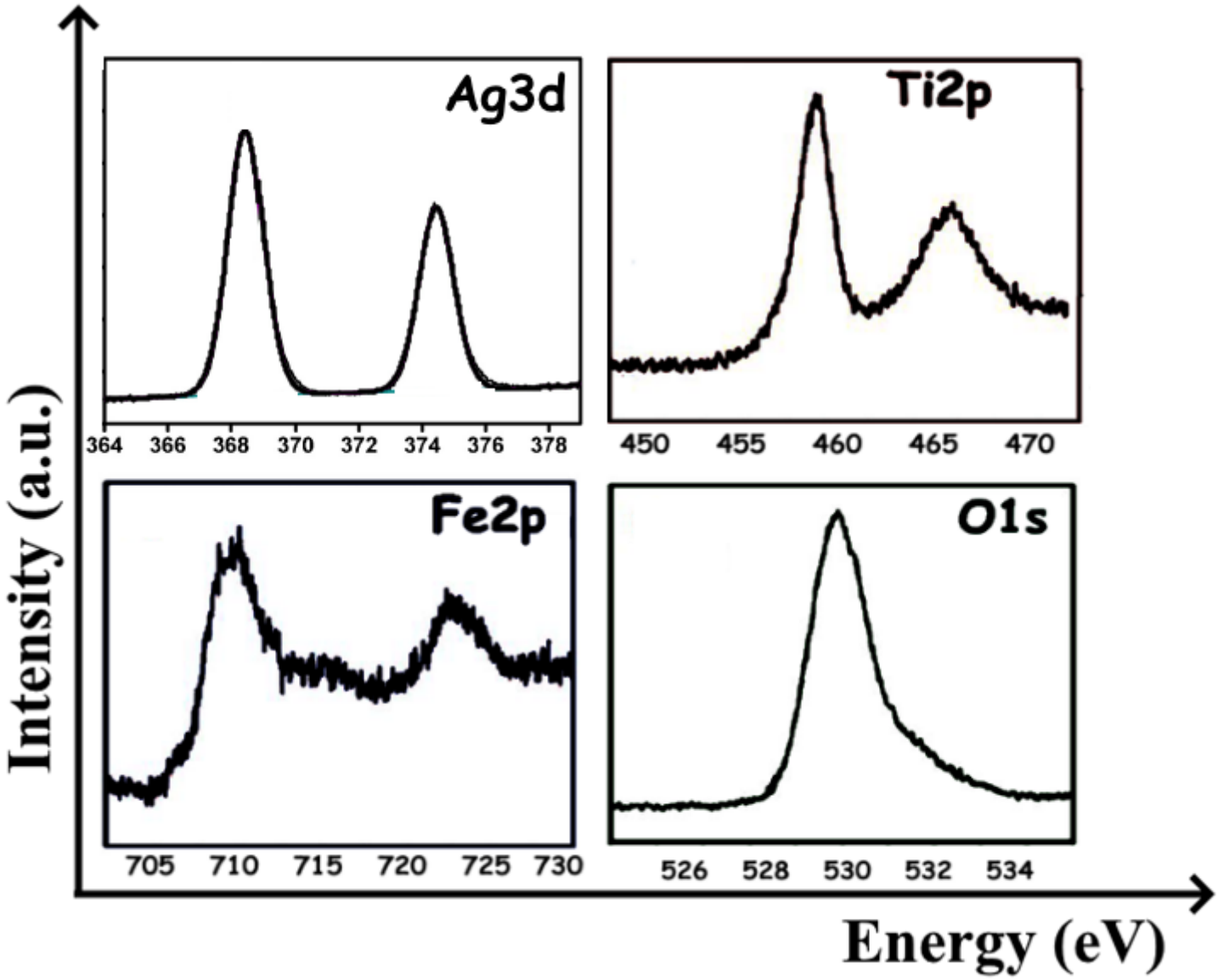

Figure 3

XPS spectra of Ag@TiO2/α-Fe2O3

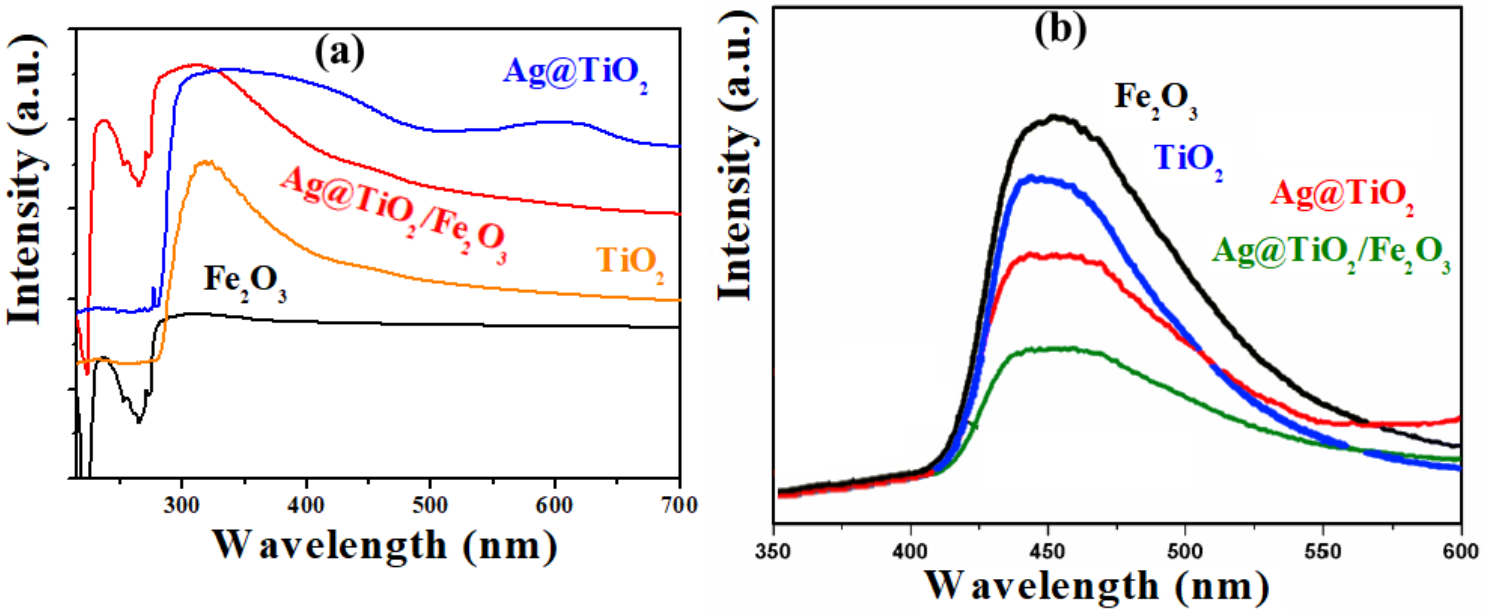

Figure 4

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

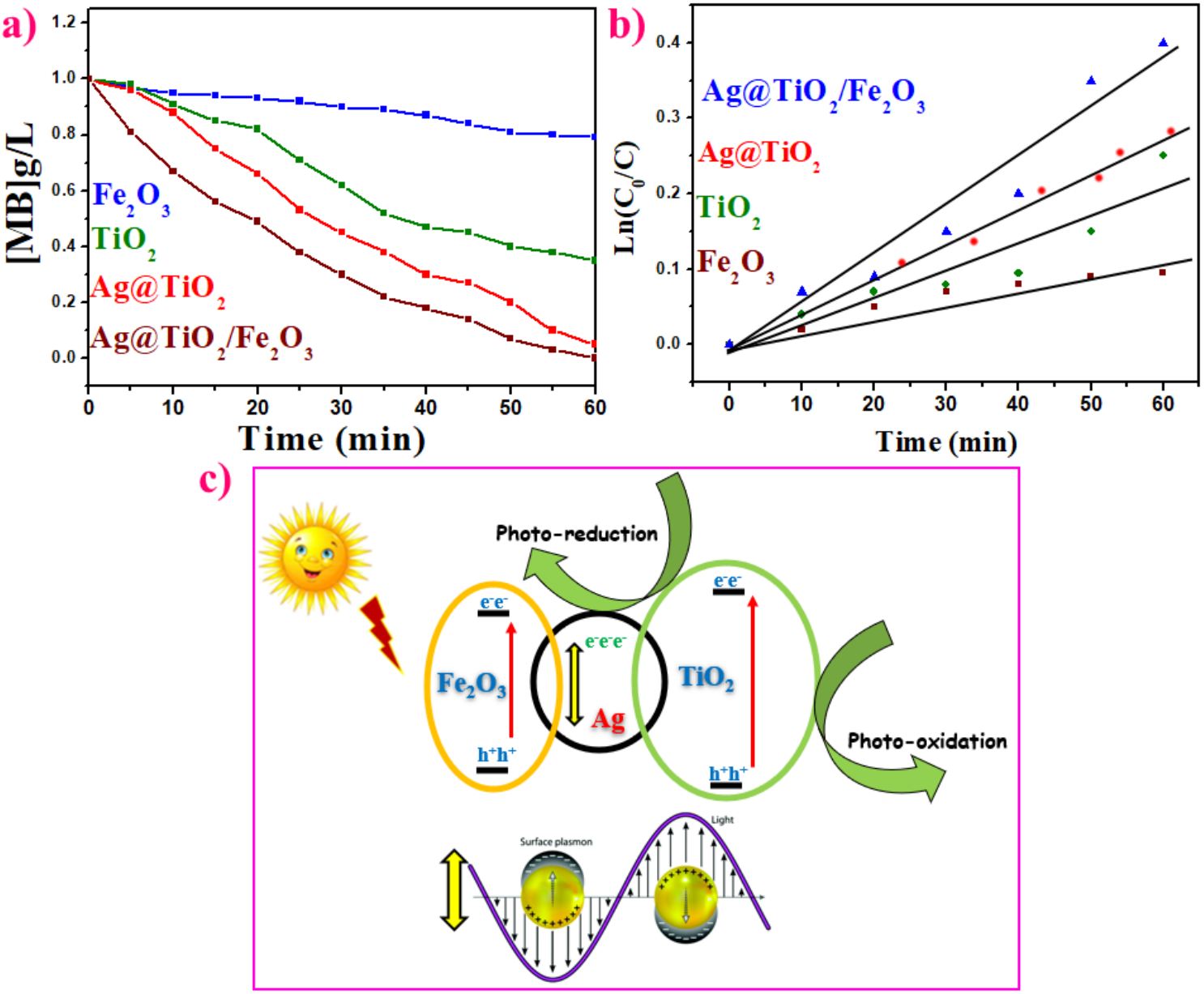

Figure 5

(a,b) Photocatalytic activity of Ag@TiO2/α-Fe2O3 Nanocomposite. (c) proposed photocatalytic mechanism

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