

Silver Reduction by Photocatalysis on α -FeOOH Surface

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Under UV light irradiation ($\lambda \geq 320$ nm), the photoreduction of silver ions on the surface of α -FeOOH occurs in an aqueous solution. The adsorption isotherm of Ag^+ on α -FeOOH was of the Langmuir type. The Langmuir-Hinshelwood kinetic model was used to describe the photoreduction reaction. From the TEM image, the average size of the produced Ag particles was about 25 nm. The mechanism of the photoinduced reduction of silver ions is semiconductor photocatalysis.

1. Introduction

Semiconductor materials acting as photocatalysts have been extensively researched for almost 40 years. One of the most important applications is to the photoreduction of metals and noble metals. The photoreduction of Au, Ag, Ph, Pd, Pt, Cu and other metals by TiO_2 , WO_3 and polyoxometallates has been often reported.^(1–9) The metal particles obtained through such reduction could be easily separated from the catalyst, and their small size induces some special functions, such as catalytic activity, optical properties, and chemical and biological sensing abilities.^(10,14)

However, in the past 20 years, sufficient attention has already been paid on green chemistry and chemistry engineering.^(15–19) The key factor in green chemistry is the application of nontoxic reagents, environmentally friendly solvents and renewable materials. In this study, we proposed a totally green approach to reclaiming silver ions. We synthesized the nanosized semiconductor material α -FeOOH and studied the photoreduction of Ag^+ over such a material, Only a few reports on the photoreduction of metals over α -FeOOH have been found.

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2. Experimental

2.1 Preparation of α -FeOOH

All the chemicals used in this work, such as AgNO_3 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ethylenediamine (EN) were of analytical grade, and used without further purification. Doubly distilled deionized water was used throughout this study.

α -FeOOH was prepared according to previous studies.^(20,21) The detailed process is as follows: Analytical-grade iron chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 20 mmol) and 25 ml of EN were dissolved in 200 ml of distilled water. The mixture was stirred for 50 min to form a solution before it was transferred into a Teflon-lined stainless steel autoclave up to 80% of the total volume, sealed, and maintained at 85°C for 12 h. After the reaction was completed, the resulting yellow solid was centrifuged, rinsed in distilled water repeatedly in order to eliminate the residual chloride ions, and finally dried at 80°C under vacuum.

2.2 Adsorption process

AgNO_3 adsorption on the catalyst was performed by mixing 50 mg of α -FeOOH and 100 mL of AgNO_3 aqueous solution of pH 8.0 in the dark. The initial Ag^+ concentrations were 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mM. The suspension was shaken at a constant rate for 60 min. 2 mL of the suspension was filtered through a membrane filter, and Ag^+ concentration was determined by inductively coupled plasma (ICP), IRIS Intrepid II XSP analysis. The amount of adsorption, Q_e , was calculated from the decreased concentration of $(C_0 - C_e)$ divided by the amount of catalyst used, i.e., 50 mg.

2.3 Photocatalysis

The light source used in the experiment was a medium-pressure mercury lamp from Philips (300 W, 365 nm in its dominant wavelength). The reactor was thermostated at 25°C. The suspension was stirred with a magnetic rod through the entire irradiation reaction. At certain intervals, 2 mL of the suspension was drawn with a syringe, filtered, and measured of its Ag^+ concentration.

2.4 Characterization

Transmission electron microscopy (TEM) was carried out using a JEOL JEM-200CX electron microscope. The surface area of the catalyst was detected using a BET instrument (F-Sorb 2400, GAPP).

3. Results and Discussion

3.1 Composition and structure of α -FeOOH

Figure 1 shows the X-ray diffraction pattern of α -FeOOH. It is clear that α -FeOOH nanocrystals are single-phased and that their crystal structure corresponds to the structure of the standard (No. 19-0629, JCPDS). The crystallinity of the prepared material is 75.21% that calculated from the XRD result. By using Scherrer's formula $D_{\text{hkl}} = K\lambda/(\beta^{1/2} \cos\theta)$, where D_{hkl} is the particle size of the (hkl) face, K is a constant (0.89), λ is

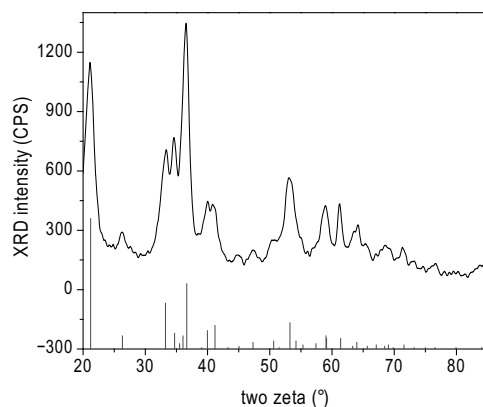


Fig. 1. XRD pattern of α -FeOOH. The vertical lines are standard patterns.

the X-ray wavelength (0.15406 for Cu K α), $\beta^{1/2}$ is the full width at half maximum (FWHM), and θ is the Bragg angle, the calculated diameter of the catalyst was found to be 13 nm. In addition, the BET detection showed that the sample surface reached 158 m²/g.

3.2 $AgNO_3$ adsorption on α -FeOOH

Owing to electrostatic interaction, Ag^+ could highly adsorb on α -FeOOH that has many negative charges. The pH of zero point of charge (pH_{PZC}) of α -FeOOH is near 8.5.⁽²⁰⁾ To ensure that no Ag^+ precipitation or Ag^+ adsorption on the surface of α -FeOOH occurs as much as possible, we decided to use pH 8.0 in this work. The concentration of α -FeOOH was 0.5 g/L and those of Ag^+ were 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mM. As we can see in Fig. 2, the adsorption isotherm is of the Langmuir type and the amount of equilibrium adsorption, Q , is plotted as a function of the equilibrium concentration C_e . According to the Langmuir equation

$$Q/Q_{\max} = KC_e/(1 + KC_e) \quad (1)$$

where Q is the amount of Ag^+ adsorbed at C_e , which is the equilibrium concentration of Ag^+ in the bulk solution, Q_{\max} is the maximum amount of adsorption, and K is the adsorption constant. The calculated Q_{\max} and K were 2.73×10^{-4} mol/g and 2.86×10^4 L/mol, which were obtained from the slope and intercept of the plot of C_e/Q vs C_e at $C_e = 0$, respectively. This indicates that Ag^+ adsorbed well on the α -FeOOH surface. No photocatalytic reaction occurred when there was no adsorption on the catalyst surface.

3.3 Photocatalytic reduction of $AgNO_3$ on α -FeOOH

Figure 3 shows the kinetics curve of Ag^+ photocatalytic reduction on α -FeOOH. As we can see, Ag^+ concentration decreased rapidly, which means that Ag^+ was photocatalytically reduced. At the same time, the suspensions changed from orange-brown to dark brown, which also indicates that Ag nanoparticles were produced. The average size of the Ag nanoparticles was estimated to be about 25 nm, seen as the black

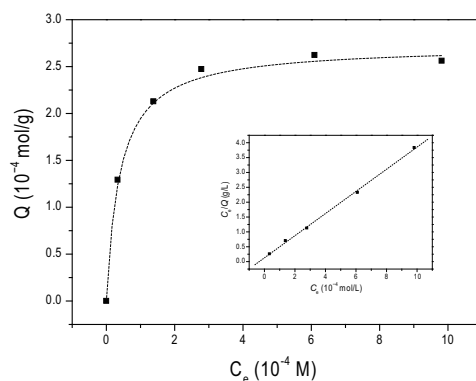


Fig. 2. Adsorption isotherm and the corresponding Langmuir plots (insert) of AgNO_3 on $\alpha\text{-FeOOH}$. pH= 8.0, $[\text{AgNO}_3]_0 = 0, 0.2, 0.4, 0.6, 0.8, \text{ and } 1.0$ mM.

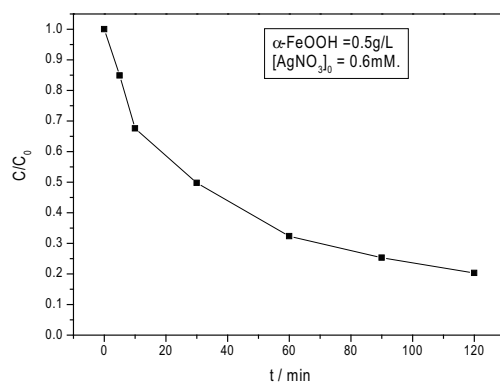


Fig. 3. Kinetics curve of Ag^+ photocatalytic reduction on $\alpha\text{-FeOOH}$.

area in the TEM image of the $\alpha\text{-FeOOH}$ sample after 120 min of irradiation in AgNO_3 solution (Fig. 4(b)). Compared with that shown in Fig. 4(a), the black area also means the production of Ag particles.

The Langmuir-Hinshelwood kinetics model was used to describe the initial photocatalytic reduction rate (r_0) for the initial Ag^+ concentration.⁽²²⁾ The initial photocatalytic degradation rate (r_0) is observed to be a function of the initial Ag^+ concentration (C_0). A linear plot of r_0^{-1} versus C_0^{-1} is obtained, as seen in Fig. 5, which gives the L-H rate constant k and the Langmuir adsorption constant K .

$$r_0 = kKC_0/1+KC_0$$

or

$$1/r_0 = 1/kK*1/C_0+1/k$$

(2)

The kinetic parameters k and K obtained using linear least-squares analysis were 10.7×10^{-6} M/min and 0.159×10^4 M/min, respectively.

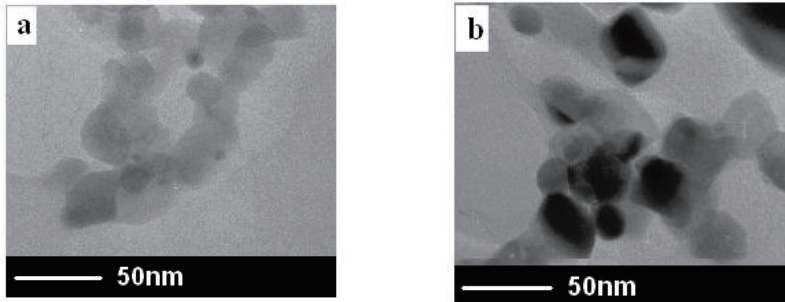


Fig. 4. TEM images of α -FeOOH of irradiation in AgNO_3 solution (a) before irradiation and (b) after 120 min of irradiation.

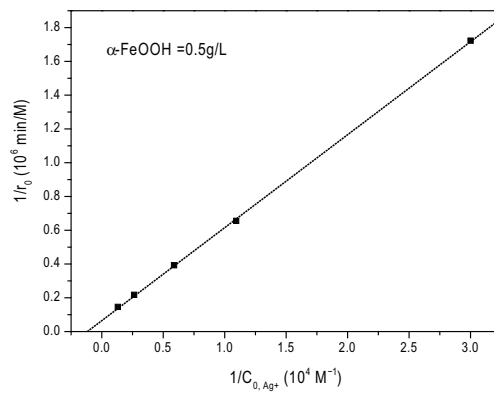
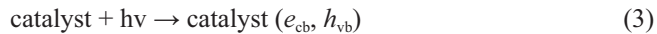


Fig. 5. Langmuir-Hinshelwood plots of $1/r_0$ vs $1/C_{0, \text{Ag}^+}$. $[\text{AgNO}_3]_0 = 0, 0.2, 0.4, 0.6, 0.8,$ and 1.0 mM .

3.4 Reaction mechanism

As a semiconductor material, silver ions on α -FeOOH are photoreduced mainly via a semiconductor photocatalytic mechanism. Under the UV light irradiation, e^- appeared in the conduction band of α -FeOOH and h^+ appeared in the valence band. e^- reduced the adsorbed Ag^+ into Ag nanoparticles and h^+ oxidized surface water into H^+ . No toxic reagents were released.



4. Conclusion

A green approach to reclaiming silver ions was proposed. The photoreduction of silver ions over α -FeOOH under UV light irradiation was researched. The Langmuir-Hinshelwood (L-H) kinetic model has been used to describe the photoreduction reaction. Nanosized Ag particles were formed and no toxic reagents were released. The reaction mechanism is a semiconductor photocatalytic mechanism.

References

- 1 Y. Taga: *Thin Solid Films* **517** (2009) 3167.
- 2 M. Hara, G. Hitoki, T. Takata, J. N. Kondo, H. Kobayashi and K. Domen: *Catal. Today* **78** (2003) 555.
- 3 D. B. Hamal and K. J. Klabunde: *J. Colloid Interface Sci.* **311** (2007) 514.
- 4 Z. Zou, J. Ye, K. Sayama and H. Arakawa: *J. Photochem. Photobiol., A* **148** (2002) 65.
- 5 B. Xin, L. Jing, Z. Ren, B. Wang and H. Fu: *J. Phys. Chem. B* **109** (2005) 2805.
- 6 W. Shangguan: *Sci. Technol. Adv. Mater.* **8** (2007) 76.
- 7 Y. Takahashi, P. Ngaotranwiwat and T. Tatsuma: *Electrochim. Acta* **49** (2004) 2025.
- 8 D. Yamashita, T. Takata, M. Hara, J. N. Kondo and K. Domen: *Solid State Ionics* **172** (2004) 591.
- 9 K. Gurunathan, J.-O. Baeg and S. M. Lee: *Int. J. Hydrogen Energy* **33** (2008) 2646.
- 10 B. Tryba, M. Piszcz, B. Grzmil, A. Pattek-Janczyk and A. W. Morawski: *J. Hazard. Mater.* **162** (2009) 111.
- 10 Y. Li, G. Chen, H. Zhang, Z. Li and J. Sun: *J. Solid State Chem.* **181** (2008) 2653.
- 11 Z. Shan, Y. Wang, H. Ding and F. Huang: *J. Mol. Catal. A* **302** (2009) 54.
- 12 H. Yan, J. Yang, G. Ma, G. Wu, X. Zong, Z. Lei, J. Shi and C. Li: *J. Catal.* **226** (2009) 165.
- 13 A. Maldotti, A. Molinari, R. Argazzi, R. Amadelli, P. Battioni and D. Mansuy: *J. Mol. Catal. A* **114** (1996) 141.
- 14 C.-C. Chang, C.-J. Liang and K.-W. Cheng: *Sol. Energy Mater. Sol. Cells* **93** (2009) 1427.
- 15 T. A. Taton: *Trends Biotechnol.* **20** (2002) 277.
- 16 J. García-Serna, L. Pérez-Barrigón and M. J. Cocero: *Chem. Eng. J.* **133** (2007) 7.
- 17 D. Fan and M. Afzaal: *Coord. Chem. Rev.* **251** (2007) 1878.
- 18 J. J. Schmidt and C. D. Montemagno: *Advanced Semiconductor and Organic Nano-Techniques* (Academic Press, New York, 2003) p. 505.
- 19 Z. Li, Z. Jia, Y. Luan and T. Mu: *Current Opinion in Solid State and Materials Science* **12** (2008) 1.
- 20 D.-E. Zhang, X.-J. Zhang, X.-M. Ni and H.-G. Zheng: *Mater. Lett.* **60** (2006) 1915.
- 21 S. Krehula, S. Popović and S. Musić: *Mater. Lett.* **54** (2002) 108.
- 22 W. Du, Q. Sun and Y. Liu: *Catal. Commun.* **10** (2009) 1854.