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Article

Synthesis of Ag/AgCl/Fe-S plasmonic catalyst for bisphenol A degradation in heterogeneous photo-Fenton system under visible light irradiation

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ARTICLE INFO

Article history:

Received 18 May 2017

Accepted 5 August 2017

Published 5 October 2017

Keywords:

Visible light

Photo-Fenton

Plasmonic catalyst

Ag/AgCl/Fe-S

Sepiolite

ABSTRACT

A novel plasmonic photo-Fenton catalyst of Ag/AgCl/Fe-S was synthesized by ion exchange and photoreduction methods. The obtained catalyst was characterized by X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscope imaging, and Brunauer-Emmett-Teller measurements. Moreover, the photocatalytic activity of Ag/AgCl/Fe-S was investigated for its degradation activity towards bisphenol A (BPA) as target pollutant under visible light irradiation. The effects of H_2O_2 concentration, pH value, illumination intensity, and catalyst dosage on BPA degradation were examined. Our results indicated that the Ag/AgCl material was successfully loaded onto Fe-sepiolite and showed a high photocatalytic activity under illumination by visible light. Furthermore, active species capture experiments were performed to explore the photocatalytic mechanism of the Ag/AgCl/Fe-S in this heterogeneous photo-Fenton process, where the major active species included hydroxyl radicals ($\cdot\text{OH}$) and holes (h^+).

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1. Introduction

Safety concerns in relation to bisphenol A (BPA) have drawn attention owing to its widespread use in producing epoxy resins and polycarbonate plastics [1]. As a representative endocrine disruptor, BPA can damage the fecundity of animals and humans [2] by disrupting endocrine effects in the reproductive systems and cause the death of some types of cells [3–5]. Thus, a rapid and efficient method of removing BPA is urgently required.

Among various technologies for removing BPA, the heterogeneous photo-Fenton process is considered to be an effective and affordable method, owing to its generation of highly active radicals and the easy separation of the catalysts from treated

wastewater [6,7]. In the past few decades, much attention has been paid to investigating heterogeneous photo-Fenton processes for organic pollutant degradation under UV irradiation. However, UV light-based heterogeneous photo-Fenton processes are limited in their practical applications because UV light accounts for only 3%–5% of solar light energy [8]. Thus, the development of heterogeneous photo-Fenton catalysts that operated based on visible light is of great importance for practical applications.

The combination of photo-Fenton catalysts and plasmonic materials might overcome this problem. Plasmonic materials based on silver/silver halide (Ag/AgX, X = Cl, Br, I) composites can strongly absorb visible light because of their surface plasmon resonance [9–11] and are extensively used as visible-light

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This work was supported by the National Natural Science Foundation of China (41573118), Research Foundation of Education Bureau of Hunan Province, China (14B177), and Special Project of Xiangtan University.

DOI: 10.1016/S1872-2067(17)62902-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 10, October 2017

photocatalytic materials [12–15]. However, Ag/AgX composites suffer from high charge carrier recombination rates, causing losses of photocatalytic efficiency [16]. Additionally, recent evidence has suggested that iron oxides, blended with semiconductor composites, can act a selective acceptor and inhibit the recombination of electron/hole pairs [17–19]. For example, Yang et al. [20] synthesized a $\text{Fe}_3\text{O}_4/\text{rGO}/\text{TiO}_2$ visible light catalyst, in which the photo-induced electrons from TiO_2 could rapidly transfer to Fe^{3+} , accelerating the redox transformation between Fe(III) and Fe(II) . On the basis of the above reports, we attempted to add Ag/AgCl composites into a heterogeneous photo-Fenton system. We expected that the Ag/AgCl might promote the charge transfer between $\text{Fe(III)}/\text{Fe(II)}$ by promoting photogenerated electrons and enhancing the photo-Fenton catalytic activity under visible light irradiation. The choice of catalyst support is also important for preparing efficient heterogeneous photo-Fenton catalysts. Sepiolite is a zeolite-like clay mineral that has a high specific surface area and good chemical stability [21,22]. Thus, in this work, sepiolite was selected as the support material to enhance the synergistic effects between Ag/AgCl and hydroxy-iron, and fabricated a quaternary-composite photo-Fenton catalyst. We investigated the photocatalytic activity and stability of our synthesized Ag/AgCl/Fe-Sepiolite (Ag/AgCl/Fe-S) photocatalyst using BPA as a target contaminant. In addition, the possible photocatalytic mechanism involved in the photo-Fenton system was discussed. This work provides new insights into the preparation of visible-light responsive photo-Fenton catalysts.

2. Experimental

2.1. Materials

The sepiolite sample used in this study was obtained from Hunan Province, China, and the clay particle size was approximately 100-mesh. All chemical reagents were of analytical grade and used without further purification. Deionized water was used throughout the experiments.

2.2. Catalyst preparation

Acidified sepiolite was prepared by pouring 50 g of raw sepiolite powders into 1 L of HNO_3 solution (2 mol/L) under continuous stirring at 40 °C for 2 h. This mixture was then filtered and washed with deionized water repeatedly until the supernatant pH value was approximately 7, and the resulting solid was vacuum dried at 100 °C overnight.

The Ag/AgCl/Fe-S catalyst was prepared by ion exchange and photoreduction methods. First, Fe-sepiolite was fabricated as follows. Na_2CO_3 (0.2 mol/L) was added dropwise into 0.2 mol/L $\text{Fe}(\text{NO}_3)_3$ solution under stirring at 25 °C until the molar ratio of Na/Fe was 1:1. This solution was aged for 24 h at 25 °C and then added into an aqueous suspension containing 2 wt% of the above-treated sepiolite under stirring at 60 °C until the final Fe/clay ratio was equal to 5 mmol/g of sepiolite. After aging for 12 h at 60 °C, the mixture was centrifuged and washed by deionized water. The resulting precipitates were

dried in air overnight at 70 °C to obtain Fe-sepiolite. Subsequently, the Fe-sepiolite was used to fabricate the AgCl/Fe-S. A 1-g portion of Fe-sepiolite was dispersed in 100 mL of deionized water and a 20-mL AgNO_3 solution (0.15 g of AgNO_3 dissolved in 20 mL of water) was added to the mixture with vigorous magnetic stirring for 12 h at 25 °C. Then, a 20-mL KCl solution (0.15 g of KCl dissolved in 20 mL of water) was added into the mixture, which was stirred for a further 30 min. The resulting product (AgCl/Fe-S) was filtered, washed, and dried at 70 °C. Finally, Ag/AgCl/Fe-S was prepared via a photoreduction method. A 1-g portion of the AgCl/Fe-S was dispersed in 100 mL of deionized water. An AgNO_3 solution (30 mg of AgNO_3 in 5 mL of water) was then added to the mixture, and the reaction stirred in the dark for 30 min. This mixture was irradiated with visible light ($\lambda > 400$ nm) for 30 min to partially reduce the Ag^+ ions to Ag^0 species. The final product was gathered by centrifugation and dried at 70 °C. For comparison, pure Ag/AgCl was also prepared by the same method without the addition of Fe-sepiolite. All of the prepared samples were crushed and screened through a 200-mesh sieve.

2.3. Characterization

The XRD patterns of the prepared materials were acquired with a diffractometer (Rigaku D/max-2550 VK/PC) equipped with $\text{Cu K}\alpha$ radiation at 40 kV and 50 mA. XPS measurements were performed on a K-alpha X-ray photoelectron spectrometer (PHI Quantera II, UIVAC) using a monochromatic Al $\text{K}\alpha$ X-ray radiation source at 1486.71 eV. The morphologies of the products were observed with a scanning electron microscope (SEM, JSM-6360LV, JEOL). The nitrogen adsorption-desorption isotherms were determined with a NOVA 2200e instrument. Prior to the adsorption tests, the samples were outgassed for 12 h at 150 °C. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas of the samples. The light absorption properties were measured with a UV-vis diffuse reflectance spectrophotometer (Shimadzu, UV-2550) with a wavelength range of 200–800 nm.

2.4. Photocatalytic reaction and analytical methods

All the experiments were conducted in a photoreaction apparatus (BL-GHX-V, Shanghai Depai Biotech. Co. Ltd., China), in which a 500 W xenon lamp equipped with a 420-nm cutoff filter was applied as the visible light source. The light source was positioned inside a cylindrical Pyrex vessel surrounded by a jacket with circulating water. The photocatalytic activities of the studied catalysts were evaluated from their ability to degrade BPA under various conditions. An appropriate amount of the catalyst was added into 100 mL of BPA solution (10 mg/L), and the initial pH of solution was adjusted by addition of NaOH or HNO_3 solutions. Prior to irradiation, the solution was magnetically stirred in the dark for 30 min to establish an adsorption-desorption equilibrium. The reaction was started when H_2O_2 was added to the solution and the light source was turned on. During the photocatalytic process, samples were taken from the reaction mixture at fixed intervals, and filtered immediately

with a 0.45 μm membrane.

The concentration of BPA in the aqueous solution was measured by high performance liquid chromatography (HPLC, Agilent 1260), and the total organic carbon (TOC) was analyzed with a Shimadzu TOC-V CPH analyzer.

An atomic absorption spectrophotometry instrument (Shimadzu AA7000) was used to measure the quantity of iron ions leached from the catalyst into solution. The concentration of Fe^{2+} in the leachate was measured by the *o*-phenanthroline spectrophotometric method ($\lambda = 510 \text{ nm}$).

The active species inducing degradation of BPA during the photocatalytic reaction were detected with the use of various scavengers. Namely, isopropanol (IPA), ammonium oxalate (AO) and benzoquinone (BQ) were separately applied as scavengers for hydroxyl radicals ($\cdot\text{OH}$), holes (h^+), and superoxide radicals ($\text{O}_2^{\cdot-}$), respectively. The processes for the active species capture experiments were similar to those for the photocatalytic experiments.

The photoluminescence (PL) spectra were measured on a fluorescence spectrophotometer (F-4600) at room temperature with excitation at 362 nm.

The generation of $\cdot\text{OH}$ radicals was also investigated by electron spin resonance spectroscopy (ESR) with a Bruker EMX-10/12 electron paramagnetic resonance spectrometer, and 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was chosen as the spin-trapping reagent (0.02 mol/L).

Electrochemical impedance spectroscopy (EIS) measurements were performed in three-electrode quartz cells with a 0.1 mol/L KCl electrolyte solution containing 5 mmol/L $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$. A glassy carbon electrode served as the working electrode, which was modified by the different catalysts. A platinum plate and saturated calomel electrode were used as the counter and reference electrodes, respectively. A CHI660 Electrochemical Workstation (Shanghai Chen Hua Instrumental Co. Ltd., China) was used to measure the EIS data over the frequency range from 100 kHz to 0.01 Hz with an AC signal amplitude of 10 mV.

3. Results and discussion

3.1. Characterization of the catalysts

Fig. 1 shows the XRD patterns of sepiolite, Fe-sepiolite, and Ag/AgCl/Fe-S. The intensities of the characteristic peaks of sepiolite at $2\theta = 7.494^\circ$ (110), 20.882° (131), and 26.654° (080) [23] decreased sharply after loading with Fe or Ag/AgCl, suggesting that the sepiolite phase became less crystalline. Furthermore, some new diffraction peaks appeared in the XRD pattern of Ag/AgCl/Fe-S at 27.792° , 32.216° , 46.203° , 54.786° , and 57.445° , which could be indexed to AgCl (JCPDS31-1238). These results indicate the successful loading of AgCl onto sepiolite. However, no distinct diffraction peaks from metallic Ag or Fe could be observed in the Ag/AgCl/Fe-S, which is likely because of the small-size of their crystallites and their high degree of dispersion. To further demonstrate the chemical compositions of Ag/AgCl/Fe-S, we performed XPS measurements, as shown in Figs. 2 and 3. The XPS survey spectrum of the raw

Fig. 1. XRD patterns of sepiolite (1), Fe-sepiolite (2), and Ag/AgCl/Fe-S (3).

sepiolite is also shown for comparison with that of Ag/AgCl/Fe-S.

The main elements found at the surface of sepiolite, were Si, Mg, C, and O. In Ag/AgCl/Fe-S clear signals from Fe and Ag also appeared. In the Fe 2p XPS spectrum of Ag/AgCl/Fe-S (Fig. 3(a)), peaks around 710.6 and 711.8 eV could be attributed to FeOOH and Fe_2O_3 [24], respectively, and indicate that the oxidation state of Fe was Fe(III) in the Ag/AgCl/Fe-S catalyst. In the Ag 3d spectrum of the catalyst (Fig. 3(b)), the peaks observed at 367.3 and 373.3 eV belong to Ag^+ , and the peaks at 368.1 and 374.1 eV were assigned to metallic Ag [25,26]. These results indicate that the Ag/AgCl structure was formed on the surface of the Fe-sepiolite.

The morphology and microstructure of the raw sepiolite, Fe-sepiolite, and Ag/AgCl/Fe-S were examined by SEM imaging (Fig. 4). Images of the raw sepiolite showed a smooth and dense surface (Fig. 4(a)); however, the surface of the Fe-sepiolite particles appeared to be rough and mesoporous (Fig. 4(b)), indicating that the hydroxyl-iron treatment etched channels into the sepiolite. Additionally, Ag/AgCl particles with a size of a few hundred nanometers to several micrometers

Fig. 2. XPS survey spectra of raw sepiolite (1) and Ag/AgCl/Fe-S (2).

Fig. 3. Fe 2p (a) and Ag 3d (b) peaks of Ag/AgCl/Fe-S.

Fig. 4. SEM images of sepiolite (a), Fe-sepiolite (b), and Ag/AgCl/Fe-S (c).

were observed to be well dispersed on the surface of the Fe-sepiolite catalyst (Fig. 4(c)).

Fig. 5 shows nitrogen adsorption-desorption isotherms of sepiolite, Fe-sepiolite, and Ag/AgCl/Fe-S. All samples exhibited a type IV isotherm with a H3 type hysteresis loop, indicating that all the samples were typical mesoporous materials with a high adsorption energy [27,28]. The specific surface areas, pore volumes, and aperture diameters of all samples are summarized in Table 1. The specific surface area and pore volume of

Fig. 5. Nitrogen adsorption-desorption isotherms of sepiolite ($\blacktriangle$, $\triangle$), Fe-sepiolite ($\blacksquare$, $\square$), and Ag/AgCl/Fe-S ($\bullet$, $\circ$).

Fe-sepiolite were much larger than those of raw sepiolite. However, the corresponding values were slightly lower in Ag/AgCl/Fe-S. These lower values were likely caused by the effects of pore blocking by the Ag/AgCl particles. Similar observations have also been reported by McEvoy *et al.* [29].

The light absorption ability of the prepared samples was examined by UV-vis diffuse reflectance spectroscopy (Fig. 6). The Ag/AgCl shows two strong absorption peaks in the range of 200–800 nm. The absorption peak at 350 nm is attributed to the indirect bandgap of AgCl [30], and the other intense absorption band observed in the visible light region (around 550 nm) is attributed to the surface plasmon resonance of Ag NPs [31]. By comparison, Fe-S showed much weaker absorption of visible light. However, after loading the Ag/AgCl onto the surface of the Fe-sepiolite, we found a notable enhancement of light absorption in both the UV and visible light regions. Hence, the Ag/AgCl/Fe-S catalyst is able to efficiently absorb visible light.

Table 1

Surface area, pore volumes and apertures of sepiolite, Fe-sepiolite, and Ag/AgCl/Fe-S.

Sample	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Aperture (nm)
sepiolite	32.6576	0.070664	8.72157
Fe-sepiolite	50.0368	0.073684	6.05682
Ag/AgCl/Fe-S	29.6332	0.053013	7.29888

Fig. 6. UV-vis spectra of Fe-sepiolite (1), Ag/AgCl/Fe-S (2), and Ag/AgCl (3).

3.2. Degradation and mineralization of BPA

The degradation and mineralization of BPA in aqueous solution by various processes were investigated. As shown in Fig. 7, in the dark, only a small amount of BPA decomposition was observed after 3 h in the presence of Ag/AgCl/Fe-S and H_2O_2 . This result indicated that no active radicals were released in the absence of light. In a system subjected to only visible light, the degradation and mineralization of BPA were also negligible, implying that BPA is stable in wastewater under ambient conditions. When H_2O_2 and visible light were combined, the degradation efficiency of BPA reached 96.24%; however, the mineralization of BPA was negligible. These results indicate that the hydroxyl radicals released in this system could degrade BPA into long-lived intermediates but could not further oxidize those intermediates into CO_2 and H_2O . The degradation of BPA reached more than 95% in the systems with Ag/AgCl, H_2O_2 , visible light; Fe-sepiolite, H_2O_2 , visible light; and Ag/AgCl/Fe-S, H_2O_2 , visible light. However, the Ag/AgCl/Fe-S, H_2O_2 , visible light system showed the highest TOC removal efficiency (60.98%) and the fastest BPA degradation rate, suggesting that Ag/AgCl/Fe-S is an efficient heterogeneous photo-Fenton cata-

Fig. 8. Effects of H_2O_2 concentration on the degradation of BPA (pH = 4; [BPA] = 10 mg/L; catalyst loading = 1.0 g/L; light intensity = 500 W).

lyst for removal of BPA.

3.3. Factors influencing the degradation of BPA

3.3.1. Effects of H_2O_2 concentration

The initial H_2O_2 concentration had a notable influence in the photo-Fenton reaction owing to its influence on the production of hydroxyl radicals [32]. Thus, we examined the effects of initial H_2O_2 concentration on the degradation of BPA in our heterogeneous photo-Fenton system with the Ag/AgCl/Fe-S catalyst.

As shown in Fig. 8, when the concentration of H_2O_2 was increased to 6 mmol/L, the kinetic constant of the BPA degradation increased from 0.057 to 0.10393 min^{-1} correspondingly. This result can be explained by the increased quantity of hydroxyl radicals produced. However, a further increase of the H_2O_2 concentration from 6 to 25 mmol/L led to a lower kinetic constant for BPA removal (0.03641 min^{-1}). This decrease may be attributed to scavenging of hydroxyl radicals by excess H_2O_2 according to Eq. (1) [33–36]:

Fig. 7. (a) Degradation and (b) mineralization of BPA under different systems. (1) Ag/AgCl/Fe-S, H_2O_2 , visible light; (2) Ag/AgCl, H_2O_2 , visible light; (3) Fe-sepiolite, H_2O_2 , visible light; (4) H_2O_2 , visible light; (5) visible light; (6) Ag/AgCl/Fe-S, H_2O_2 . Experimental conditions: [H_2O_2] = 6 mmol/L; pH = 4; [BPA] = 10 mg/L; catalyst loading = 1.0 g/L; light intensity = 500 W.

Fig. 9. Effects of initial pH value on the degradation of BPA ($[\text{H}_2\text{O}_2] = 6 \text{ mmol/L}$; $[\text{BPA}] = 10 \text{ mg/L}$; catalyst loading = 1.0 g/L ; light intensity = 500 W).

3.3.2. Effects of pH value

The pH value of the reaction medium also plays an important role in photo-Fenton system; pH value not only affects the efficiency of photo-Fenton reaction but also determines the extent of Fe leaching from catalyst. To investigate the influence of initial pH value on the degradation of BPA, we performed experiments at five different pH values (pH = 2, 3, 4, 5, and 6) as shown in Fig. 9.

The kinetic constant of BPA degradation increased from 0.10882 to 0.12838 min^{-1} as the pH was increased from 2 to 3. However, increasing the solution pH value from 3 to 6 resulted in a decrease of the kinetic constant from 0.12838 to 0.03889 min^{-1} . These results confirmed that the optimum pH for BPA degradation efficiency in the studied system was approximately pH = 3. However, as shown in Fig. 10, leaching of Fe in the system at pH = 3 was almost 3 times as high as that in the pH = 4 system by the end of reaction. This high leaching rate might cause more rapid catalyst degradation. Considering that the kinetic constant of BPA degradation in the system at pH = 4 was 0.10393 min^{-1} , and only slightly lower than that of the pH = 3

Fig. 10. Release of Fe as a function of time in pH = 3 (1) and 4 (2) systems.

Fig. 11. Release of Fe (1) and Fe^{2+} (2) as a function of time in the pH = 4 system.

system, we used solutions with pH = 4 for the following experiments.

The concentration of Fe^{2+} in the system of pH = 4 was measured, and the results are shown in Fig. 11. The Fe^{2+} content as a proportion of total Fe was low, which may be attributed to the rapid oxidation of Fe^{2+} by H_2O_2 .

3.3.3. Effect of irradiation intensity

The effects of light intensity on BPA removal in the heterogeneous photo-Fenton process were investigated by varying the visible light intensity from 250 to 500 W . These results are shown in Fig. 12.

The degradation of BPA was highly sensitive to the visible light intensity. When the power of the light source was increased from 250 to 500 W , the kinetic constant of BPA degradation increased from 0.00775 to 0.10393 min^{-1} over a reaction time of 60 min. This result can be explained by the higher light intensity contributing more photons for activation of the Ag/AgCl/Fe-S catalyst, which in turn promoted the degradation of BPA.

Fig. 12. Effects of light intensity on the degradation of BPA ($[\text{H}_2\text{O}_2] = 6 \text{ mmol/L}$; pH = 4; $[\text{BPA}] = 10 \text{ mg/L}$; catalyst loading = 1.0 g/L).

Fig. 13. Effects of catalyst loading on the degradation of BPA ($[\text{H}_2\text{O}_2] = 6$ mmol/L; pH = 4; $[\text{BPA}] = 10$ mg/L; light intensity = 500 W).

3.3.4. Effects of catalyst loading

The effects of the catalyst loading on BPA degradation are shown in Fig. 13. The BPA was degraded more rapidly as the catalyst loading was increased from 0.1 to 1.5 g/L. However, for a catalyst loading higher than 1.5 g/L, the BPA removal rate was slightly decreased. Thus, higher catalyst loadings provided more active sites for H_2O_2 activation and produced more active radicals to degrade BPA; however, at catalyst loadings exceeding 1.5 g/L, the visible light penetration was decreased owing to the screening effects of excess catalyst particles in the solution [37]. Thus, the optimal catalyst loading used in this system was 1.5 g/L.

3.4. Stability of the photocatalyst

To evaluate the stability of Ag/AgCl/Fe-S in the heterogeneous photo-Fenton reaction, the catalyst was recycled three times under the conditions of 20 mg/L BPA, 6 mmol/L H_2O_2 , pH = 4.0, 500-W irradiation intensity, and 1.5 g/L catalyst loading. As shown in Fig. 14, a BPA degradation of 95.41% was achieved in the first run. In the second and third runs, the BPA degradation decreased to 94.86% and 93.28%, respectively, indicating that the catalyst can be effectively reused at least three times without any major loss of its catalytic activity.

Fig. 14. Recycling runs with Ag/AgCl/Fe-S catalyst.

3.5. Proposed photo-Fenton mechanism

To gain insight into the reactive species involved in the heterogeneous photo-Fenton system catalyzed by Ag/AgCl/Fe-S, specific scavengers (IPA, BQ, and AO) were used in the photocatalytic process under the above optimized conditions. IPA is known to be an effective scavenger for $\cdot\text{OH}$ radicals ($k_{\text{I-PrOH}, \cdot\text{OH}} = 1.9 \times 10^9 \text{ L}/(\text{mol} \cdot \text{s})$) [35,36,38]. Fig. 15(a) shows the effects of different concentrations of IPA on the degradation of BPA. As the concentration of IPA was increased the degradation of BPA decreased. The inhibition caused the BPA degradation to approach 65.21% when the IPA concentration was increased to 15 mmol/L. This result suggests that $\cdot\text{OH}$ is the main oxidative species in the studied heterogeneous photo-Fenton system.

BQ was used to determine the contribution of $\text{O}_2^{\cdot-}$ radicals to BPA degradation [39,40]. In this study, the addition of BQ had a slight effect on the degradation rate of BPA (Fig. 15(b)), indicating that $\text{O}_2^{\cdot-}$ has less effect on degradation of BPA than $\cdot\text{OH}$. Holes are another possible active species in semiconductor photocatalytic systems, and AO is a typically used hole scavenger [41,42]. As shown in Fig. 15(c), when the concentration of AO was increased from 0 to 10 mmol/L, the BPA degradation efficiency decreased from 100% to 49.23%, which indicated that holes are also an important active species in this system.

Fig. 15. Effects of (a) isopropanol, (b) *p*-benzoquinone, and (c) ammonium oxalate on the degradation of BPA in heterogeneous photo-Fenton system with Ag/AgCl/Fe-S catalyst ($[\text{H}_2\text{O}_2] = 6$ mmol/L; pH = 4; $[\text{BPA}] = 10$ mg/L; catalyst loading = 1.5 g/L; light intensity = 500 W).

Fig. 16. ESR spectra of DMPO•OH adducts in Ag/AgCl (1), Fe-S (2), and Ag/AgCl/Fe-S (3) system under visible light irradiation.

On the basis of the above experiments, we concluded that •OH radicals play the most important role in the studied heterogeneous photo-Fenton system. To further characterize the •OH radical generation ability in the different systems, we performed ESR spin-trapping measurements with DMPO as a spin trap. These results are shown in Fig. 16. No significant ESR signal was detected in the system with Ag/AgCl and visible light, indicating that no •OH radicals were generated in this system. A weak signal from DMPO•OH adducts characterized by an intensity ratio of 1:2:2:1 was observed in the Fe-S, H₂O₂, visible light system, implying that •OH generation was relatively slow because Fe circulation was restricted. For the Ag/AgCl/Fe-S, H₂O₂, visible light system, the intensity of the •OH signal was much higher than that for the Fe-S system. This result suggests that the introduction of Ag/AgCl into Fe-S induces an increase in the amount of •OH radicals produced in photo-Fenton systems.

We performed EIS measurements of the systems based on Fe-S, Ag/AgCl, and Ag/AgCl/Fe-S to investigate the charge transfer resistance and the separation efficiency between the photogenerated electrons and holes in the different catalysts

Fig. 17. EIS Nyquist plots of systems based on Fe-S (1), Ag/AgCl (2), Ag/AgCl/Fe-S (3).

Fig. 18. PL emission spectra of the Ag/AgCl (1) and Ag/AgCl/Fe-S (2).

[43]. According to previous reports [16,44], a lower charge transfer resistance indicates more effective separation of electron-hole pairs. The results in Fig. 17 show that the charge transfer resistance of Ag/AgCl/Fe-S was lower than that of the Fe-S and Ag/AgCl individual components suggesting that the combination of Ag/AgCl and Fe-S effectively promoted separation and transfer of photogenerated electron-hole pairs.

To further understand the transfer and recombination processes of the photogenerated electron hole pairs in the studied plasmonic catalyst, we measured the photoluminescence (PL) emission spectra of Ag/AgCl and Ag/AgCl/Fe-S under excitation at 362 nm. As shown in Fig. 18, two emission peaks at approximately 475 and 550 nm were observed in the PL spectrum of pure Ag/AgCl, which indicated recombination of photo-induced electron and holes [16,45]. The intensity of the emission peaks of Ag/AgCl/Fe-S was clearly lower than that of Ag/AgCl. This result suggests that hydroxyl-iron on the sepiolite surface acted as a trap to capture photo-induced electrons, and thus inhibited recombination of electron-hole pairs.

On the basis of the above results, a possible mechanism for BPA degradation catalyzed by Ag/AgCl/Fe-S and H₂O₂ under visible light is proposed. As shown in Fig. 19, under visible light irradiation, the metallic Ag nanoparticles absorb photons by a surface plasmon resonance effect to generate electron-hole pairs. The plasmon-excited electrons rapidly migrate to the conduction band (CB) of AgCl [46], leaving holes on the surface of the Ag nanoparticles, which can oxidize BPA. The electrons in the CB of AgCl are captured by Fe³⁺ to generate Fe²⁺, which can then react with H₂O₂ to generate •OH radicals through a typical Fenton reaction. Thus, the •OH radicals and holes are the main active species that degrade BPA in this system.

Fig. 19. Proposed mechanism for the reaction system.

4. Conclusions

A promising heterogeneous photo-Fenton catalyst, Ag/AgCl/Fe-S, was fabricated by impregnation of Ag/AgCl onto a hydroxy-iron modified sepiolite. The photo-Fenton catalytic activity of the catalyst was tested under various reaction conditions with BPA as a target contaminant. Our results showed that the Ag/AgCl/Fe-S catalyst exhibited excellent activity and stability under visible light illumination. Active species capture experiments revealed that the major active species in the heterogeneous photo-Fenton system catalyzed by Ag/AgCl/Fe-S were $\cdot\text{OH}$ radicals and holes. These active species exhibited synergistic effects in the heterogeneous photo-Fenton system, leading to higher photocatalytic activity than that of Ag/AgCl and Fe-sepiolite.

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Graphical Abstract

Chin. J. Catal., 2017, 38: 1726–1735 doi: 10.1016/S1872-2067(17)62902-4

Synthesis of Ag/AgCl/Fe-S plasmonic catalyst for bisphenol A degradation in heterogeneous photo-Fenton system under visible light irradiation

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In a heterogeneous photo-Fenton system $\cdot\text{OH}$ radicals and holes are the major active species contributing to the high photocatalytic activity of Ag/AgCl/Fe-S catalyst.

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Ag/AgCl/铁-海泡石异相可见光Fenton催化降解双酚A

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摘要: 光-Fenton技术是高级氧化技术中的一种,常用于难降解废水处理,由于其反应速度快、毒性低、反应条件温和而受到广泛关注.然而,传统的光-Fenton体系具有可见光利用率低、回收困难等缺点.为了解决这些问题,本文采用廉价易得、无污染、吸附能力强的天然矿物海泡石作为催化剂载体,并利用Ag/AgCl能够吸收可见光的表面等离子响应这一光学性质,合成了一种有潜力的非均相等离子体光催化剂Ag/AgCl/铁-海泡石催化剂(Ag/AgCl/Fe-S),并对该催化剂的形貌结构、性能和机理等进行了系统研究.

通过XRD, SEM, XPS, BET, UV-vis等表征手段对催化剂形貌、结构和可见光性能进行了分析.其中, XRD和SEM结果显示, Ag/AgCl粒子已经成功负载在Fe-海泡石上; XPS结果显示,铁氧化物的组成主要为FeOOH和Fe₂O₃; UV-vis结果显示,催化剂有较好的可见光吸收性能.

以双酚A为目标污染物,分别考察了Ag/AgCl/Fe-S, Ag/AgCl和Fe-海泡石的光-Fenton催化性能.结果显示, Ag/AgCl/Fe-S降解双酚A的效果明显优于另外两种催化剂,在H₂O₂浓度为6 mmol/L, pH为4,光照强度500 W, Ag/AgCl/Fe-S催化剂量为1.0 g/L,双酚A初始浓度为10 mg/L的条件下,1 h时,双酚A基本被完全降解,且3 h时,其矿化率达到61.2%;而Ag/AgCl和Fe-海泡石催化剂在同样的条件下完全降解双酚A至少要3 h,且其矿化率分别只有46.61%和28.85%.另外,还分别探讨了H₂O₂浓度、pH值、光照强度和催化剂剂量对双酚A降解的影响.

最后,通过活性物种捕获、ESR、电化学和PL实验对该体系的反应机理进行了探讨.活性物种捕获实验和ESR实验结果表明,羟基自由基(·OH)和空穴(h⁺)是该体系中的主要活性物种,且Ag/AgCl/Fe-S + H₂O₂ + vis体系产生的·OH明显多于Fe-S + H₂O₂ + vis体系.为了探讨·OH增多的原因,我们进行了电化学实验和PL实验.电化学实验结果显示, Ag/AgCl/Fe-S催化剂具有更低的阻抗,因此有利于电子-空穴分离. PL结果显示, Ag/AgCl/Fe-S催化剂的电子-空穴复合率更低.结合以上实验,我们提出了Ag/AgCl/Fe-S + H₂O₂ + vis体系对双酚A的降解机理,即一方面催化剂能够发生Fenton反应而产生·OH,另一方面,催化剂中的Ag/AgCl在可见光下由于表面等离子响应而产生电子-空穴,空穴本身可作为活性物种降解双酚A.同时,产生的电子被体系中的Fe³⁺捕获生成Fe²⁺,从而促进了铁循环,有利于体系中产生更多的·OH.最后,空穴和羟基自由基发生协同作用共同促进污染物降解.

关键词: 可见光; 光-Fenton; 等离子催化剂; Ag/AgCl/Fe-S; 海泡石

收稿日期: 2017-05-18. 接受日期: 2017-08-05. 出版日期: 2017-10-05.

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基金来源: 国家自然科学基金(41573118); 湖南省教育厅优秀青年项目(14B177); 湘潭大学专项基金.

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).