Synthesis of Ag@AgCl Core–Shell Structure Nanowires and Its Photocatalytic Oxidation of Arsenic (III) Under Visible Light

Yanyan Qin, Yanping Cui*, Zhen Tian, Yangling Wu and Yilian Li*

Abstract
Ag@AgCl core–shell nanowires were synthesized by oxidation of Ag nanowires with moderate FeCl₃, which exhibited excellent photocatalytic activity for As(III) oxidation under visible light. It was proved that the photocatalytic oxidation efficiency was significantly dependent on the mole ratio of Ag:AgCl. The oxidation rate of As(III) over Ag@AgCl core–shell nanowires first increased with the decrease of Ag₀ percentage, up until the optimized synthesis mole ratio of Ag nanowires:FeCl₃ was 2.32:2.20, with 0.023 mg L⁻¹ min⁻¹ As(III) oxidation rate; subsequently, the oxidation rate dropped with the further decrease of Ag₀ percentage. Effects of the pH, ionic strength, and concentration of humic acid on Ag@AgCl photocatalytic ability were also studied. Trapping experiments using radical scavengers confirmed that h⁺ and ·O₂⁻ acted as the main active species during the visible-light-driven photocatalytic process for As(III) oxidation. The recycling experiments validated that Ag@AgCl core–shell nanowires were a kind of efficient and stable photocatalyst for As(III) oxidation under visible-light irradiation.

Keywords: Arsenic (III), Photocatalytic oxidation, Ag@AgCl core–shell structure nanowires, Visible light

Background
As(III) is prevalent in anoxic groundwater, more harmful to human health, more mobile, and less efficiently removed than As(V); thus, pre-treatment by transforming As(III) to As(V) using different types of oxidation technologies is highly desirable for enhancing the immobilization of arsenic and is a prerequisite step for the use of sequent arsenic removal technologies such as coagulation, sorption, and membrane filtration. In recent years, photocatalytic oxidation technology has been considered as a potential and environmentally acceptable technique for As(III) oxidation [1]. Up to now, the photocatalyst TiO₂ has been reported to be widely used for the oxidation from As(III) to As(V) in many literatures [2]. Rapid oxidation from As(III) to As(V) can be realized in TiO₂ suspensions under UV irradiation [3]. The photocatalysis mechanism of TiO₂ involves the generation of valence band holes and conduction band electrons under UV illumination and the subsequent generation of hydroxyl (HO⁻) and superoxide radical (·O₂⁻) [4]. However, as we know, TiO₂ crystalline phase can only be photoexcited by UV light (λ < 388 nm, a small fraction of solar spectrum) which only accounts for about 5% of the solar light energy owing to its large band gap (3.2 eV). This practically rules out the use of sunlight as a light source.

In order to expand the absorption band of TiO₂-based photocatalysts, numerous attempts such as deposition with metal cations or nonmetal ions [5], decoration with another semiconductor [6, 7], and coating with organic matters [8] have been devoted to modify the photocatalyst TiO₂. By far, TiO₂-based nanoparticles functionalized with noble metal Pt nanoparticles [9] and sensitized with ruthenium dye [10, 11] have been used for As(III) oxidation, and all exhibited excellent photocatalytic oxidation performance for As(III) under visible light. Recently, visible-light driving photocatalysts were firstly used in As(III) oxidation by Hu et al. [12]; they found BiOI showed its great potential application value in photocatalytic oxidation of As(III). Later, Kim et al. firstly verified that tungsten trioxide (WO₃) [13] was also active under visible light and could successfully oxidize As(III) to As(V).
Considering energy utilization and saving, the investigation of the development of visible-light-driven photocatalysts has currently been considered to be a hot topic. Recently, various Ag-based compounds such as silver/silver halides (Ag/AgX, X = Cl, Br, and I), Ag₃PO₄ [14], Ag₂CO₃, Ag₃AsO₄, Ag₃SiO₅ [15], and Ag₃(SiO₄)₃(NO₃)₂ [16] were demonstrated to be a new family of highly efficient visible-light photocatalytic materials. Among the Ag-based visible-light-energized photocatalysts, silver/silver chloride (Ag/AgCl) is one of the most attractive candidates that can meet the requirements of excellent visible-light absorption, high photocatalytic efficiency, and stability, owing to the surface plasmon resonance (SPR) characteristics of metallic silver nanoparticles (NPs) which can promote charge separation/transfer efficiently [17]. It is mainly used in water photolysis, water disinfection, pollutant degradation [18], carbon dioxide reduction, etc. Core–shell structured nanomaterials have aroused considerable attention in recent years because of their unique and tunable properties by changing either the constituting materials or the ratio of core to shell. Such adjustable structures with suitable shell materials enable these functional materials to meet application requirements in protection, modification, and functionalization of core particles [19].

One-dimensional (1-D) nanostructure-based catalysts such as wires, rods, and tubes [20] have been the focus of many recent studies due to their intrinsic large aspect ratio which favors a directional charge transport with a reduced grain boundary. The superior charge transport property of the catalytic species generally plays an important role for the enhancement of photocatalytic performances [21]. Among them, 1-D core–shell nanowires (NW) have recently become of particular interest because the function of the fabricated core–shell nanostructure can be further tuned or enhanced by coating the nanowires with a thin layer of another material and adjusting their core and shell with different materials [21]. As the consequence, considering the specific and excellent properties of 1-D core–shell nanowires, Ag nanowires were first used as chemical templates for the synthesis of Ag@AgCl core–shell nanowires by Bi and Ye [22] through an in situ oxidation reaction between Ag nanowires and FeCl₃ solution, which exhibited and Ye [22] through an in situ oxidation reaction be-cause the function of the fabricated core-shell (NW) have recently become of particular interest be-

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Fe²⁺ ions could efficiently decompose methylene blue molecules under illumination of white light [25]. All these works illustrated that Ag@AgCl core–shell nanowires exhibited unique photocatalytic ability.

While As(III) photocatalytic oxidation performance using Ag@AgCl core–shell nanowires with different ratios of Ag nanowires:Ag⁺ was not researched, in this work, Ag@AgCl core–shell nanowires with different ratios of Ag: AgCl were synthesized to realize the rapid oxidation of As(III) under visible-light irradiation. Photocatalytic mechanism in this oxidation process for As(III) and recycling tests of Ag@AgCl core–shell nanowires were also studied.

**Methods**

**Materials**

Twenty milligrams per liter Ag nanowire dispersion was purchased from Xianfeng (China). Polyvinylpyrrolidone (PVP) was purchased from Sigma-Aldrich (USA), FeCl₃ and EDTA were purchased from Aladdin (USA), high-performance liquid chromatography (HPLC) grade methanol was purchased from Fisher (USA) for HPLC analysis, and tetrabutylammonium hydroxide was purchased from PerkinElmer (America). One thousand milliliters of As(III) standard solution (1000 mg/L) was prepared by dissolving 1.3203 g of As₂O₃ in the minimum amount of 4.0 M NaOH solution and then adjusting pH to 3.0 with 1.0 M H₂SO₄ solution. All solutions and subsequent dilutions were prepared using deionized water from a scientific nanopure water purifier (Thermo fisher, America) with a resistivity of less than 0.055 µS/cm.

**Instruments**

Morphological analysis was performed on a Hitachi SU8010 field-emission scanning electron microscope (FE-SEM) (Japan) with an acceleration voltage of 2 kV. The X-ray diffraction (XRD) data was detected via a XAXS D8-Focus X-ray diffractometer using Cu Kα radiation (Bruker, Germany). The operated conditions were controlled at 40 kV and 40 mA with a scan step width of 0.01°, and the scan range was 20°–90°.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a RBD upgraded PHI-5000C ESCA system (PerkinElmer, America) with Al X-ray source operating at 250 W. All the binding energies were referenced to the C 1 s peak at 284.8 eV of the surface adventitious carbon.

To detect concentration of As(III) and As(V), an ELAN DRC II inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer, America) equipped with an atomizer and a spray chamber was used. The ICP-MS normal operating parameters were as follows: RF power 1100 W, lens voltage 7.25 V, nebulizer gas...
flow rate 0.98 L/min, auxiliary gas flow rate 1.2 L/min, and plasma gas flow rate 15.00 L/min. Arsenic species were separated by Series 200 HPLC (PerkinElmer, America) with an automatic sample injector and directly introduced into ICP-MS. A C8 chromatographic column (PerkinElmer, America) was used with the mobile phase containing 1 mM tetrabutylammonium hydroxide, 0.05 mM dipotassium EDTA, and 0.05% methanol (pH 6.8).

Preparation of Ag@AgCl Core–Shell Nanowires
Ag@AgCl core–shell nanowire dispersions with different mole ratios of Ag:AgCl were synthesized using an in situ oxidation method. In a typical procedure, 250 μL dispersion of 20 mg/L Ag nanowires was added to 10 mL deionized water in every 25-mL beaker. One hundred fifty microliters aqueous solution of 1 M PVP was added to the dispersion of Ag nanowires. The dispersion was vigorously stirred with a magnetic stirrer for 5 min before different volume of 20 mM FeCl₃ solution was dropwise injected into the dispersion. The adding volume of 20 mM FeCl₃ solution which was freshly prepared in order to avoid hydrolysis was 0.5, 1, 1.5, 2.0, 2.2, and 4.0 mL, respectively. The reaction solution was stirred for 1 h until the color of the solution became stable. The reaction of the Ag nanowires with different volume FeCl₃ transformed them to Ag@AgCl core–shell nanowires with different mole ratios of Ag:AgCl. The resulting Ag@AgCl core–shell nanowires were centrifuged to remove excess FeCl₃ and PVP after reaction. Every kind of Ag@AgCl core–shell nanowires was dispersed in 0.5 mL of deionized water after being washed by water and alcohol. The synthesis was carried out at room temperature and could be scaled up.

The quality of Ag@AgCl core–shell nanowires synthesized with 250 μL Ag nanowire dispersion and 2.2 mL FeCl₃ solution was equal to 6 mg, and the mole ratio of Ag nanowires:FeCl₃ used in the preparation of this kind of Ag@AgCl core–shell nanowires was 2.32:2.20. Subsequently, this kind of synthesized Ag@AgCl core–shell nanowire dispersion was prepared in a large scale according to the above process, then dried in the air at 50 °C for 8 h, and grinding to obtain the solid powder of Ag@AgCl core–shell nanowires with the mole ratio of Ag nanowires:FeCl₃ = 2.32:2.20. The dry solid was used in the subsequent batch tests for influence factors, mechanism, and recycling.

Photocatalytic Oxidation for As(III)
Photocatalytic activities for As(III) oxidation were conducted in a 25-mL quartz beaker. The initial arsenite concentration of the solution with 0.02 mol/L Na₂SO₄ was fixed at 2.0 mg/L, and the pH was adjusted with H₂SO₄ or NaOH solution to 7.0. Prior to each As(III) oxidation, Ag@AgCl core–shell nanowires were added in the arsenite solution with a fixed volume of 20 mL. Prior to the irradiation, the suspension was kept in dark environment for 30 min to achieve adsorption/desorption equilibrium for arsenite. Then, the sample was exposed to 300 W halogen lamp equipped with a UV (less than 420 nm wavelength) cutoff filter, and the illumination intensity is shown in Fig. 1. In the whole photocatalytic process, air was aerated continuously through the suspension, which caused the reaction mixture to continuously stir. Water samples were withdrawn by a 0.4-mL pipette intermittently during photoreaction and filtered through a 0.22-μm PTFE filter. Duplicate or triplicate experiments were performed for each set.

To study the effect of the mole ratio of Ag:AgCl on photocatalytic oxidation for As(III), 0.5 mL suspension of Ag@AgCl core–shell nanowires with different mole ratios of Ag:AgCl for As(III) was respectively added in the 20 mL aqueous solution of 2.0 mg/L As(III).

In the subsequent batch experiments for influence factors, mechanism, and recycling, 6 mg solid of the Ag@AgCl core–shell nanowires synthesized with the mole ratio of Ag nanowires:FeCl₃ = 2.32:2.20 was added in the 20 mL aqueous solution of 2.0 mg/L As(III) in every test.

Results and Discussion
Physicochemical Characterization of Ag@AgCl Core–Shell Nanowires
Morphology Study (SEM)
Figure 2 presents a series of SEM images from samples containing 250 μL dispersion of Ag nanowires (20 mg/L) before and after they reacted with different volumes of 20 mM FeCl₃ solution, clearly showing the morphological evolution involved in the conversion of Ag nanowires to Ag@AgCl core–shell nanowires. As shown in Fig. 2a, the Ag nanowires exhibited smooth surfaces and
have diameters of 50–65 nm and lengths of 20–60 μm. After the addition of a small amount of FeCl₃ (i.e., 0.5 mL), some defect sites with higher surface energies on the surface of Ag nanowires were decorated with cubic nanocrystals, which made the surface to become rough (Fig. 2b); this indicated that Ag atoms around the defects of the Ag nanowire were oxidized to Ag⁺ ions, and Ag⁺ ions immediately reacted with Cl⁻ ions to nucleate and condense into AgCl nanocrystals at these defect sites on the surface of Ag nanowires. As the consequence, cubic AgCl nanocrystals were formed on the surface of Ag nanowires, and the surface area of the composite became larger. With the increasing additional amount of FeCl₃, more Ag atoms on the surface of Ag nanowires were converted into more AgCl nanocrystals (Fig. 2f), and the smooth surface of Ag nanowires gradually become the rough and thick shells of AgCl nanocrystals. It was observed that the surface area of Ag@AgCl core–shell nanowires became larger and larger with the mole ratio of AgCl. By theoretical calculation, 250 μL dispersion of 20 mg/L Ag nanowires totally changed to AgCl; 2.32 mL of 20 mM FeCl₃ solution was needed. Figure 2f also proved that the whole surface of Ag nanowires were completely converted into AgCl nanocrystals with the addition of 2.2 mL FeCl₃ solution, and the Ag nanowires thoroughly became the Ag@AgCl core–shell nanowires.

**Phase and Compositional Study (XRD)**

The corresponding XRD patterns of Ag nanowires were shown in Fig. 3a. The diffraction peaks at 2θ = 38.1°, 44.3°, 64.4°, and 77.5° marked with “black diamond” were assigned to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes of metallic Ag (JCPDS cards no. 04-0783). Figure 3b–f shows the XRD patterns of Ag@AgCl core–shell nanowires synthesized with different amount of FeCl₃. Apart from the peaks which ascribed to metallic Ag crystals, the diffraction peaks at 2θ = 27.8°, 32.2°, 46.3°, 54.8°, 57.6°, 67.4°, 74.5°, and 76.6°, which were marked with “white diamond,” were assigned to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), and (4 2 0) planes of AgCl crystal (JCPDS cards no. 31-1238). With the increase of the additional volume of FeCl₃ solution, the peak strength of metallic Ag gradually weakened after the oxidation reaction with FeCl₃ and the peaks of AgCl crystals significantly increased. When the volume of FeCl₃ solution was 2.2 mL, the SEM image (Fig. 2f) indicated that the surface of silver nanowires was almost completely covered by AgCl nanocrystals, and XRD diagrams showed that only a small amount of silver element still existed.
**X-ray Photoelectron Spectroscopy (XPS)**

XPS analysis was carried out to identify the chemical composition and binding states on the surface of Ag@AgCl core–shell nanowires synthesized with the mole ratio of Ag:FeCl₃ = 2.32:2.20. It was shown from Fig. 4a that the XPS spectrum of Cl 2p displayed two bands at 197.3 and 199.1 eV, which could be ascribed to Cl (2p½) and Cl (2p½), respectively [26]. The XPS spectrum of Ag 3d in Fig. 4b showed that the 3d½ and 3d¾ signals were located at 373.151 and 367.051 eV, respectively, and the splitting of the 3d doublet was about 6.0 eV. However, the two bands could not be divided into different peaks and were both attributed to the Ag⁺ of AgCl, which indicated that the peaks of metallic Ag centered at 368.73 and 374.91 eV were not contained in this XPS spectra, which meant that only AgCl crystals existed on the surface of Ag@AgCl core–shell nanowires.

**Photocatalytic Oxidation Experiments for As(III)**

**Photocatalytic Oxidation of Ag@AgCl Core–Shell Nanowires Synthesized with Different Mole Ratios of Ag Nanowires:FeCl₃ for As(III)**

To evaluate the photocatalytic activity of Ag@AgCl core–shell nanowires synthesized with different ratios of Ag:AgCl for As(III) oxidation, the photocatalytic oxidation of As(III) was carried out in aqueous solution under visible-light irradiation (Fig. 5a). For comparison, As(III) oxidation was also performed in Ag nanowire suspensions under the same condition. Ag nanowires showed no photocatalytic activity with visible light in 120 min. However, when Ag nanowires were etched into Ag@AgCl nanowires by FeCl₃, the transformation from As(III) to As(V) occurred (Fig. 5a), and it was clear that the photocatalytic oxidation rate of As(III) over Ag@AgCl core–shell nanowires increased with the rise of the mole ratio of AgCl first. The sample Ag@AgCl core–shell nanowires synthesized with the mole ratio of Ag nanowires:FeCl₃ = 2.32:2.20 showed highest activity than other core–shell Ag@AgCl and pure Ag nanowires. Afterwards, the photocatalytic activity decreased with the further rise of the mole ratio of AgCl. This result was the same as the study of Ma et al., which also indicated that the photocatalytic activity of Ag@AgCl was significantly dependent on the mole ratio of Ag⁺:Ag⁺ on the surface of the catalyst, the optimum ratio being 0.035 [19]. The ratio of Ag and AgCl was a significant factor influencing the photocatalytic oxidation rate. When the amount of metallic silver was very scarce, the generation of the electron–hole pairs on the metallic Ag may be decreased due to the SPR effect on the metallic Ag, and the active species were also cut down, which could reduce the photocatalytic activity. But when the amount of Ag was too high, some of the Ag nanoparticles became the active sites promoting the recombination of the photoelectrons and the holes, which also reduced the photocatalytic activity [27].

Because of the strong photosensitive property of AgCl phase without Ag, under the sunlight, the photogenerated electron combines with an Ag⁺ ion to form an Ag⁰ atom; ultimately, a cluster of silver atoms is formed within a AgCl particle upon the repeated absorption of photons. So AgCl is instable under sunlight and seldom used as a photocatalyst. However, when a certain amount of Ag nanoparticles are deposited onto AgCl particles, electron–hole separation occurs smoothly in the presence of Ag nanoparticles, so metallic Ag plays an important role on the photoinduced stability of Ag/AgCl composite [28].

From the SEM images (Fig. 2), it could be observed that the surface area of Ag@AgCl core–shell nanowires became larger and larger with the mole ratio of AgCl. As we know, a large specific surface area as a photocatalytic material is conducive to adsorption of pollutants [29]. The investigation of Matsui et al. clearly demonstrated that the catalytic activity of ZrO₂/carbon cluster composite materials increased with the increase of their surface areas [30]. Generally, the performances of semiconductor oxide photocatalysts are dependent on the surface area, mesoporosity, crystallinity, morphology [31], and active facets exposed [32]. The exposed high-index facets (1 1 1) of the AgCl crystals in the Ag@AgCl
core–shell nanowires also caused high photocatalytic oxidation efficiency for As(III).

**Kinetic Study of As(III)**

An exponential decay of As(III) concentration with the irradiation time was evident, indicating the photocatalytic oxidation of As(III) was fitted to pseudo-first-order kinetics (Fig. 5b).

\[
-\ln\left(\frac{C_t}{C_0}\right) = k_r t = k_{\text{app}} t
\]

where \(C_t\) is the concentration of As(III) at time \(t\), \(t\) is the reaction time, \(C_0\) is the initial concentration of As(III) solution (mg/L), and the slope \(k_{\text{app}}\) (min\(^{-1}\)) is the apparent pseudo-first-order reaction rate constant and is calculated from the slope of the plot of \(-\ln(C_t/C_0)\) vs. time.

In this case, \(C_0 = 2.669 \times 10^{-5}\) mol/L.

The rate constants \(k_{\text{app}}\) (Table 1) of Ag@AgCl core–shell nanowires which were synthesized with different ratios of Ag nanowires:FeCl\(_3\) from 2.32:0.5 to 2.32:4.0 were increased from 0.009 to 0.023 min\(^{-1}\) and then decreased to 0.016 min\(^{-1}\). The rate of oxidation (mg L\(^{-1}\) min\(^{-1}\)) was proportional to the rate constant \(k_{\text{app}}\) (min\(^{-1}\)).

**Effects of pH and Ionic Strength**

To investigate the effect of pH on photocatalytic oxidation of As(III) over Ag@AgCl core–shell nanowires, the experiment was carried out at different values of initial pH (3.0, 7.0, and 10.0), with an initial As(III) concentration of 2.00 mg/L. The As(III) oxidation percentages at initial solution pH 3.0, 7.0, and 10.0 in 2 h were found to be 39.60, 75.55, and 83.13%, respectively (Fig. 6). Thus, it was concluded that the conversion rate of As(III) was significantly influenced by pH and increased with the rise of the initial pH. In the acid reaction solution, the reactive radical of \(\cdot\text{O}_2^-\) combined with \(\text{H}^+\) to form \(\text{HO}_2\) and then generated \(\text{H}_2\text{O}_2\) (Eqs. 2 and 3). The oxidation activity of \(\text{H}_2\text{O}_2\) for As(III) was less than \(\cdot\text{O}_2^-\), which might be the reason why the oxidation of As(III) decreased as the pH of the solution dropped.

\[
\cdot\text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^-.
\]
\[
2\text{HO}_2^- \rightarrow \text{O}_2 + \text{H}_2\text{O}_2
\]
\[
\text{H}_3\text{AsO}_3 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{AsO}_4^- + \text{H}_2\text{O} + \text{H}^+ \quad \text{(when pH is less than 6.76)}
\]

**Table 1** Pseudo-first-order kinetic parameters of As(III) photocatalytic oxidation

| Quantity of FeCl\(_3\) (mL) | \(C_0\) (Exp.) | \(C_0\) (cal.) | \(R^2\) | \(k_{\text{app}}\) |
|-----------------------------|----------------|----------------|--------|--------------|
| 0.5                         | 1.711          | 1.586          | 0.927  | −0.009       |
| 1.0                         | 1.738          | 1.555          | 0.930  | −0.010       |
| 1.5                         | 1.625          | 1.489          | 0.958  | −0.010       |
| 2.0                         | 1.668          | 1.565          | 0.973  | −0.015       |
| 2.2                         | 1.635          | 1.494          | 0.965  | −0.023       |
| 4.0                         | 1.629          | 1.406          | 0.910  | −0.016       |
When NaSO₄ concentrations in As(III) solution was 0.02 and 0.06 M, the conversion percentages of As(III) were 75.55 and 66.75%, respectively. It is known that Na⁺ is an alkaline metal ion and at its maximum oxidation state; therefore, it will not compete as hole scavenger and does not show distinct effect on photocatalytic reaction [33].

**Effect of Humic Acids**

The concentration of humic substance in natural water varies from 0.03 to 30 mg/L. Arsenic-contaminated groundwater often contains high levels of dissolved organic carbons. The influence of humic acids (HA) on the photocatalytic oxidation of As(III) over Ag@AgCl core–shell nanowires was tested, as shown in Fig. 7. The addition of HA slightly enhanced the oxidation rate of As(III) over Ag@AgCl core–shell nanowires at pH 7.0 and pH 10.0. HA could serve as a hole scavenger which could facilitate the production of superoxides and H₂O₂ under visible-light illumination; as the consequence, the As(III) photooxidation rate was enhanced [34]. Therefore, the HA-enhanced effect should be ascribed to the hole scavenging effect.

**Photocatalytic Mechanism**

It has been widely accepted that series of active species may be generated to degrade pollutants in photocatalytic process, including superoxide radical (·O₂⁻), photogenerated holes (h⁺) in the valence bond, and hydroxyl radicals (·OH) [35]. Herein, p-benzoquinone (1,4-BQ) was employed for quenching ·O₂⁻, tertiary butanol (TBA) for ·OH, and EDTA for h⁺, to study the photocatalytic mechanism of Ag@AgCl (as shown in Fig. 8). The photocatalytic oxidation of As(III) over Ag@AgCl core–shell nanowires was not almost affected by the addition of TBA (Fig. 8a), indicating that ·OH was not produced in the photocatalytic reaction system of Ag@AgCl core–shell nanowires. However, the photocatalytic performance was strongly restrained in the presence of BQ or EDTA. The oxidation rate of As(III) was decelerated obviously from 75.55 to 0% in the presence of EDTA (1 mmol/L). It could be elucidated that h⁺ was generated in the photodegradation process and h⁺ was acted as the dominant active species responsible for the photocatalytic oxidation of As(III) under visible-light irradiation. The oxidation rate of As(III) was reduced to 25.25% by 1,4-BQ (4 mmol/L) addition, indicating that ·O₂⁻ played an important role in the photocatalytic process. Therefore, it could be concluded that h⁺ and ·O₂⁻ were the main active species for the photocatalytic oxidation of As(III) on Ag@AgCl core–shell nanowires under visible-light irradiation.

In a hybrid composite, the band positions of individual components are crucial to determine the excitation, migration, and recombination of the photogenerated electrons and holes, which is also important for the efficiency of the photocatalytic activity. The valence band (VB) and conduction band (CB) potentials of Ag@AgCl at the point of zero charge are calculated by the following empirical Eqs. (5) and (6):

\[
E_{vb} = X - E_0 + 0.5E_g
\]  
(5)

\[
E_{cb} = E_{vb} - E_g
\]  
(6)

Where \(E_{vb}\) is the VB edge potential, \(X\) is the absolute electronegativity of the semiconductor, \(E_0\) is the energy of free electrons on the hydrogen scale (ca. 4.5 eV), and \(E_g\) is the band gap energy of the semiconductor. Thus, the CB and VB potentials of AgCl are estimated to be −0.06 and 3.19 eV, respectively [36].

Based on the above observations and the literature, the possible transfer routes of the photoexcited electrons and holes and a feasible photocatalytic oxidation mechanism for As(III) in the presence of Ag@AgCl core–shell nanowires under visible light are proposed and schematically illustrated in Fig. 8b. Because AgCl has a direct band gap of 5.15 eV (241 nm) and an indirect bandgap of 3.25 eV (382 nm) [37], it cannot be excited under the illumination of visible light (\(\lambda_{ex} > 420\) nm). However, metallic Ag nanoparticles (Ag NPs) can absorb a photon under visible-light irradiation leading to electron–hole (e⁻–h⁺) separation because of its strong intrinsic plasmon resonance (SPR) effect (Eq. (7)). The photoinduced electrons transiently occupy the CB of Ag and then sequentially transfer to the CB of AgCl, while the plasmon-induced holes (h⁺) remained on the surface of Ag NPs. This electrons transfer process can effectively promote the charge separation and inhibit the recombination.
of the electron–hole pair. Since the CB energy level of AgCl (−0.06 V vs NHE) is more negative than the potential of \( \text{O}_2/\cdot\text{O}_2^- \) (−0.046 V vs NHE), the electrons in the CB of AgCl will be trapped by the surface adsorbed molecular \( \text{O}_2 \) to generate \( \cdot\text{O}_2^- \) (Eq. (8); [38]). \( \cdot\text{O}_2^- \) is a kind of active species with strong oxidation power that can convert As(III) to As(V) (Eqs. (11) and (12)). In the meantime, a few electrons combine with Ag\(^+\) ions to form Ag\(0\) atoms with the lixiviation of chloridion (Cl\(^-\)) , which is another competing trapping route for the photoinduced electrons (Eq. (9); [17]). Plasmon-induced h\(^+\) on the surface of Ag NPs can directly oxidize As(III) to As(V) (Eq. (13)).

\[
\begin{align*}
\text{AgNPs(SPR) + hv} & \rightarrow \text{e}^-(\text{electron}) + \text{h}^+(\text{hole}) \\
\text{O}_2 & \rightarrow \cdot\text{O}_2^- \\
\text{AgCl} + \text{e}^- & \rightarrow \text{Ag}^0 + \text{Cl}^- \\
\text{h}^+ + \text{Cl}^- & \rightarrow \text{Cl}^0 \\
\text{H}_3\text{AsO}_3 + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{AsO}_4^- + \text{H}_2\text{O} + \text{H}^+ \\
(\text{pK}_a = 6.76, \text{when pH is less than 6.76}) & \\
3\text{H}_3\text{AsO}_3 + 2\cdot\text{O}_2^- + 4\text{OH}^- & \rightarrow 3\text{H}_2\text{AsO}_4^- + 5\text{H}_2\text{O} \\
(\text{pK}_a = 6.76, \text{when pH is greater than 6.76}) & \\
2\text{h}^+ + \text{As(III)} & \rightarrow \text{As(V)} \\
(14)
\end{align*}
\]

**Recycling**

In addition to efficiency, stability and recyclability of practical photocatalysts are also important for applications. As we know, lifetime of photocatalysts is an important factor for practical application as well as its photocatalytic activity. To test the stability and reusability, Ag@AgCl core–shell nanowires synthesized with Ag nanowires:FeCl\(_3\) = 2.32:2.20 were selected as the model photocatalysts to test the repeatability of As(III) oxidation and were reused for photocatalytic oxidation of As(III) 20 times with same conditions. Results are shown in Fig. 9a. The oxidation percentage of As(III) decreased from 77.3% in the 1st run to 22.4% in the 20th cycle. The decrease of the oxidation efficiency was due to some catalyst washout during the recycling steps. To better understand the decrease reason of photocatalytic oxidation efficiency during recirculation process, the samples of Ag@AgCl core–shell nanowires after 20 cycles of photocatalytic oxidation for As(III) were tested by XRD and SEM. It was found that the diffraction peak of Ag\(^0\) at 38.2° with enhanced intensity could be observed in the XRD pattern of the sample after the twentieth cycle (Fig. 9b). This revealed the continuous transformation from AgCl into Ag\(^0\) with the leaching of chloridion (Cl\(^-\)) during the recycling process. Such kind of transformation led to a deviation from the optimum ratio of AgCl to Ag with the best photocatalysis performance, which should be responsible for the continuous and slight decrease of photocatalysis activity in the recycle runs. What is more, the formation of Ag nanoparticles resulted in the decrease of the interface area between Ag and AgCl, which was another reason for the decrease of photocatalytic activity. This phenomenon was also found in other Ag@AgCl nano-composites [39]. The SEM image (Fig. 9c) showed that
the core–shell nanowires cracked during the photocatalytic activity.

The 20th recycled Ag@AgCl nanowires were collected and reacted with FeCl₃ solution again; the SEM image showed that Cl-afresh core–shell nanowires structure was rebuilt, but cracked more seriously which might be caused in the process of ultrasonic dispersion, and became thicker because of the agglomeration (Fig. 9d). The XRD patterns showed that the mole ratio of Ag:AgCl in regenerated Ag@AgCl core–shell nanowires returned the optimum again (Fig. 9b). The As(III) oxidation rate of regenerated Ag@AgCl core–shell nanowires was increased to 40.2% (Fig. 9a), which proved Cl-afresh of recycled Ag@AgCl core–shell nanowires could efficiently prolong the lifetime of prepared photocatalysts.

Conclusions

In order to exploit more visible-light-responding photocatalysts for As(III) oxidation, Ag@AgCl core–shell nanowires synthesized via a controllable oxidation reaction with different mole ratios of Ag nanowires:FeCl₃ in solution were selected to conduct the photocatalytic oxidation experiment for As(III). Ag@AgCl core–shell nanowires showed excellent photocatalytic activity toward As(III) oxidation and the mole ratio of Ag nanowires:FeCl₃ had obvious influence on its photocatalytic ability. Photocatalytic oxidation rate of As(III) was favored at high pH and could be promoted by humus acid. High concentration of Na₂SO₄ in solution will slightly inhibit the photocatalytic oxidation reaction. With quenching agent, the holes and ·O₂⁻ were proved to be the main active materials in the photocatalytic oxidation process for As (III). The photocatalytic ability of Ag@AgCl core–shell nanowires gradually decreased with recycle times, and Ag@AgCl core–shell nanowires after recycling could be efficiently regenerated by Cl-afresh. The prepared Ag@AgCl core–shell nanowires were proved to be an efficient and relatively stable visible-light-induced photocatalyst for As(III) oxidation in water with high humic substance.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (No: 40902070), Fundamental Research Funds for the Central Universities, China University of Geosciences (Wuhan) (2017, No: CUG110414), Nature Science Foundation of Hubei Province (No: 2016CFB609), and Experimental Technology Program of China University of Geosciences (Wuhan) (No: SJ-201509).

Authors’ Contributions

YQ prepared the nanomaterials, carried out the structural analyses of the samples, conducted the photocatalytic experiments, and drafted the manuscript. ZT and YW took part in the experimental section. YC and YL proposed, designed, and guided the experiments. YC edited the manuscript. All the authors read and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

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1. Mohan D, Pittman CU Jr (2007) Arsenic removal from water/wastewater using adsorbents—a critical review. J Hazard Mater 142:1–53
2. Tsimas ES, Tyrovola K, Xekoukoulotakis NP, Nikolaidis NP, Diamadopoulos E, Mantzavinos D (2009) Simultaneous photocatalytic oxidation of As(III) and humic acid in aqueous TiO2 suspensions. J Hazard Mater 169:376–385
3. Blissen M, Veillard-Baron MM, Schindelien AI, Frimmel FH (2001) TiO2-catalyzed photooxidation of arsenite to arsenate in aqueous samples. Chemosphere 44:751–757
4. Ryu J, Choi WY (2006) Photocatalytic oxidation of arsenite on TiO2: understanding the controversial oxidation mechanism involving superoxide and the effect of alternative electron acceptors. Environ Sci Technol 40:7094–7099
5. Chen H, Chen K, Lai S, Dang Z, Peng Y (2015) Photoelectrochemical oxidation of azo dye and generation of hydrogen via C-N co-doped TiO2 nanotube arrays. Sep Purif Technol 146:143–153
6. Gao X, Liu X, Wang X, Zhu Z, Xie Z, Li J (2016). Photodegradation of unsymmetrical dimethylhydrazine by TiO2 nanorod arrays decorated with CdS nanoparticles under visible light. Nanoscale Res Lett 11:496–476.
7. Cai H, Liang P, Hu Z, Shi L, Yang X, Sun J, et al (2016) Enhanced photoelectrochemical activity of ZnO-coated TiO2 nanotubes and its dependence on ZnO coating thickness. Nanoscale Res Lett 11:104–115
8. Giovannetti R, D’Amato CA, Zannotti M, Rommizzo E, Gonnella R, Minicucci M, et al (2015) Visible light photoactivity of polypropylene coated nano-TiO2 for dyes degradation in water. Sci Rep 5:17901–17913.
9. Qin Y, Li Y, Tian Z, Wu Y, Cui Y (2016). Efficiently Visible-light driven photoelectrocatalytic oxidation of As(II) at low positive biasing using Pt/TiO2 nanotube electrode. Nanoscale Res Lett 11:32–45.
10. Li X, Leng W (2012) Highly enhanced dense sensitized photocatalytic oxidation of arsenite over TiO2 under visible light by I− as an electron relay. Electrochem Commun 22:185–188
11. Li X, Leng W, Cao C (2013) Quantitatively understanding the mechanism of highly enhanced regenerated dye sensitized photooxidation of arsenite over nanostructured TiO2 electrodes under visible light by I−. J Electroanal Chem 703:70–79
12. Hu J, Weng S, Zheng Z, Pei Z, Huang M, Liu P (2014) Solvents mediated-synthesis of BiOCl photocatalysts with tunable morphologies and their visible-light driven photocatalytic performances in removing arsenic from water. J Hazard Mater 264:293–302
13. Kim J, Moon G, Kim S, Kim J (2015) Photocatalytic oxidation mechanism of arsenite on tungsten trioxide under visible light. J Photoch Photobio A 311:35–40
14. Bi Y, Ouyang S, Umezawa N, Cao J, Ye J (2011) Facet effect of single-crystalline Ag3PO4 sub-microcrystals on photocatalytic properties. J Am Chem Soc 133:6490–6492
15. Zhu X, Wang P, Huang B, Ma X, Qin X, Zhang X et al (2016) Synthesis of novel visible light response Ag8W4O16/AgCl-nanoparticle core-shell nanorods. J Mater Chem 22:1487–1494
16. Li W, Ma Z, Bai G, Hu J, Guo X, Dai B et al (2015) Dopamine-assisted one-step fabrication of Ag@AgCl nanophotocatalyst with tunable morphology, composition and improved photocatalytic performance. Appl Catal B: Environ 174:43–48
17. Ma B, Guo J, Dai W, Fan K (2012) Ag-AgCl/WO3 hollow sphere with flower-like structure and superior visible photocatalytic activity. Appl Catal B: Environ 123:193–199
18. Wang P, Huang B, Qin X, Zhang X, Dai Y, Wei JY et al (2008) Ag@AgCl: a highly efficient and stable photocatalyst active under visible light, Angew Chem Int Ed 47:7931–7933
19. Cheng P, Wang Y, Xu L, Sun P, Su Z, Jin F et al (2016) High specific surface area urchin-like hierarchical ZnO-TiO2 architectures: hydrothermal synthesis and photocatalytic properties. Mater Lett 175:52–55
20. Matsui H, Ohkura N, Karpuchcarmy S, Yoshihara M (2013) The effect of surface on the photocatalytic behavior of ZrO2/Carbon clusters composite materials. Ceram Int 39:5827–5831
21. Chen D, Huang F, Cheng Y, Caruso RA (2009) Mesoporous anatase TiO2 beads with high surface areas and controllable pore sizes: a superior candidate for high-performance dye-sensitized solar cells. Adv Mater 21:2206–2210
22. Lou Z, Huang B, Qin X, Zhang X, Cheng H, Li Y et al (2012) One-step synthesis of AgCl concave cubes by preferential overgrowth along <111> and <110> directions. Chem Commun 48:3488–3490
23. Wang D, Li Y, Li G, Wang C, Zhang W, Wang Q (2013) Modeling of quantitative effects of water components on the photocatalytic degradation of 17 alpha-ethynylestradiol in a modified flat plate serpentine reactor. J Hazard Mater 254:64–71
24. Lee H, Choi W (2002) Photocatalytic oxidation of arsenite in TiO2 suspension: kinetics and mechanisms. Environ Sci Technol 36:3872–3878
25. Serpone N (1995) Brief introductory remarks on heterogeneous photocatalysis. Sol Energ Mat Sol C 38:3869–379
26. Ye L, Liu J, Gong C, Tian L, Peng T, Zan L (2012) Two different roles of metallic Ag on Ag/AgCl/BIOX (X = Cl, Br) visible light photocatalysts: surface plasmon resonance and Z-scheme bridge. ACS Catal 2:1677–1683
27. Glaus S, Calzaferri G (2003) The band structures of the silver halides AgF, AgCl, and AgBr: a comparative study. Photoch Photobiol Sci 2:398–401
28. Tang Y, Jiang Z, Xing G, Li A, Kanhere PD, Zhang Y et al (2013) Efficient Ag@AgCl cubic cage photocatalysts profit from ultrafast plasmon-induced electron transfer processes. Adv Funct Mater 23:2922–2940
29. Daupor H, Wongnawa S (2014) Urchinlike Ag/AgCl photocatalyst: synthesis, characterization, and activity. Appl Catal A-Gen 473:59–69
30. Zhu MS, Chen PL, Liu MH (2012) Highly efficient visible-light-driven plasmonic photocatalysts based on graphene oxide-hybridized one-dimensional Ag/AgCl heteroarchitectures. J Mater Chem 22:21487–21494
31. Sun YG (2013) Conversion of Ag nanowires to Ag3O4 nanowires decorated with Au nanoparticles and their photocatalytic activity. J Phys Chem C 117:2127–2133
32. Li W, Ma Z, Bai G, Hu J, Guo X, Dai B et al (2015) Synthesis of high efficient visible-light-driven photocatalysts based on graphene oxide-hybridized one-dimensional Ag/AgCl heteroarchitectures. J Mater Chem 22:21487–21494
33. Daupor H, Wongnawa S (2014) Urchinlike Ag/AgCl photocatalyst: synthesis, characterization, and activity. Appl Catal A-Gen 473:59–69
34. Qin et al. Nanoscale Research Letters (2017) 12:247

References

Received: 10 December 2016 Accepted: 21 March 2017

Published online: 04 April 2017

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