Cubic-shape hematite decorated with plasmonic Ag-Au bimetals for enhanced photocatalysis under visible light irradiation

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Abstract

Cubic-shape hematite (C-Fe₂O₃) was facilely prepared by hydrothermal autoclave reaction of Fe³⁺ in the presence of 1,12-diaminododecane at 130 °C for 10 h. The surface of C-Fe₂O₃ was decorated with nanosilvers through the sonochemical reduction of Ag precursor (0.1–0.4 ml of 1.0 wt.% AgNO₃), so-called C-Fe₂O₃@Ag. After then, the C-Fe₂O₃@Ag was plated with Au layer via galvanic-assisted reduction of Au precursor (0.04–0.14 ml of 1.0 wt.% HAuCl₄), so-called C-Fe₂O₃@Ag-Au. Scanning electron microscopy demonstrated the formation of cubic-shape hematite deposited with plasmonic nanometals. X-ray photoelectron spectroscopy analysis confirmed the existence of Ag and Au crystals. Photocatalytic performance of the hematite samples was estimated towards the degradation of methylene blue (MB) under visible light. The C-Fe₂O₃@Ag (0.2 ml) exhibited the five-fold increase of photocatalytic activity to that of the pristine C-Fe₂O₃. Furthermore, Au-deposited C-Fe₂O₃@Ag (0.2 ml), i.e., C-Fe₂O₃@Ag-Au, exhibited the 200% increase of photocatalytic activity to that of the C-Fe₂O₃@Ag (0.2 ml), owing to the plasmonic coupling effect on the extended visible light absorbance and enhanced separation efficiency of electron-hole pairs on the hematite surface.

1. Introduction

At present, environmental pollution caused by organic toxic chemicals is getting more aggravated because of the rapid and reckless development of industrialization, i.e., air pollutant and industrial wastewater are significantly uprising [1, 2]. In solving these serious problems, conventional biological and chemical technologies are quite restricted mainly due to the generation of secondary pollutants during their applications [3, 4]. On the other hand, photocatalytic treatment using renewable sunlight is an environmental friendly and low-cost process that can effectively decompose organic materials into harmless components [5].

Titanium dioxide (TiO₂) is generally known as the gold standard photocatalyst because of its abundance, nontoxicity, photostability, and high activity. However, TiO₂ has a wide bandgap (3.2 eV), and the absorbance wavelength is ranged in the ultraviolet region (λ ≤ 390 nm) [6]. Thus, the photocatalytic activity of TiO₂ is poor under visible light (or sunlight) irradiation. In addition, it is difficult to control the particle size owing to the aggregation of TiO₂ nanoparticles (NPs) during the sol-gel process [7–10]. Accordingly, many researches are focused on searching low bandgap and size-controllable photocatalysts such as Fe₂O₃ (2.1 eV), WO₃ (2.6 eV), CdS (2.4 eV), and Cu₂O (2.2 eV) that are easily activated under visible light [11–14].

Among many semiconductors as alternative photocatalysts, Fe₂O₃ can absorb broader wavelength of visible light because of low bandgap energy of 2.1 eV. In addition, it is chemically stable, non-toxic, and earth-abundant material as a promising sunlight-driven photocatalyst [15]. However, its photocatalyst activity is quite restricted due to the rapid recombination of electron-hole (e⁻–h⁺) pairs, very short diffusion length of hole carrier (2–4 nm), and low electrical conductivity [16, 17]. Therefore, it is absolutely needed to improve the photocatalytic activity of Fe₂O₃ using various synthetic routes controlling structural design (nanosheets,
nanorods), heterostructure formation, and plasmonic nanometal deposition [18]. The heterostructure formation usually follow the combination strategy of two or three semiconductors that have different bandgap energies [19–22]. For instance, the heterostructure of Fe₂O₃–CdS improved the photocatalytic activity of pristine Fe₂O₃ because of efficient separation of photo-generated charge carriers and extended visible light absorption [23–26].

As an alternative strategy, the deposition of plasmonic nanometals (Au, Ag, Pt, and Cu) can increase the separation efficiency of e⁻−h⁺ pairs on the hematite because the deposited nanometals can trap the photo-excited electrons temporarily and reduce the recombination of photo-generated carriers [27–30]. Bimetallic NPs are formed as the alloys of two different nanometals and/or core-shell nanostructures. Thus, bimetallic nanostructures can optimize surface plasmon energy resonance and provide additional degrees of freedom, consequently leading to enhanced optical, electronic and catalytic effects. Furthermore, plasmonic coupling effect is beneficial for enhancing charge separation and extending visible light absorption [31–34].

In this work, hydrothermal autoclave reaction was carried out to prepare cubic hematite particles (so-called C-Fe₂O₃) at 130 °C for 10 h. The C-Fe₂O₃ was subsequently decorated with nanosilvers via a sonochemical reduction of Ag precursor (0.1–0.4 ml of 1.0 wt.% AgNO₃) [35]. Ag-deposited C-Fe₂O₃ (C-Fe₂O₃@Ag) was further plated with Au layer, i.e., the formation of Ag-Au bimetals via galvanic-assisted plating of Au precursor, so-called C-Fe₂O₃@Ag-Au [36]. The C-Fe₂O₃@Ag-Au exhibited the significantly enhanced photocatalytic activity as compared to nanometal-free analogue, because of the plasmonic coupling effect on the visible light harvesting and separation efficiency of e⁻−h⁺ pairs. This work provides the simple and cost-effective synthetic route for plasmonic hematite as highly efficient photocatalyst under visible light.

2. Experimental procedures

2.1. Chemical and material
Iron (III) chloride hexahydrate (FeCl₃•6H₂O), 1,12-diaminododecane, AgNO₃ (99%), gold chloride trihydrate (HAuCl₄•3H₂O), ethyl alcohol (EtOH) were purchased from Sigma–Aldrich. (South Korea). NH₄OH (28.0 ~ 30.0%), isopropanol, polyvinylpyrrolidone (PVP), L-ascorbic acid, hydrochloric acid (HCl, 36%) were purchased from Samchun Co, Ltd (South Korea). Deionized (DI) water was purchased from J.T. Baker. Co. (South Korea).

2.2. Synthesis of cubic hematite particles (C-Fe₂O₃)
C-Fe₂O₃ was synthesized by the hydrothermal autoclave reaction. The synthetic procedures are as follows. FeCl₃•6H₂O (324 mg, 2 mmol) and 1,12-diaminododecane (DA-12) (200 mg) were mixed with DI water and ethanol (1:1 v/v%) solution for 2 h. After then, the homogeneous mixture of 50 ml was put into a Teflon-lined reactor at 130 °C for 10 h. The product was centrifuged at 7000 rpm for 20 min and washed with DI water to purify the sample. Finally, the C-Fe₂O₃ product was dried overnight at 60 °C [37].

2.3. Ag-deposited C-Fe₂O₃ (C-Fe₂O₃@Ag)
First, 10 mg of C-Fe₂O₃ was dispersed in 50 ml of ethanol, and aliquot (0.1–0.4) ml of 1.0 wt% AgNO₃ was added and ultrasonically dispersed for 5–10 min. Then, 50 μl of NH₄OH (28–30 wt.%) and 13 μl of isopropanol were added to the C-Fe₂O₃ solution and the mixed solution was stirred for 5 min. Lastly, Ag-deposited Fe₂O₃ (C-Fe₂O₃@Ag) was prepared using ultrasound irradiation (20 kHz, 300 W) for 0.5 h. The final product was also separated by the same purification procedures [35, 38].

2.4. Au-plated C-Fe₂O₃@Ag (C-Fe₂O₃@Ag-Au)
Ag-deposited C-Fe₂O₃ (C-Fe₂O₃@Ag) was dispersed in aqueous solution containing 66 mg of PVP and 100 mg of ascorbic acid (AA). After that, 1.8 ml of 0.1 M HCl was added to make acidic solution of pH 2–3. An aliquot (0.04 ml, 0.09 ml, 0.14 ml) of 1.0 wt% HAuCl₄ was slowly injected into the acidic solution for 1 h under vigorously stirring at room temperature (RT) [39, 40]. The final product, C-Fe₂O₃@Ag-Au, was purified by centrifuging at 7500 rpm for 20 min, followed by washing with DI water.

2.5. Photocatalytic tests
The photocatalytic activities of the samples (C-Fe₂O₃, C-Fe₂O₃@Ag and C-Fe₂O₃@Ag-Au) were estimated towards the degradation of methylene blue (MB) under visible light. The photocatalyst was dispersed in 30 ml of DI water containing 10 ppm MB. During photocatalytic reaction under visible light, 1.2 ml of solution was sampled at predetermined time and centrifuged at 10 000 rpm to remove the photocatalyst. Then, 0.5 ml of the supernatant was diluted with 3 ml of DI water to measure the absorbance at 664 nm using a UV–vis spectrophotometer.
3. Results and discussion

3.1. Synthesis and characterization of C-Fe₂O₃ samples

Scheme 1 shows the stepwise procedures for fabricating the final product. First, C-Fe₂O₃ was synthesized by the hydrothermal autoclave reaction of Fe³⁺ in aqueous solution (containing 50 vol.% of ethanol). The sonochemical reduction of Ag⁺ led to the deposition of nanosilvers on the C-Fe₂O₃. Then, the surface coverage of nanosilver was controlled by changing the loading volume of Ag precursor (1.0 wt.% AgNO₃). The Ag-deposited C-Fe₂O₃ was added to the aqueous solution containing PVP (capping agent) and L-Ascorbic acid. After the addition of Au precursor (1.0 wt.% of HAuCl₄), Au-Ag bimetals were finally formed on the C-Fe₂O₃ via a galvanic-assisted plating of Au layer, referred to as C-Fe₂O₃@Ag-Au.

3.2. Ag-deposited C-Fe₂O₃ (C-Fe₂O₃@Ag)

Figures 1(a)–(d) shows the scanning electron microscopy (SEM) image of Ag-deposited C-Fe₂O₃ samples prepared by the consecutive hydrothermal reaction and ultrasonic-assisted deposition method. Using the dynamic light scattering (DLS) instrument at the Smart Materials Research Center for IoT at Gachon University, the particle size of cubic-shape hematite was measured as ± 83.9 nm, which was well matched with the SEM images of C-Fe₂O₃ (figure S1 is available online at stacks.iop.org/MRX/7/095014/mmedia). The surface morphology of C-Fe₂O₃ was retained after nanosilver deposition, and the size of Ag NPs was estimated as ~30–40 nm. The surface coverage of nanosilver was increased with loading volumes of Ag precursor, and the size of Ag NPs was increased probably due to their aggregation at a high loading volume (0.4 ml of 1.0 wt.% AgNO₃). Figure 1(e) is the energy-dispersive x-ray spectroscopy (EDX) data showing the presence of Ag element on the C-Fe₂O₃.

Figure 2 shows the x-ray diffraction (XRD) patterns of C-Fe₂O₃ and C-Fe₂O₃@Ag in the 2θ range of 10–80°, respectively. The C-Fe₂O₃@Ag exhibited the pronounced XRD peaks at 2θ = 24.1° (012), 33.1° (104), 35.6° (110), 41.0° (113), 49.5° (024), 54.2° (116), and 62.5° (214), all of which were corresponding to the hexagonal phase of hematite (JCPDS card No. 33-0664). In the XRD pattern of C-Fe₂O₃@Ag, two additional peaks were observed at 38.1° (111) and 44.3° (200) that were assigned as the crystalline phase of cubic Ag NPs (JCPDS card No. 04-0783).

Scheme 1. Overall synthetic procedures for fabricating cubic-shape hematite (C-Fe₂O₃) decorated with Ag and Ag-Au bimetals.

Figure 1. SEM images of (a) pristine C-Fe₂O₃, (b) C-Fe₂O₃@Ag (0.1 ml of 1.0 wt.% AgNO₃), (c) C-Fe₂O₃@Ag (0.2 ml of 1.0 wt.% AgNO₃), and (d) C-Fe₂O₃@Ag (0.4 ml of 1.0 wt.% AgNO₃), (e) EDX analysis of C-Fe₂O₃@Ag (0.4 ml of 1.0 wt.% AgNO₃).
Figure 3 compares the UV-vis absorbance of C-Fe₂O₃@Ag (0.1–0.4 ml) samples. The absorbance of C-Fe₂O₃@Ag was not significantly different from that of C-Fe₂O₃ when the loading volume of Ag precursor was less than 0.2 ml. When the loading volume of Ag precursor was 0.4 ml, a new peak appeared at ∼480 nm more distinctly due to the plasmon resonance of nanosilvers deposited on the C-Fe₂O₃. In addition, the absorbance of C-Fe₂O₃@Ag (0.4 ml) showed the distinct hypochromic shift (i.e., blue-shift), owing to the high Ag coverage on the hematite surface.

Photocatalytic activity of C-Fe₂O₃@Ag was estimated towards the degradation of MB under visible light. The photocatalytic activities of C-Fe₂O₃@Ag samples were compared at different loading volumes of AgNO₃ (0.1–0.4 ml). Figures 4(a)–(d) shows the time evolution profiles of UV–vis absorbance during the photocatalytic reaction. Among as-prepared samples, the Fe₂O₃@Ag (0.2 ml) exhibited the highest photocatalytic activity, indicative of optimal deposition of Ag on the hematite. However, figure 4(e) shows higher loading volume (0.3 ml and 0.4 ml of Ag precursor) decreased their photodegradation efficiencies, probably due to the excessive nanosilvers that played as recombination centers and reduced the active sites for MB adsorption [37, 41, 42].

3.3. Au-plated C-Fe₂O₃@Ag (C-Fe₂O₃@Ag-Au)

Figure 5(a) shows the SEM image of Ag-deposited C-Fe₂O₃ (0.2 ml) prepared by sonochemical deposition of Ag NPs. The Fe₂O₃@Ag (0.2 ml) exhibited the suitable size of 35 nm for galvanic-assisted Au plating process. Figures 5(b)–(d) shows the SEM images of C-Fe₂O₃@Ag-Au prepared with different loading volumes of Au.
precursor (0.04–0.14 ml of 1.0 wt.% HAuCl4). Au precursor (Au3+) was directly plated on the surface of nanosilvers deposited on the C-Fe2O3, and the size of Ag–Au bimetal was increased with loading volume of Au precursor. The size of bimetallic Ag–Au was estimated as ∼50–70 nm. In addition, the surface morphology of Ag–Au bimetals became more roughened without significantly reducing the exposed surface area of C-Fe2O3.

Figure 4. Time-evolution of absorbance change of methylene blue (MB) under visible light irradiation over a) C-Fe2O3@Ag (0.1 ml of 1.0 wt.% AgNO3), (b) C-Fe2O3@Ag (0.2 ml of 1.0 wt.% AgNO3), (c) C-Fe2O3@Ag (0.3 ml of 1.0 wt.% AgNO3), (d) C-Fe2O3@Ag (0.4 ml of 1.0 wt.% AgNO3), (e) comparative photodegradation efficiencies of MB dye over C-Fe2O3@Ag samples.

Figure 5. SEM images of (a) C-Fe2O3@Ag, (b) C-Fe2O3@Ag-Au (0.04 ml of 1.0 wt.% HAuCl4), (c) C-Fe2O3@Ag-Au (0.09 ml of 1.0 wt.% HAuCl4), and (d) C-Fe2O3@Ag-Au (0.14 ml of 1.0 wt.% HAuCl4), (e) UV-vis absorption spectra of C-Fe2O3, C-Fe2O3@Ag (0.2 ml of 1.0 wt.% AgNO3) and C-Fe2O3@Ag-Au (0.04 ml of 1.0 wt.% HAuCl4) samples.

X-ray photoelectron spectroscopy (XPS) was performed to investigate the chemical state and elemental composition of Fe2O3@Ag–Au. According to the survey scan of XPS spectrum of figure 6(a), typical peaks of Fe 2p, O 1s, N 1s, C 1s and Ag 3d, Au 4f are clearly observed. The peaks of C1s and N 1s are attributed to diamine linker (1, 12-diaminododecane) incorporated into the hematite structure during the hydrothermal synthesis. Figure 6(b) shows two distinct peaks of Fe2p3/2 at 709.58 eV and Fe2p1/2 at 723.08 eV, and the separation of the 2p doublet is ∼13.5 eV. In addition, two satellites with binding energies of 718.08 and 732.78 eV are clearly
observed [41]. Figure 6(c) shows the O1s spectrum that is deconvoluted into three peaks. The peaks at 528.68 eV and 530.48 eV are attributed to lattice oxygen species of FeO and FeOH, respectively. The peak at 533.1 eV represents adsorbed water molecules [42–44]. Figure 6(d) shows the spectrum of Ag 3d, in which the peaks at 366.88 eV and 372.88 eV are assigned to Ag 3d3/2 and Ag 3d7/2 components, respectively [45]. Figure 6(e) shows the spectrum of Au 4f, in which the peaks at 82.88 eV and 86.58 eV are assigned to Au 4f7/2 and Au 4f5/2 components, respectively. When compared with the pure metals (368 eV for Ag 3d3/2 and 84 eV for Au 4f7/2), Ag-Au bimetals exhibited the negative shift of binding energies by 1.1 eV (366.88 eV for Ag 3d3/2 and 82.88 eV for Au 4f7/2), suggesting the plasmonic coupling effect by Ag-Au bimetals [45, 46].

The photocatalytic activities of as-prepared samples were tested towards the degradation of MB dye under visible light irradiation. The C-Fe2O3@Ag-Au sample was prepared by plating the C-Fe2O3@Ag (0.2 ml of 1 wt% AgNO3) with different loading of Au precursor (0.04 and 0.14 ml of 1 wt% HAuCl4). Figure 7 compares the degradation efficiency of MB dye depending on the deposition of nanometals on the hematite. The C-Fe2O3@Ag-Au showed the higher photocatalytic activity than any other samples (C-Fe2O3 and C-Fe2O3@Ag). The reason may be that Ag-Au bimetals induce the plasmonic coupling effect, consequently leading to the enhanced photocatalytic activity. In the meantime, the C-Fe2O3@Ag-Au showed the similar degradation efficiency irrespective of loading amounts of Au (0.04 ml and 0.14 ml), indicating the direct deposition of Au layer on Ag NPs. The EDX analysis

Figure 6. Survey and core-level spectra of Fe2O3@Ag-Au by XPS: (a) Survey, (b) Fe 2p, (c) O 1s, (d) Ag 3d, (e) Au 4f.

Figure 7. Comparative photodegradation of Methylene blue (MB) over as-prepared samples: pristine C-Fe2O3, C-Fe2O3@Ag (0.2 ml of 1 wt% AgNO3), C-Fe2O3@Ag-Au (0.04 ml and 0.14 ml of 1 wt% HAuCl4) under visible light for 4 h.
did not show the significant difference of Au elements among the samples, which was ranged in 0.43–0.59% of atomic composition.

Prior to the photodegradation reaction of MB dye (10 ppm), the photocatalyst sample was first dispersed in the aqueous solution for 5 min in the dark. Figure 8(a) shows the temporal evolution photodegradation of MB dye over the hematite samples (C-Fe₂O₃, C-Fe₂O₃@Ag, C-Fe₂O₃@Ag-Au) under visible light. The C-Fe₂O₃ exhibited 17% degradation of MB dye under visible light after 4 h, and the C-Fe₂O₃@Ag exhibited the much higher degradation efficiency of ~51% at the same condition. The C-Fe₂O₃@Ag-Au exhibited the maximal degradation efficiency of ~70%. The hematite samples showed the following increasing order of photocatalytic activity: C-Fe₂O₃ < C-Fe₂O₃@Ag < C-Fe₂O₃@Ag-Au. These experimental results clearly indicated that the deposition of plasmonic nanometals improved the photocatalytic activity of C-Fe₂O₃.

Figure 8(b) shows the Langmuir–Hinshelwood (L-H) kinetics for the degradation of MB dye under visible light. The experimental data were fitted by $\ln(C_0/C) = kt$, where k is the rate constant, and $C_0$ and C are the concentrations at time zero and t, respectively. The linear plot of $\ln(C_0/C)$ versus time indicated that the photodegradation rate followed the pseudo-first-order kinetics. The rate constant of C-Fe₂O₃, C-Fe₂O₃@Ag, C-Fe₂O₃@Ag-Au were calculated as $k = 6.59 \times 10^{-3}$, $3.04 \times 10^{-3}$, $6.05 \times 10^{-3}$, respectively. The C-Fe₂O₃@Ag exhibited five-fold increase of photocatalytic activity to that of the pristine C-Fe₂O₃, and the C-Fe₂O₃@Ag-Au exhibited 200% increase of photocatalytic activity to that of C-Fe₂O₃@Ag. The significantly enhanced photocatalytic activity was mainly attributed to the plasmonic coupling effect of Ag-Au bimetals, which could harvest wider range of visible-light and enhance the separation efficiency of photo-generated charge carriers.

PL emission spectra represent the excited state of the photocatalyst through the recombination process of photo-excited electrons and remained holes in the valence band. Thus, the intensity of PL emission indicates the degree of recombination rates of $e^-\cdot h^+$ pairs. Figure 8(c) showed the increasing order of PL emission intensity under an excitation wavelength of 340 nm as follows: C-Fe₂O₃@Ag-Au < C-Fe₂O₃@Ag < C-Fe₂O₃. The C-Fe₂O₃@Ag-Au exhibited the lowest PL intensity (i.e., the lowest recombination rate), resulting in the highest photocatalytic activity among the samples. Figure 8(d) shows the time-evolution of change in absorbance at 360 nm during the photocatalytic degradation of colorless tetracycline hydrochloride (5 ppm) over Fe₂O₃@Ag-Au. The degradation efficiency of tetracycline hydrochloride under visible light was found to be 64.3%, which was lower than that of the MB dye (75.6%). Figure 8(e) shows that the photocatalytic efficiency was gradually decreased with cycling numbers, probably due to the slight loss of photocatalyst during a recovery process. However, the photocatalytic efficiency after 5 cycles was slightly decreased by 9.5%, indicating the sustainability of C-Fe₂O₃@Ag-Au as a visible-light photocatalyst.

The photocatalytic degradation of organic pollutants usually involves active species such as hydroxyl radical (·OH), hole (h$^+$), and superoxide radical anions (·O$_2^-$). Typically, disodium ethylenediaminetetraacetate

![Figure 8](image-url)
(Na$_2$–EDTA) (1 mmol l$^{-1}$), isopropyl alcohol (IPA) (1 mmol l$^{-1}$), and benzoquinone (BQ) (1 mmol l$^{-1}$) are used as a scavenger agent for hole (h$^+$), hydroxyl radicals (·OH), and superoxide radical anion (·O$_2^-$), respectively [47, 48]. Therefore, active species trapping experiments were carried out to unfold the main species in the photodegradation of MB dye under visible light. As shown in figure S2, the photodegradation efficiency of C-Fe$_2$O$_3$@Ag-Au was distinctly diminished to 15.40% and 30.25% by adding IPA and BQ scavengers, suggesting that ·OH and ·O$_2^-$ are the main active species for the photodegradation of MB dye. On the other hand, the Na$_2$–EDTA had a very little effect on the photodegradation efficiency of MB dye (i.e., 7.2% decrease), signifying that h$^+$ played a minor role in the photodegradation of MB dye. Furthermore, optical band gap of C-Fe$_2$O$_3$@Ag-Au was calculated as ~1.93 eV (versus 2.0 eV of pristine C-Fe$_2$O$_3$) (figure S3), suggesting that band gap was decreased due to the surface plasmon resonance (SPR) effect of noble metals. Using the Mulliken electronegativity theory, conduction band (E CB) and valence band (E VB) potentials of C-Fe$_2$O$_3$@Ag-Au were calculated as 0.42 eV and 2.35 eV, respectively [49].

The schematic diagram of photocatalytic mechanism of C-Fe$_2$O$_3$@Ag-Au was briefly described in figure 8(f). The hematite with low bandgap receives wide range of visible-light, and the activated photoelectrons are easily separated from e$^-$–h$^+$ pairs. Nonetheless, the hematite has poor electrical conductivity and very short length of hole diffusion, and the separated electrons are quickly recombining with the remained holes, leading to the decreased photocatalytic activity. On the other hand, plasmonic nanometals deposited on the hematite can play as a temporary reservoir of photo-generated electrons and reduce the recombination rates of e$^-$–h$^+$ pairs. In particular, Ag–Au bimetal shows the better photocatalytic performance than monometallic Ag, because the work function of Ag is higher than that of Au, thereby transferring more electrons from Fe$_2$O$_3$ to Ag–Au bimetal. When compared with nanometal-free analogue, the C-Fe$_2$O$_3$@Ag–Au exhibited the more enhanced absorbance of visible light and electron trapping effects owing to the plasmonic coupling effect of Ag–Au bimetal [50–52]. The photo-generated charge carriers produced superoxide (·O$_2^-$) and hydroxyl radicals (·OH) that mainly participated in the photodegradation of MB dye under visible light.

4. Conclusions

In this work, cubic hematite particles (C-Fe$_2$O$_3$) were facilely prepared by hydrothermal autoclave reaction of Fe$^{3+}$ in the presence of DA-12 at 130 °C for 10 h. After then, nanosilvers were directly deposited on the hematite surface via sonochemical reduction of Ag precursor. The C-Fe$_2$O$_3$@Ag was further plated with Au layer via galvanic-assisted reduction method, forming so-called C-Fe$_2$O$_3$@Ag–Au. SEM and UV–vis spectroscopy analysis clearly demonstrated the formation of cubic-shape hematite deposited with plasmonic nanometals. XRD patterns of the C-Fe$_2$O$_3$@Ag clearly exhibited the pronounced XRD peaks corresponding to hematite and deposited Ag. XPS analysis of C-Fe$_2$O$_3$@Ag–Au confirmed the co-existence of Ag and Au crystals on the hematite. As-prepared samples were subjected to the photocatalytic degradation of MB dye under visible light. The Fe$_2$O$_3$@Ag (0.2 ml) showed the higher photocatalytic activity than those of C-Fe$_2$O$_3$@Ag (0.1 ml, 0.3 ml, and 0.4 ml), due to the optimal deposition of nanosilvers on the hematite surface. Furthermore, the C-Fe$_2$O$_3$@Ag–Au exhibited the 200% increase of photocatalytic activity to that of C-Fe$_2$O$_3$@Ag, probably because of plasmonic coupling effect of Ag–Au bimetal on the extended absorption of visible light and increased separation efficiency of photo-generated electrons. Optical band gap of C-Fe$_2$O$_3$@Ag–Au was calculated as ~1.93 eV (versus 2.0 eV of pristine C-Fe$_2$O$_3$) from the diffuse reflectance spectrum, suggesting that the bandgap was decreased due to the SPR effect of noble metals. In addition, the reusability test confirmed the sustainability of C-Fe$_2$O$_3$@Ag–Au as a visible-light photocatalyst. This work provides the facile synthetic route for plasmonic cubic hematite with enhanced photocatalysis under visible light.

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