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Enhanced photocatalytic activity of Bi₄Ti₃O₁₂ nanosheets by Fe³⁺-doping and the addition of Au nanoparticles: Photodegradation of Phenol and bisphenol A

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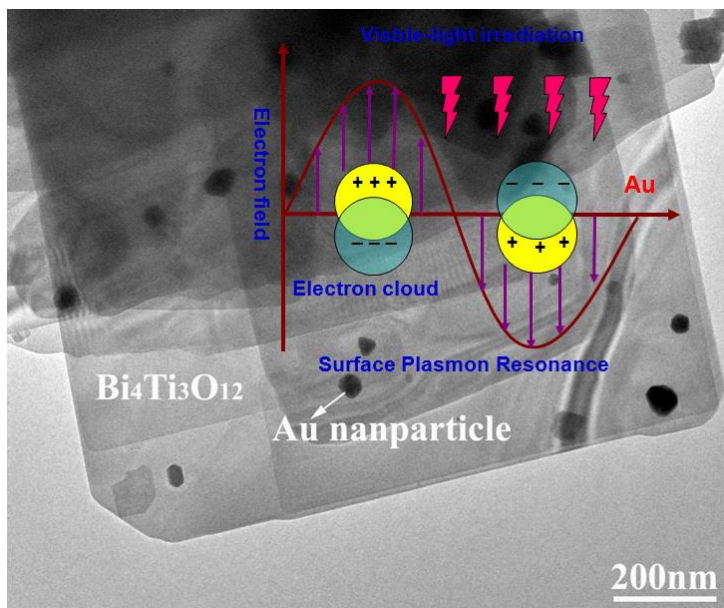
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Graphical abstract



Highlights

- A novel photocatalyst consisting of Fe-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets with added Au nanoparticles is synthesized.
- Enhanced photodegradation of phenol and bisphenol A has been observed.
- The improved photocatalytic property can be attributed to the combined effect of electron-hole pair separation by Fe^{3+} and SPR of Au nanoparticles.

Abstract

Pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BTO) and Fe-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (Fe/BTO) nanosheets with exposed {001} facets were synthesized by a one-step molten salt method. Au nanoparticles with a diameter range of 20-50 nm were loaded on 2%Fe-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (Au-2%Fe/BTO) nanosheets via a room-temperature hydrogen peroxide reduction method. The UV-vis diffuse reflectance spectra showed that the Fe/BTO and Au-2%Fe/BTO samples exhibit an obvious red shift in visible light absorption band in comparison with the pure BTO. Phenol and bisphenol A solutions were chosen

as model organic pollutants to verify the influence of Fe³⁺-doping and plasmonic effect of Au nanoparticles on the photocatalytic activity of the catalyst. The Au-2%Fe/BTO sample exhibited the highest photocatalytic activity compared with other samples. The high photocatalytic activity of Au-2%Fe/BTO rises from two contributions: i) the Fe³⁺ ion acts as an efficient scavenger to trap electrons, and hence promotes the separation of photo-induced electron-hole pairs; ii) the visible light response of the catalyst is enhanced by the surface plasmon resonance effect from the Au nanoparticles.

Keywords: Molten-salt method; nanosheet; facet; plasmonic; photocatalytic activity

1. Introduction

The rapid expansion of global industry has led to serious environmental problems such as water and air pollution, which present health problems to mankind [1]. In recent years, a number of technologies (such as biological, thermal, chemical, etc) have been developed for the removal of toxic organic compounds from industrial wastewater [2-4]. Among them, photocatalysis is one of green technologies that allows the utilization of solar light for organic pollutants degradation, hence providing a potential route for cleaning up the environment [5,6]. Phenol and bisphenol A (BPA) are the most abundant organic contaminants in industrial wastewater [7,8]. They are toxic at rather low concentrations and relatively stable against biodegradation. Therefore, finding effective methods to remove phenol and BPA from wastewater has become an important issue for environmental scientists.

The Aurivillius phase of Bi₄Ti₃O₁₂ (BTO) has received much attention for its photocatalytic activity in degrading organic pollutants and water splitting [9-12]. The structure of Bi₄Ti₃O₁₂, i.e., (Bi₂O₂)²⁺(Bi₂Ti₃O₁₀)²⁻, is achieved by alternative stacking of a triple layer of TiO₆ octahedral and a monolayer of (Bi₂O₂)²⁺ along the *c* axis. (Bi₂O₂)²⁺ and (Bi₂Ti₃O₁₀)²⁻ layers form an inner electric field, which promotes the separation of photo-generated electrons and holes giving rise to an enhanced photocatalytic activity [10,13]. However, pure Bi₄Ti₃O₁₂ is not very efficient for photocatalysts due to its large band gap ($E_g=2.95$ eV) and high recombination rate of photo-generated electron-hole pairs [14]. Much effort has been devoted to the modification of

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with a view to increasing its photocatalytic activity during recent years [15,16]. There is evidence that metal-doping is an effective method for enhancing visible light response and reducing the recombination rate of photo-induced electron-hole pairs [17-20]. Many experimental results show that metal-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has higher photocatalytic activity than pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, for instance, La-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [21], Cr-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [22], Zn-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [23], and Nd-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [24].

Among the transition metal ions, Fe^{3+} ions can form a dopant energy-band and reduce the band gap of the photocatalysts, hence electrons can be excited by photons of lower energy. More importantly, Fe^{3+} can turn into Fe^{2+} or Fe^{4+} ions by trapping photo-generated electrons or holes, respectively, which can hinder the recombination process and enhance the photocatalytic activity [25]. In addition, the radius of Fe^{3+} (0.79Å) is similar than that of Ti^{4+} (0.75Å) [25], so Fe^{3+} ions can be easily accommodated into the crystal lattice of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Therefore, it is expected that the photocatalytic activity of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ for removing organic pollutants can be improved by Fe^{3+} -doping. The effect of Fe^{3+} -doping on photocatalytic reactivity has been studied and reported in a number of previous publications, for instance, Fe^{3+} -doped BiOCl [26], Fe^{3+} -doped Bi_2O_3 [27], Fe^{3+} -doped Bi_2WO_6 [28], and Fe^{3+} -doped BiVO_4 [29].

By considering a much related topic, highly dispersed noble metal nanoparticles (Au, Ag, Cu, etc) loaded on the surface of semiconductor materials exhibit extraordinary high activity for photocatalytic degradation of organic contaminants [30-33]. There are plenty of experimental results reporting the effectiveness of this method involving model catalysts such as Au/ TiO_2 [34], Ag/ Bi_2O_3 [35], Ag/ C_3N_4 [36], Ag/ BiVO_4 [37], Ag/ Bi_2WO_6 [38], and Ag/ BiPO_4 [39]. The high activity is related to the retardation of electron-hole recombination due to the trapping of electrons. Moreover, noble metal nanoparticles has a wide range of absorption spectrum in the visible light region because of the surface plasmon resonance (SPR), which is defined as the collective oscillation of the conduction electrons [40-44]. As a result, photocatalytic activity is improved by the SPR effect of noble metal nanoparticles on the semiconductor surface.

In this work, Au nanoparticles loaded on the Fe/BTO photocatalysts with exposed {001} facets were synthesized by molten salt method and low-temperature hydrogen peroxide reduction method. Phenol and bisphenol A were chosen as model organic pollutants to evaluate the photocatalytic activity of Fe/BTO and Au-2%Fe/BTO photocatalysts. Compared with pure BTO, the as-prepared

Au-2%Fe/BTO composites photocatalysts displayed a much higher photocatalytic activity for photo-degradation of phenol and bisphenol A under light irradiation. Furthermore, a comprehensive photocatalytic mechanism of Au-Fe/BTO composites was also proposed and discussed in detail.

2. Experimental

2.1. Sample preparation

All the chemical reagents were analytical grade and used without further purification. All the Fe^{3+} -doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ samples were prepared by a one-step molten salt synthesis method. A typical procedure for preparing Fe^{3+} -doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ sample is described in the following: First, the powders of α - Bi_2O_3 , P25, and Fe_2O_3 were mixed according to the composition of $\text{Bi}_4\text{Fe}_x\text{Ti}_{3-x}\text{O}_{12}$, with NaCl and KCl the co-solvents at a molar ratio of NaCl: KCl: $\text{Bi}_4\text{Fe}_x\text{Ti}_{3-x}\text{O}_{12}$ = 60: 60: 1. Secondly, the above mixture was ground thoroughly for over 15 minutes with an agate mortar and pestle. The resulting mixture was then heated at 750°C for 2 hours in air. The obtained product was washed in an ultrasonic bath with deionized water for 6 times, before washing twice with ethanol. Finally, the as-prepared powders were dried at 80°C . The $\text{Bi}_4\text{Fe}_x\text{Ti}_{3-x}\text{O}_{12}$ samples were achieved by adjusting the "x" to 0, 0.02, 0.04, and 0.06. After that, the as-prepared samples were denoted as BTO, 2%Fe/BTO, 4%Fe/BTO, and 6%Fe/BTO, respectively. For the preparation of Au-2%Fe/BTO sample, 0.5 g of 2%Fe/BTO sample was dispersed in 100 mL glass beaker with 20 mL deionized water, then 2 mL HAuCl_4 (0.01 mol/L) and 20 mL H_2O_2 (0.1 mol/L) were added into the 2%Fe/BTO dispersion under continuously stirring. After stirring for 2 hours, the obtained precipitates were washed with deionized water and ethanol for several times, and then dried at 80°C .

2.2. Characterization

The crystalline phases were determined using X-ray powder diffraction (XRD) at room temperature with Cu $K\alpha$ radiation on a Bruker D8 Advance instrument in 2θ range of 10 - 80° . The scanning electron microscopy (SEM) images were recorded by a field emission scanning electron microscopy (Nova NanoSEM 450, FEI). The transmission electron microscopic (TEM) images of the samples were acquired using a JEM-2100 electron microscope (JEOL, Japan). The chemical states of elements in the samples were determined by X-ray photoelectron spectroscopy (XPS) using a VG ESCALAB MKII X-ray photoelectron spectrometer (VG Scienta, USA) with Mg $K\alpha$ radiation. Photoluminescence (PL) spectra of the as-prepared samples were observed with a He-Cd

laser (325 nm) as the excitation source at room temperature. The UV-vis adsorption spectra of the samples were measured on a Perkin-Elmer Lambda 950 UV-VIS-NIR spectrophotometer.

2.3. Photocatalytic test

Phenol and bisphenol A (BPA) were used as probe organic pollutants, and a 400W halogen lamp was employed as a visible light source. The photo-degradation reaction temperature was maintained at 25°C by the circulation of water. Prior to irradiation, the as-prepared samples as photocatalyst for phenol and BPA were continuously stirred in the dark for 30 min to ensure an adsorption-desorption equilibrium. During the irradiation, 2 mL of suspension was taken out at a given interval for subsequent pollutant concentration analysis by using a U-3010 UV-vis spectrophotometer. The wavelength of phenol and BPA was detection at 270 nm and 277 nm, respectively. Total organic carbon (TOC) concentration was measured by automatic total organic carbon analyzer (VARIO, Elementar, Germany).

3. Results and discussion

3.1 XRD analysis

Figure 1a shows the XRD patterns of all the as-synthesized samples. All the diffraction peaks in Figure 1a can be indexed according to the standard data of orthorhombic BTO with the space group $Aba2$ (JCPDS 72-1019). The Orthorhombic BTO is described with a general formula of $(Bi_2O_2)^{2+}(Bi_2Ti_3O_{10})^{2-}$, which is constructed by alternative stacking with a triple layer TiO_6 octahedral and a monolayer of $(Bi_2O_2)^{2+}$, as shown in Figure 1b. The $BiOCl$, Fe_2O_3 or $FeTiO_3$ phase were not detected in the XRD patterns of all the Fe/BTO samples (Figure 1a). In addition, the diffraction peaks of the cubic Au phase are also absent in the XRD patterns of Au-2%Fe/BTO. This may attribute to the low concentration of gold in the composite sample. Although, the XRD patterns did not provide evidence for the presence of Au in the Au-2%Fe/BTO composite powders. However, the color of Au-2%Fe/BTO composite photocatalysts became gray (inset in Figure 1a) after modified with Au particles. Apparently, it can be deduced that Au has been incorporated into the samples.

3.2 XPS analysis

To investigate the chemical state of elements and the surface defects, X-ray photoelectron spectroscopy (XPS) analysis was carried out on the 2%Fe/BTO and Au-2%Fe/BTO samples and the

results are shown in Figure 2. The obtained binding energies in XPS analysis were corrected by specimen charging which was executed by referencing the C1s line to 284.6 eV. The survey XPS spectrum in Figure 2a clearly reveals that the Au-2%Fe/BTO sample mainly consists of Bi, Ti, O, Fe and Au. XPS signals of Bi 4f (Figure 2b) were observed at binding energies around 164.3 eV (Bi 4f_{5/2}) and 158.8 eV (Bi 4f_{7/2}), which are perfectly consistent with the data of Bi₂O₃ powders [45]. The XPS signals in Figure 2c are related to Ti 2p, which were observed at binding energies at around 465.1 eV (Ti 2p_{1/2}) and 457.8 eV (Ti 2p_{3/2}). This is in agreement with that of pure TiO₂ [46]. In Figure 2d, it can be seen that the O 1s peak is deconvoluted into two symmetric Gaussian curves at peak positions around 529.6 and 531.2 eV. These two peaks are assigned to oxygen in the prepared sample lattice [47] and surface-adsorbed oxygen, respectively. Consequently, the peaks around 710 and 724 eV (Figure 2e) are related to the binding energies of Fe 2p_{3/2} and Fe 2p_{1/2} for the ferric (III) ion [48]. In Figure 2f, doublet peaks are observed at 82.8 and 86.6 eV, which are from the Au 4f_{7/2} and Au 4f_{5/2} levels. The observation of the Au 4f peaks prove that Au exists as Au⁰ in Au-2%Fe/BTO sample [49]. From the above results, it is concluded that the Fe³⁺ ions and Au nanoparticles were successfully incorporated into the BTO sample.

3.3 SEM analysis

The morphologies of the as-prepared pure BTO, Fe/BTO, and Au-2%Fe/BTO are shown in Figure 3. As shown in Figure 3a, the as-prepared BTO sample consists of uniform sheet-like sub-microstructures, with a thickness of ~45 nm and the average side length of the sheets is ~500-1000 nm. The inset spectrum in Figure 3a is the EDS spectrum of the sheet-like sub-microstructure, which shows the Bi/Ti ratios is 1.33:1. This is close to ratio from the stoichiometric BTO. The signal of aluminum is detected due to the aluminum sample stage. The detection of Cl is due to residuals in the synthesized samples. It can be seen from the SEM images in Figures 3b-d that there is no significant changes on morphology after Fe³⁺-doping. Figure 3e shows the SEM image of Au-2%Fe/BTO sample. The nanoparticles with diameter around 20-50 nm could be attributed to the dispersed Au nanoparticles on the surface of the nanosheets. It can see clearly that most of these Au nanoparticles are loaded on the surface of the nanosheets, but there are also some Au nanoparticles loaded on the side of the nanosheet (the circle inset in Figure 3e). The EDS pattern in Figure 3f shows that there are Bi, Ti, Fe, Au and Cl elements in the Au-2%Fe/BTO sample. The Fe/Bi ratios is 0.97:200, which is close to the theoretical value of 1/200. The EDS

Mapping was selected for further analysis of elemental distribution on the Au-2%Fe/BTO sample. As shown in Figures 4b-e, the Bi, Fe, Ti, O elements were well distributed in the region. Figure 4f shows the elemental distribution of Au in the square area in Figure 4a, which gives a very clear signal of the presence of Au nanoparticles. From the above results of XRD, XPS, SEM, EDS and EDS mapping, it can be concluded that the Fe³⁺ ions are well doped into the BTO lattice and Au nanoparticles are located on the surface of the BTO nanosheets.

3.4 TEM and HRTEM analysis

The microstructures and morphological details of the 2%Fe/BTO and Au-2%Fe/BTO samples were further observed by TEM and HRTEM. According to Figure 5a, the 2%Fe/BTO sample has a sheet structure, which is consistent with the SEM results shown in Figure 3b. Figure 5b shows the HRTEM image of a single 2%Fe/BTO sheet that the lattice fringes is spacing with: $d = 0.270$ nm and $d = 0.272$ nm. This is ascribed to the (020) and (200) crystallographic planes of BTO respectively, and implies the exposed facets of sheet-like 2%Fe/BTO nanostructures as {001} facets [12]. The inset image in Figure 5b is SAED, which indicates that the as-prepared sheet-like 2%Fe/BTO nanostructures has a single crystal characteristic. Figure 5c shows the TEM image of the Au-2%Fe/BTO sample, it can see clearly that some of the nanoparticles are present with an average diameter around 20-50 nm and located on the sheets surface. From the HRTEM image in Figure 5d, the nanoparticles can be seen to sit on the surface of the sheet. The spacing of the lattice is $d = 0.272$ nm, which is ascribed to the (200) crystallographic plane of BTO, whereas the lattice fringes with the spacing of $d = 0.240$ nm match the (111) crystallographic planes of Au nanoparticles. **Error! Reference source not found. Error! Reference source not found.** From the TEM and HRTEM results in Figure 5, we confirm that most of the Au nanoparticles were deposited on the flat surfaces of the 2%Fe/BTO nanosheets with exposed {001} facets. However, there is also some possibility that some Au nanoparticles are attached to the sides of the Fe/BTO nanosheet with exposed {001} facets, as evidenced from TEM and HRTEM images in Figures 5e-h. From the above results, it is concluded that the Fe³⁺ ions were successfully incorporated into the BTO lattice and Au nanoparticles are mostly located on the surface of the BTO sheets, consistent with the XRD, XPS, SEM, and EDS mapping results.

3.5 UV-vis DRS analysis

Figure 6 shows the UV-vis diffuse reflectance spectra of BTO, Fe/BTO and Au-2%Fe/BTO

samples. It can see clearly that the BTO exhibits an optical response at wavelengths shorter than 450 nm. This indicates that the BTO sample is active under UV light and a narrow region of the visible light. The light absorption edge in the UV-vis diffuse reflectance spectrum of Fe/BTO was extended to the visible light region (450-600 nm) after Fe³⁺-doping. More importantly, the Au-2%Fe/BTO shows a slight red shift in the absorption edge, and a significant enhancement of visible light absorption can be noted at 420-800 nm. Another absorption band at about 500 nm can be seen in the UV-vis spectra of Au-2%Fe/BTO. The similar effect has been reported and the reason of this feature is attributed to the surface plasmon absorption of spatially confined electrons in Au nanoparticles [50,51], and the optical absorption near the band edge follows the Tauc equation:

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (1)$$

where A is constant, α , h , ν , and E_g , are the absorption coefficient, Planck's constant, light frequency, and band gap, respectively. The power index n depends on the type of electronic transition, n equals to 1 for a direct band-gap material and 4 for an indirect band-gap material. For semiconductors, the square of absorption coefficient is usually linearly proportional to the energy ($h\nu$) in the absorption edge region during the direct optical transition process. The plots of $(\alpha h\nu)^{1/2}$ versus energy ($h\nu$) is shown in Figure 6 (inset). The E_g values of pure BTO, 2%Fe/BTO, 4%Fe/BTO and 6%Fe/BTO samples can be calculated to be 2.92, 2.43, 2.36, and 2.28 eV, respectively.

3.6 Photo-degradation of bisphenol A and phenol

The photocatalytic activities of pure BTO and Fe/BTO samples were investigated by the degradation of BPA under visible light irradiation. Temporal changes in the concentration of BPA were monitored by examining the variation in maximal absorption in the UV-vis spectra at 277 nm. Figure 7a shows the variation of BPA concentration (C/C_0) over BTO, 2%Fe/BTO, 4%Fe/BTO, and 6%Fe/BTO photocatalysts against reaction time under light irradiation. To provide a point of reference, experiments were also performed on directly photolysis of BPA (a blank experiment) in the absence of photocatalysts. As a result, no obvious change in the BPA concentration within 60 min light irradiation was observed. Meanwhile, the photodegradation of BPA over BTO sample is around 75% after 60 min light irradiation, which indicates that the pure sheet-like BTO powders with photocatalytic is activated for the degradation of BPA under light irradiation. Moreover, under the same experimental conditions, the percentage of photodegraded BPA over 2%Fe/BTO, 4%Fe/BTO and 6%Fe/BTO photocatalysts has reached 89.6%, 84.2% and 79.8%, respectively. The above results indicate that the 2%Fe/BTO sample exhibits the highest photocatalytic activity. Furthermore, Phenol was also chosen for further examination of the photocatalytic activity with the

pure BTO and Fe/BTO photocatalysts. Temporal changing for the concentration of phenol was monitored by examining the variation in maximal absorption in the UV-vis spectra at 270 nm. Figure 7c shows the variation of phenol concentration (C/C_0) over pure BTO and Fe/BTO photocatalysts against different durations of light irradiation. Under light irradiation, 2%Fe/BTO photocatalysts (Figure 7c) also shows the best photocatalytic activity for the degradation of phenol compared to pure BTO powders and other Fe/BTO photocatalysts. The total photodegradation of phenol over BTO, 2%Fe/BTO, 4%Fe/BTO, and 6%Fe/BTO photocatalysts is 37.0%, 54.1%, 41.1%, and 28.8%, respectively.

According to the Langmuir–Hinshelwood (L–H) kinetics model [5], the photocatalytic process of BPA and phenol can be expressed as the following apparent pseudo-first-order kinetics equation:

$$\ln(C_1/C) = kt \quad (2)$$

where C_1 is the concentration of organic pollutant after the establishment of an absorption-desorption equilibrium ($t = 0$) and C is the concentration of organic pollutant at time t (inset in Figures 7b and d). According to Figures 7b and d, the k of BTO, 2%Fe/BTO, 4%Fe/BTO, and 6%Fe/BTO were calculated as: 0.0214, 0.0349, 0.0296, and 0.0260 min^{-1} for BPA in (Figure 7b), and 0.0047, 0.0081, 0.0056, and 0.004 min^{-1} for phenol in (Figure 7d), respectively. The results in Figure 7 show that the 2%Fe/BTO sample has the highest activity for breaking down BPA and phenol.

Under identical experimental conditions, the effect of adding Au nanoparticles to the Au-2%Fe/BTO composite photocatalysts was studied. Figure 8 shows the variation of BPA and phenol concentrations (C/C_0) over pure BTO, 2%Fe/BTO, and Au-2%Fe/BTO photocatalysts as a function of reaction time under light irradiation. Figure 8a shows the percentage of photodegraded BPA over pure BTO, 2%Fe/BTO, and Au-2%Fe/BTO photocatalysts reaches 72.3%, 87.6%, and 99.2%, after 50 min light irradiation. It can be seen clearly that compared with pure BTO and 2%Fe/BTO, the degradation efficiency of BPA by Au-2%Fe/BTO has been improved by 26.9% and 11.6%, respectively. After 80 min light irradiation, the percentages of photodegraded phenol (Figure 8c) over BTO, 2%Fe/BTO, and Au-2%Fe/BTO photocatalysts are 37.0%, 54.1%, and 64.3%, respectively. Figure 8 (b) and (d) give the k values of BPA and phenol over BTO, 2%Fe/BTO, and Au-2%Fe/BTO, which are 0.0214, 0.0349, and 0.0789 min^{-1} for BPA; 0.0047, 0.0081, and 0.0096 min^{-1} for phenol. From the above results in Figure 8, the Au-2%Fe/BTO sample can present a higher degradation rate for BPA and phenol in comparison with pure BTO and 2%Fe/BTO. The Au

metal nanoparticles have a great effect on the photocatalytic activity for the composite of Au-2%Fe/BTO. According to previously reported data, the photocatalytic enhancement property was described with an enhancement factor " E_f " when the metal particle was loaded on the semiconductor [52]. Therefore, the enhancement factor E_f was also evaluated in our analysis and the values of 2.0 for phenol and 3.7 for BPA. The kinetics study of the phenol and BPA degradation over BTO, 2%Fe/BTO, and Au-2%Fe/BTO under visible light irradiation are generally evidence the synergism of Fe³⁺-doping and Au nanoparticles loading in the Au-2%Fe/BTO, especially the photocatalytic degradation for BPA. From the above results, it can also be seen that photodegradation of BPA occurs at a faster rate than that for phenol. This behavior is similar to that reported in previous works that some semiconducting photocatalysts have different selective photocatalytic properties for different types pollutants [53,54].

The removal of total organic carbon (TOC) was chosen as a mineralization index to characterize the phenol and BPA degradation. Under light irradiation, the time independence TOC data of phenol and BPA solution is measured with Au-2%Fe/BTO catalyst in Figure 9. It is observed that 95.7% of the TOC was eliminated for BPA after 50 min of light irradiation and 59.2% of the TOC was eliminated for phenol after 80 min of light irradiation, These results indicate that most of the phenol and BPA were mineralized in the photocatalytic process, which is important for practical applications of Au-2%Fe/BTO photocatalysts to avoid secondary pollution.

3.7 Trapping experiment

It is well known, in the photocatalytic oxidation process of organic pollutants, there are series of photoinduced reactive species, including $\bullet\text{OH}$, $\bullet\text{O}_2^-$, and h^+ , which will be directly involved in the process after the electron-hole pairs are generated under light irradiation [55]. In order to evaluate the kind of reactive species, the quenchers of ammonium oxalate (AO), isopropyl alcohol (IPA) and benzoquinone (BQ) were used to scavenge the relevant reactive species during the photodegradation of BPA and phenol over Au-2%Fe/BTO photocatalysts under light irradiation. According to this work, the AO (1.0 mmol/L), IPA (1.0 mmol/L), and BQ (1.0 mmol/L) were adopted as hole (h^+) and hydroxyl radicals ($\bullet\text{OH}$) superoxide anions ($\bullet\text{O}_2^-$) scavengers, respectively, and the corresponding results were shown in Figure 10. Under the addition of AO and BQ, there is only about 15% and 35.3% of BPA in the solution that was degraded under light irradiation, and 19% and 31.2% of phenol was degraded under the same condition. Overall, the above results can

demonstrate that the photo-generated h^+ and $\bullet O_2^-$ species could play the dominant roles for the degradation of BPA or phenol over the Au-2%Fe/BTO photocatalysts under light irradiation and the photo-generated h^+ plays more significant part than the $\bullet O_2^-$ species.

3.8 PL spectra and I-V analysis

The separation rate of photoexcited electron-hole pairs is also an important factor for the photocatalytic activity of a photocatalyst. The transient photocurrent (I - V) and photoluminescence (PL) spectroscopic measurements are useful in demonstrating the photo-induced charge separation in photocatalysts [35,55]. The transient photocurrent responses for BTO, 2%Fe/BTO, and Au-2%Fe/BTO were also recorded under 300W Xenon lamp irradiation through light-on and light-off cycles. In Figure 11a, the Au-2%Fe/BTO photoelectrode shows 6.2 and 1.7 times higher photocurrent density compared with the BTO and 2%Fe/BTO photoelectrode, which indicates the more efficient photo-induced charge separation and faster charge transfer in the Au-2%Fe/BTO. Efficiency of photo-induced charge carrier trapping, transfer, and separation on the semiconductor surface or near-surface was further examined by photoluminescence spectrum [56], and the results are shown in Figure 11b. The prepared samples show a broad peak in the range of 350-600 nm and the Au-2%Fe/BTO and 2%Fe/BTO samples show a lower PL intensity than BTO sample. What is more, Fe^{3+} will be oxidized to Fe^{4+} by holes [25,26], after it doped in the Fe/BTO photocatalyst. This leads to the separation of electron-hole pairs. With the Au nanoparticles on the surface of 2%Fe/BTO, the Schottky barrier is formed at the Au-Fe/BTO interface. Therefore, Au nanoparticles can easily capture the photo-excited electrons from Fe/BTO, resulting in a lower recombination rate of e^-/h^+ pairs. The lower intensity PL spectra for the Au-2%Fe/BTO composite photocatalysts can exhibit lower recombination rate of photoelectron and holes pairs if we compare with BTO and 2%Fe/BTO samples and generate the higher photocatalytic activity.

3.9 Photocatalytic mechanism

From the demonstration above, Au-2%Fe/BTO shows high photocatalytic activity for photodegradation of BPA and phenol under light irradiation, and the possible mechanisms for the enhancement in photocatalytic activity of Au-2%Fe/BTO were shown in Figure 12a. Firstly, the results of HRTEM images in Figure 5 show that 2%Fe/BTO nanosheets exposed {001} facets. The photoinduced electron-hole pairs are formed under light irradiation and then driven apart by the internal electric fields [12]. Therefore, the separation of photogenerated electron-hole pairs along

[001] direction of Fe/BTO nanosheet can be promoted. On the other hand, the depolarisation fields can cause the separation of carriers, which will also suppress recombination rates, thereby increasing carrier lifetimes. Secondly, the photogenerated electrons and holes can be trapped by Fe^{3+} , which can turn into Fe^{2+} and Fe^{4+} ions by trapping photogenerated electrons and holes, respectively, hence, holding up the recombination process. However, the Fe^{2+} and Fe^{4+} ions have half-filled $3d^5$ orbital and become relatively unstable than the Fe^{3+} ions. Therefore, the trapped charges can easily release from Fe^{2+} or Fe^{4+} ions and then migrate to the surface to initiate the photocatalytic reaction. Fe^{2+} ions can be oxidized to Fe^{3+} ions by transferring electrons to absorbed O_2 on the surface of BTO, and the adsorbed O_2 is reduced to superoxide radical. This process can further degrade BPA and phenol. Similarly, Fe^{4+} ions are also reduced to Fe^{3+} ions by releasing electrons, while surface hydroxyl group can translate into hydroxyl radical. The trapped electrons can be further transferred to oxygen, which is adsorbed on the BTO surface hence generate superoxide radical. The trapped holes can also play a role in degradation of BPA and phenol. Thirdly, the loaded metal Au nanoparticles are remarkably enhance the absorption in the light region. This is due to the surface plasmonic resonance effect (as shown in Figure 12b), and create the plasmon induced electric field around Au. This promotes the formation rate of electrons and holes [57], and the Schottky barrier could enhance the interfacial electron transfer [58,59]. The detailed photo-degradation reaction processes are as follows:



4. Conclusions

A plasmonic Au-2%Fe/BTO composite photocatalysts was successfully prepared by a two-step chemical method. The SEM, TEM, and HRTEM observations revealed that the 2% Fe^{3+} -doped BTO

samples are composed of nanosheets with exposed {001} facets. The Au-2%Fe/BTO composite photocatalysts exhibited a higher photocatalytic activity for the photodegradation of phenol and bisphenol A than pure BTO sample. This is due to a combined effect of its special morphology, Fe³⁺-doping, and surface plasmon resonance of Au nanoparticles. The synthesized Au-2%Fe/BTO composite photocatalysts is thus of potential importance for some industrial wastewater treatment in the future.

Acknowledgments

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Figure Captions

Figure 1. (a) XRD patterns of pure BTO, 2%Fe/BTO, 4%Fe/BTO, 6%Fe/BTO and Au-2%Fe/BTO samples; (b) crystal structure of orthorhombic BTO.

Figure 2. (a) Survey XPS spectrum of the 2%Fe/BTO and Au-2%Fe/BTO samples; The high-resolution XPS spectra of (b) Bi 4f, (c) Ti 2p, (d) O 1s, (e) Fe 2p, and (f) Au 4f.

Figure 3. (a) SEM images of BTO and the inset spectrum shows the corresponding EDS patterns; SEM images of (b) 2%Fe/BTO, (c) 4%Fe/BTO, (d) 6%Fe/BTO and (e) Au-2%Fe/BTO; (f) EDS patterns of Au-2%Fe/BTO sample.

Figure 4. (a) SEM image for Au-2%Fe/BTO sample; (b)-(f) EDS mapping images of the Bi, Fe, Ti, O, Au elements respectively.

Figure 5. (a) TEM and (b) HRTEM images of 2% Fe/BTO; (c,e) TEM and (d,f-h) HRTEM images of Au-2%Fe/BTO (c-h) samples

Figure 6. UV-vis adsorption spectra of the pure BTO, Fe/BTO and Au-2%Fe/BTO samples and inset the plots of $(\alpha h\nu)^{1/2}$ versus energy ($h\nu$)

Figure 7. (a) and (c) are the variation of bisphenol A and phenol; (b) and (d) are the concentration (C/C_0) over BTO, 2%Fe/BTO, 4%Fe/BTO and 6%Fe/BTO photocatalysts samples with time under light irradiation and the pseudo-first-order kinetics for bisphenol A and phenol.

Figure 8. (a) and (b) are the photocatalytic activity for degradation of BPA with different sample of BTO, 2%Fe/BTO and Au-2%Fe/BTO under light irradiation.; (c) and (d) are the photocatalytic activity for degradation of phenol with different sample of BTO, 2%Fe/BTO and Au-2%Fe/BTO

under light irradiation.

Figure 9. TOC removal in the presence of Au-2%Fe/BTO photocatalysts for phenol and BPA under light irradiation

Figure 10. Photocatalytic activity for degradation of BPA and phenol with different quenchers under light irradiation.

Figure 11. Transient photocurrent (a) and photoluminescence spectra (b) of BTO, 2%Fe/BTO and Au-2%Fe/BTO samples.

Figure 12. (a) Schematic illustration of the charge separation and transfer in the Au-2%Fe/BTO composites under light irradiation; and (b) schematic for the surface plasmon resonance (SPR) effect of Au nanoparticles.

Fig. 1

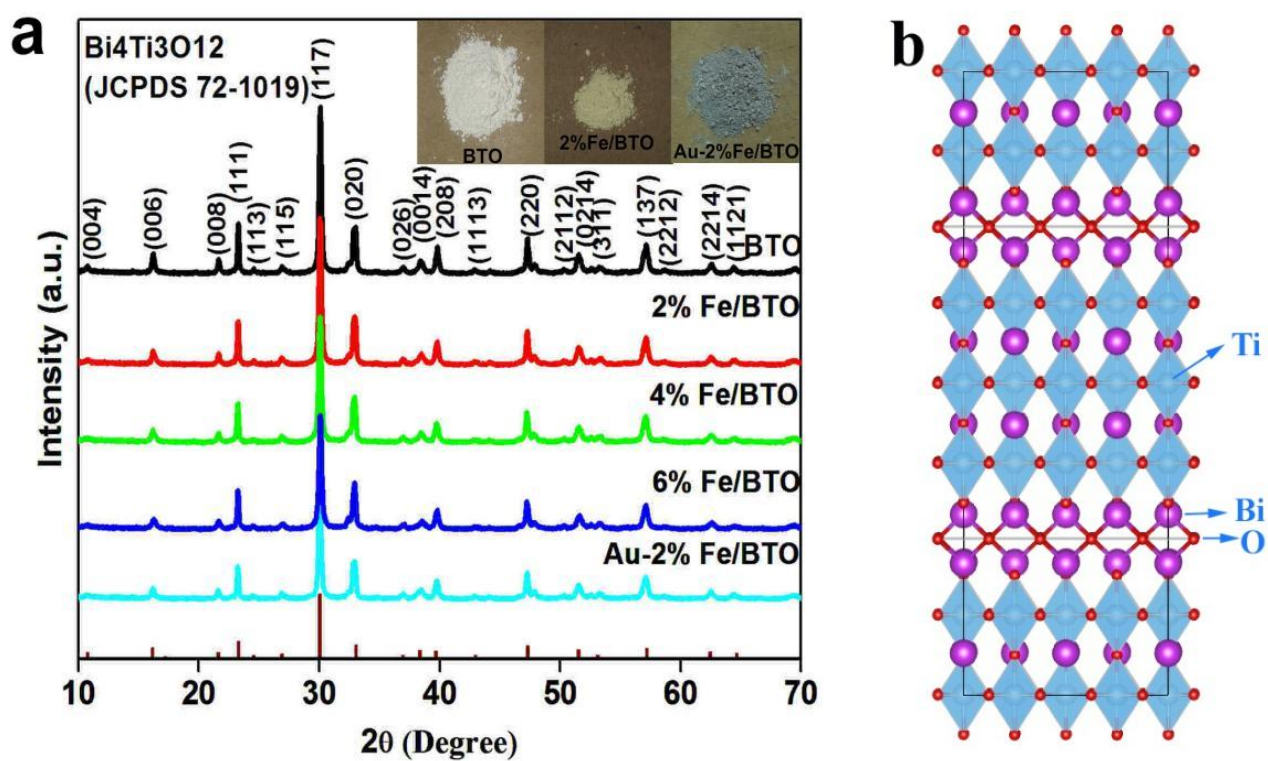


Fig. 2

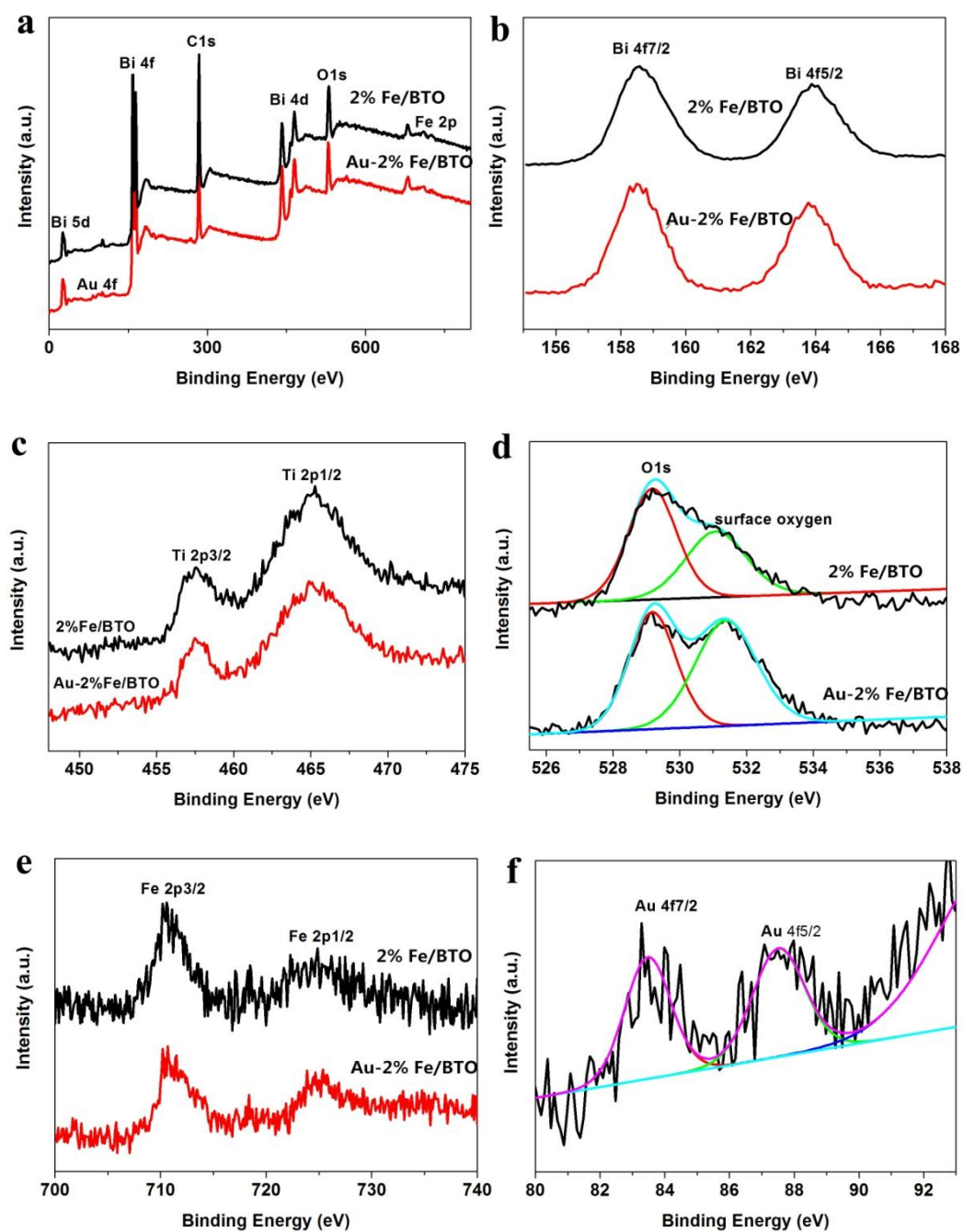


Fig. 3

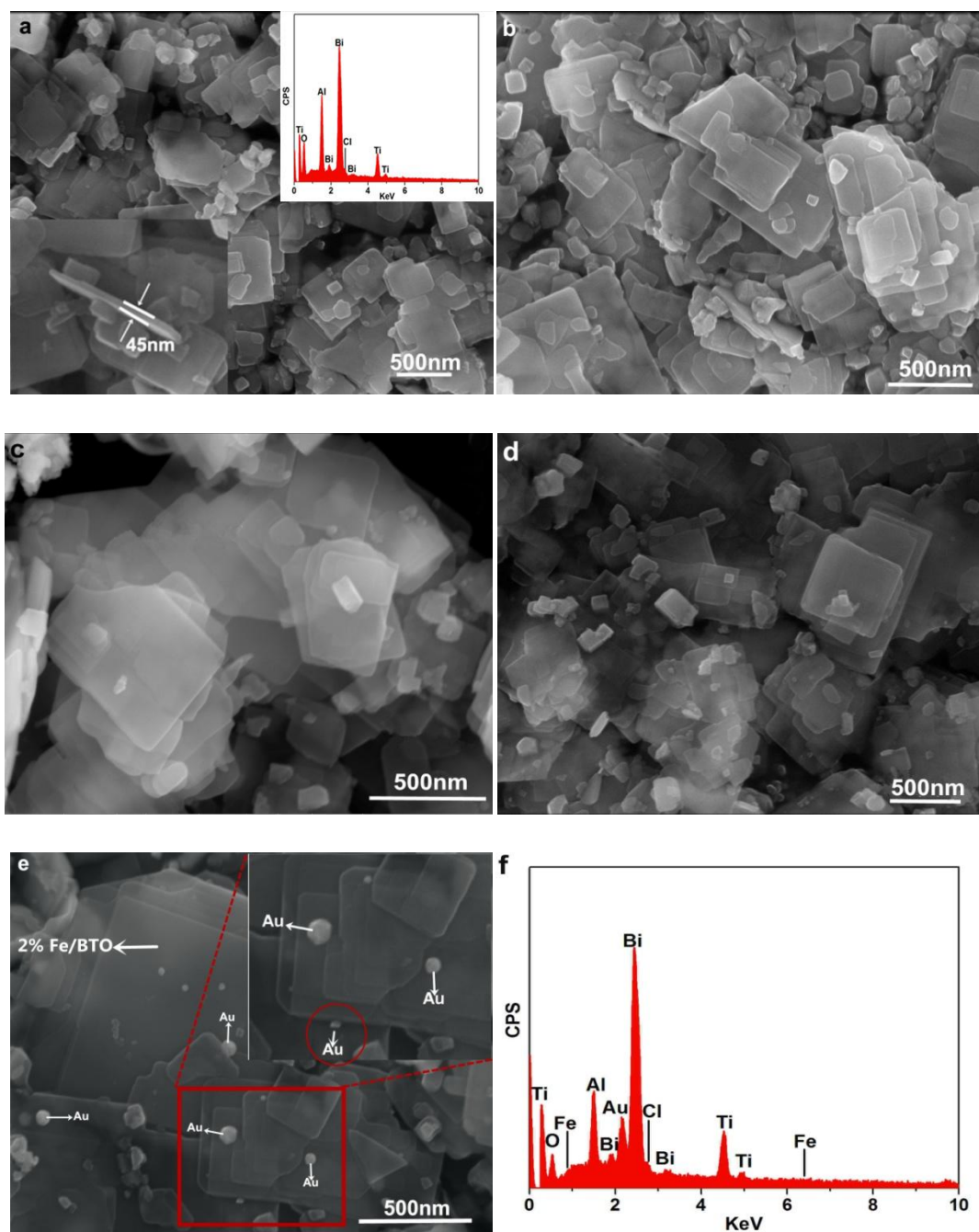


Fig. 4

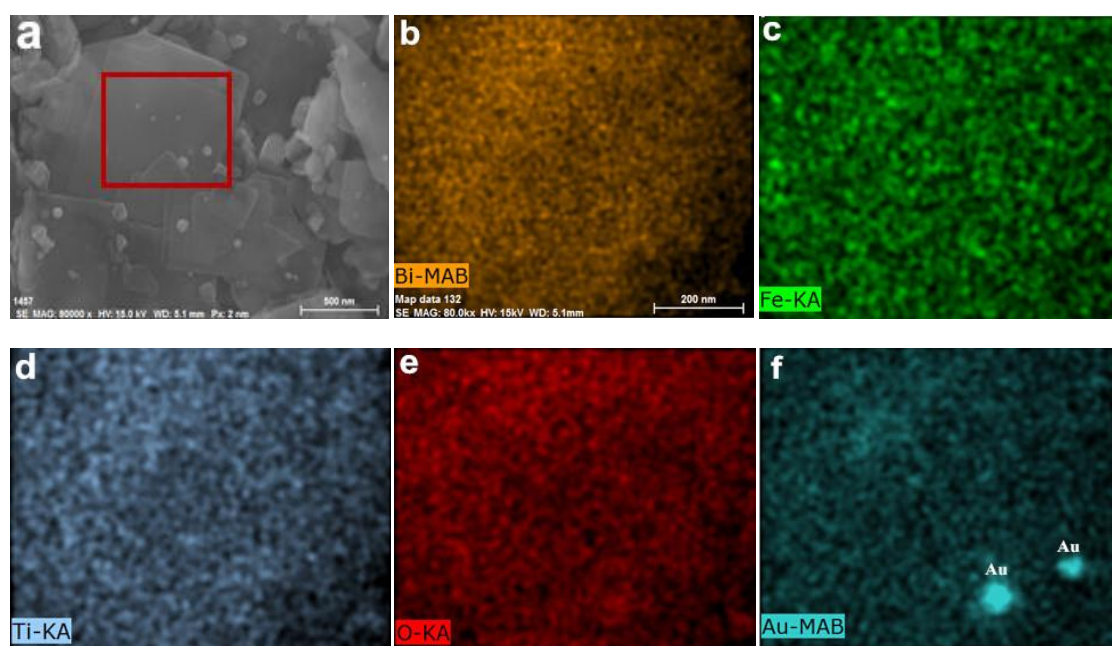


Fig. 5

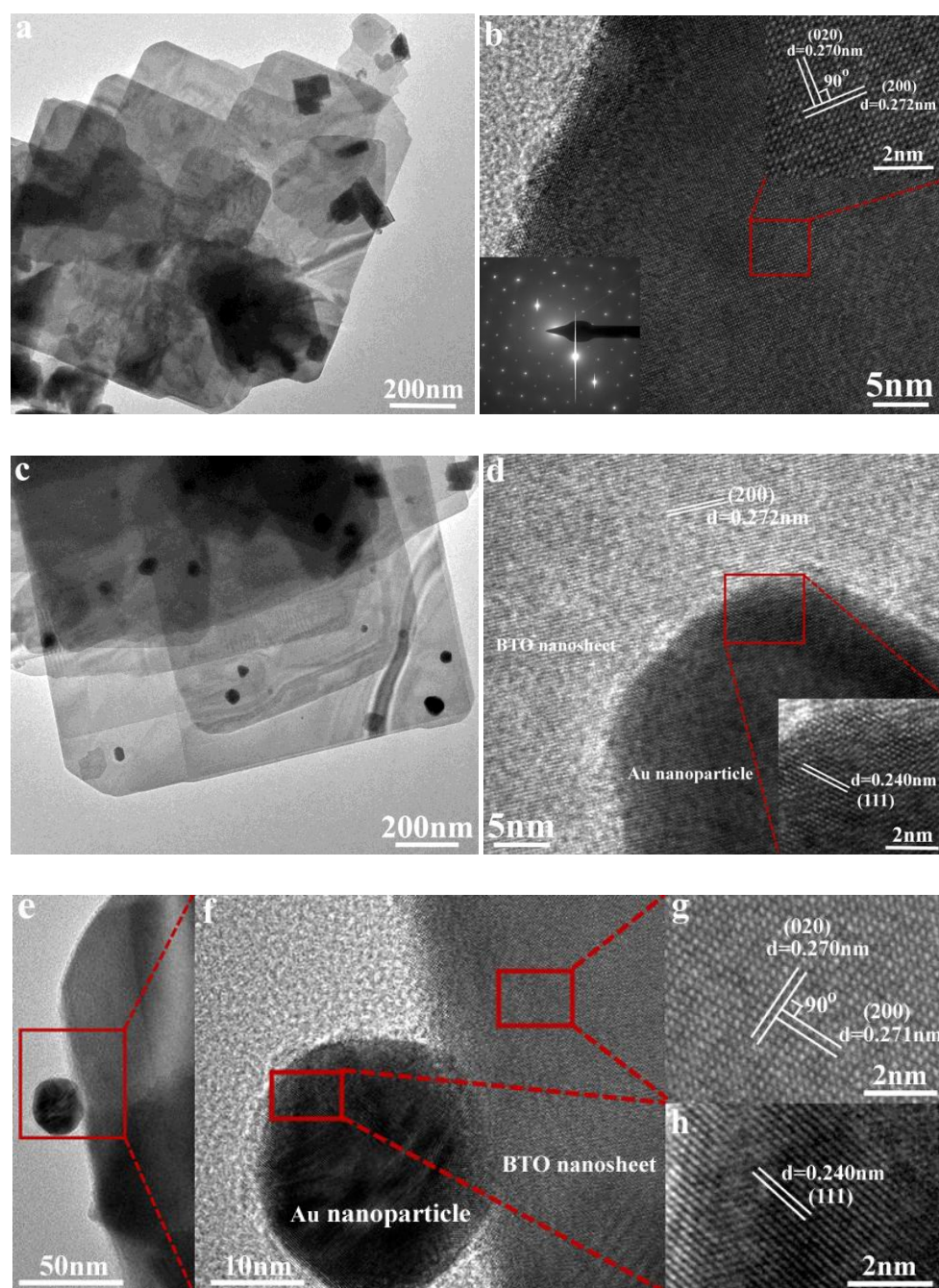


Fig. 6

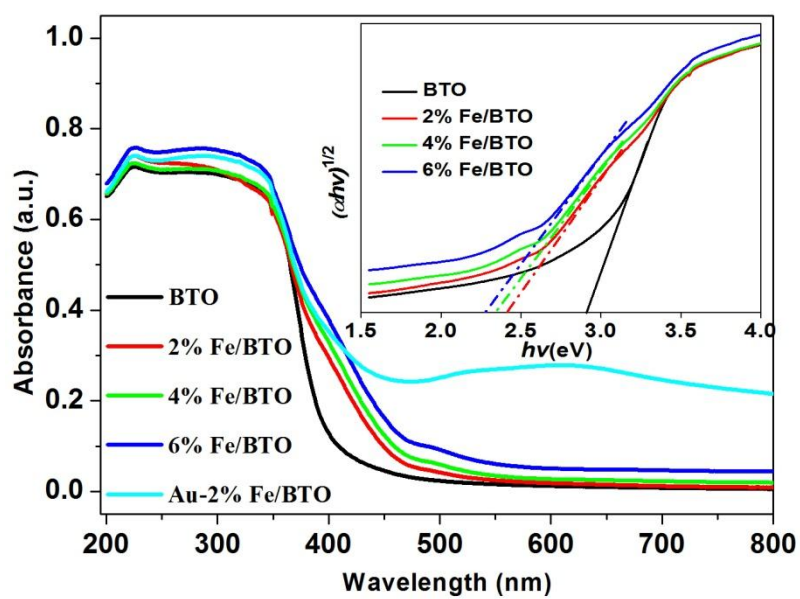


Fig. 7

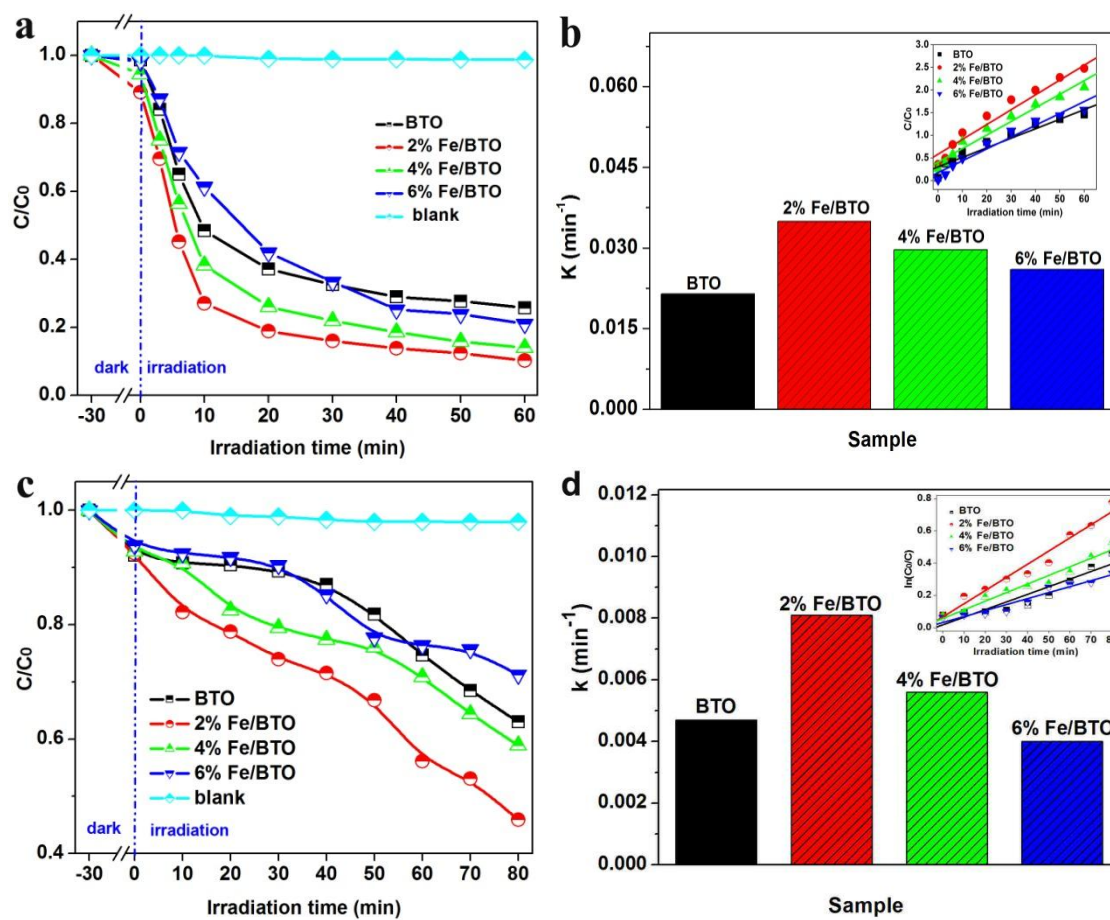


Fig. 8

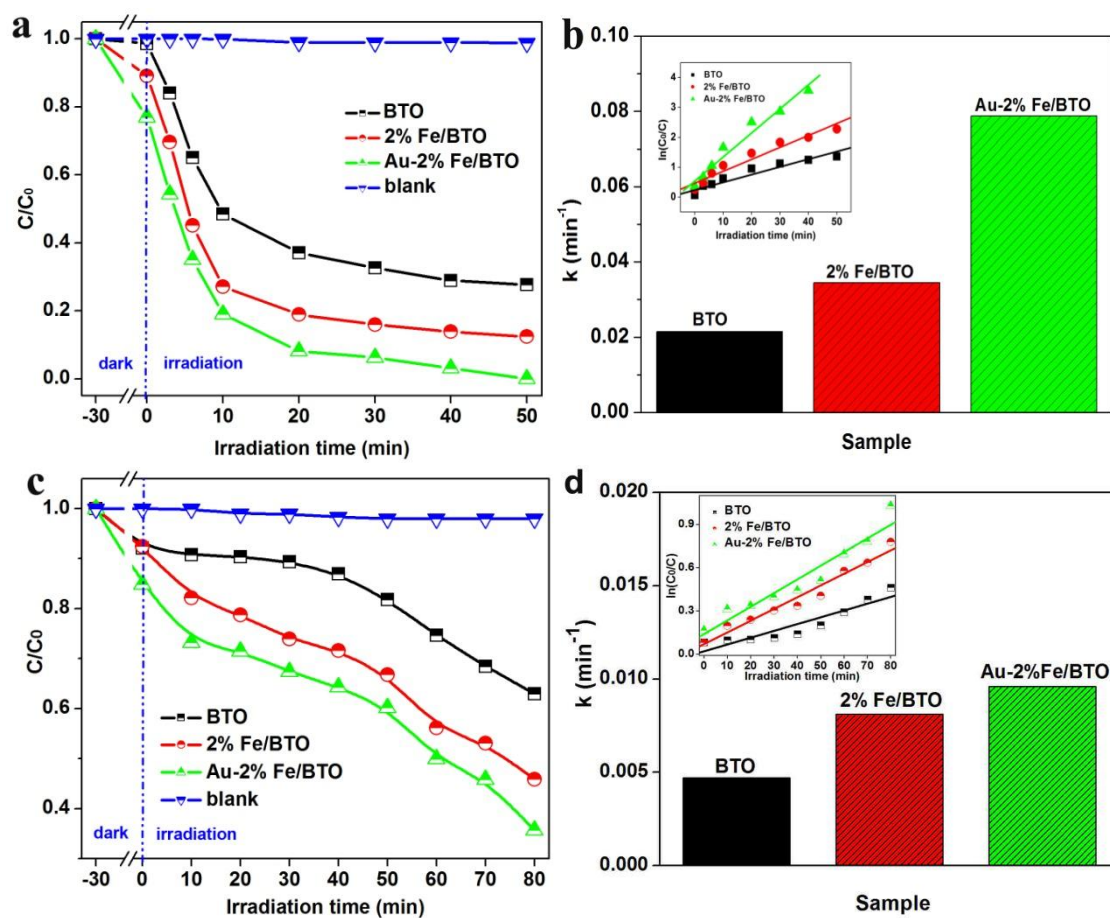


Fig. 9

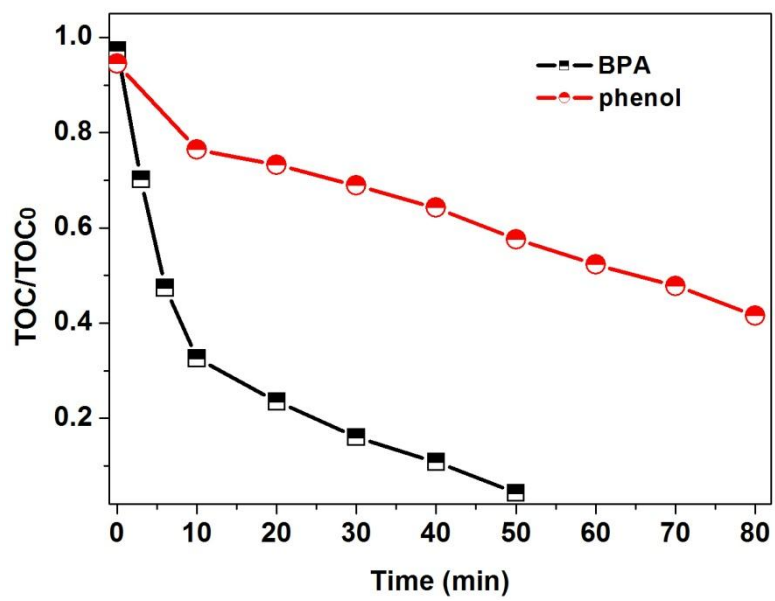


Fig. 10

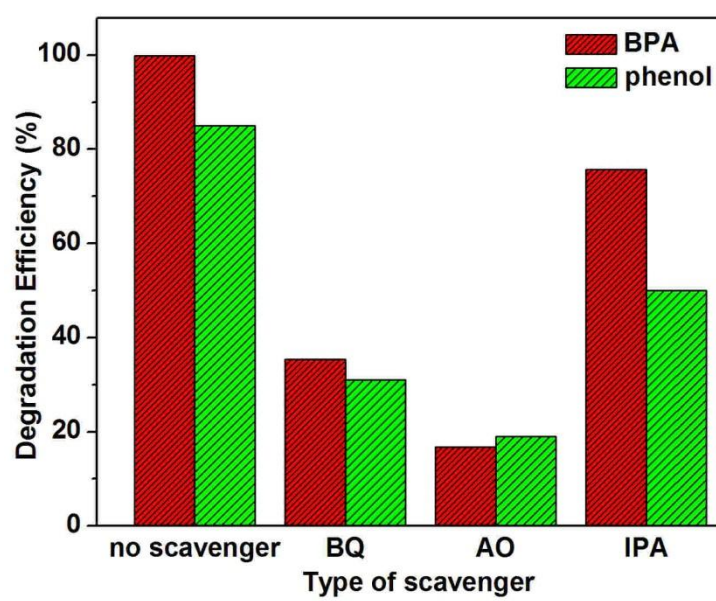


Fig. 11

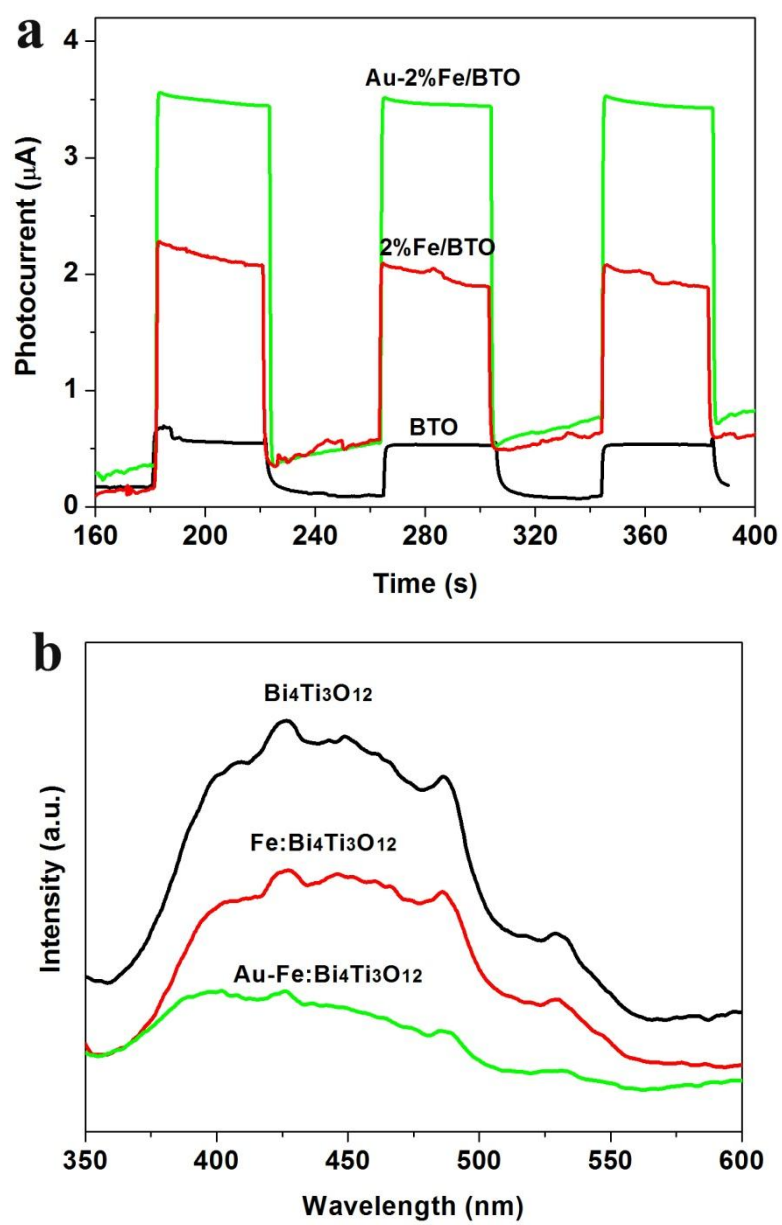


Fig. 12

