Regular Article

Silver chloride enwrapped silver grafted on nitrogen-doped reduced graphene oxide as a highly efficient visible-light-driven photocatalyst

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GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:

Received 18 April 2017

Revised 10 June 2017

Accepted 12 June 2017

Available online 13 June 2017

Keywords:

AgCl@Ag/N-rGO
 Interfacial contact
 Photocatalyst
 Visible light

ABSTRACT

The visible-light-driven plasmonic photocatalyst silver chloride enwrapped silver/nitrogen-doped reduced graphene oxide (AgCl@Ag/N-rGO) was prepared by a facile hydrothermal *in situ* oxidation method and characterized by Scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform-infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and UV–vis diffuse reflectance spectroscopy (UV–vis DRS). The characterization results reveal that Ag nanoparticles (NPs) were first grafted on N-rGO via N-groups as anchor sites and then enwrapped by AgCl by *in situ* oxidation. Close interfacial contact favors efficient electron transfer, leading to high photoactivity and photostability for the degradation of various toxic organic pollutants. The photocatalytic performance of this photocatalyst was significantly higher than that of AgCl@Ag/rGO and other related photocatalysts due to the *in situ* introduction of N-groups. Additionally, the used catalyst can be recycled without an appreciable loss of catalytic activity. Based on electron spin resonance and cyclic voltammetry analyses, the electron transfer processes were confirmed to occur from plasmon-induced Ag NPs to AgCl and from N-rGO to Ag NPs, and pollutants could be oxidized through the loss of electrons to N-rGO by the interaction between the pollutants and N-rGO. The active species of superoxide anion radicals ($O_2^{\cdot-}$), photogenerated holes (h^+) and surface-adsorbed $\cdot OH$ played roles in pollutant photodegradation. Accordingly, the plasmon-induced electron transfer processes elucidated photostability of AgCl@Ag/N-rGO. AgCl@Ag/N-rGO has a potential application in water purification due to its high photoactivity and photostability.

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1. Introduction

With the rapid growth of worldwide industrialization, severe environmental problems have become a major concern [1,2]. Photocatalysis is an attractive approach for solving environmental issues using solar energy conversion [3,4]. The most widely investigated photocatalyst is TiO_2 owing to its low cost and structural stability. Unfortunately, due to the wide band gap of TiO_2 , it is only activated under ultraviolet irradiation [5]. For solar energy utilization, the search for visible-light-driven photocatalysts is still one of the most challenging tasks.

Among the various types of visible-light-driven photocatalysts, plasmonic photocatalysts comprising metal nanoparticles (NPs) (such as Au, Pt, and Ag) have attracted particular attention in the past several years due to the surface plasmon resonance (SPR) effect of the metal NPs in the visible region [6,7]. More specifically, silver/silver halide-based (Ag/AgX , $\text{X} = \text{Br}, \text{Cl}$) nanomaterials have been reported for their excellent photocatalytic performances in the degradation of pollutants under visible-light irradiation [8,9]. For example, several Ag/AgX -based photocatalysts, including Ag/AgCl [10], Ag/AgBr [11] and Ag/AgI [12] have been developed. The high photocatalytic activity of these catalysts is mainly ascribed to the SPR effect of the Ag NPs and the interaction between Ag and AgX. However, the low surface area of pure Ag/AgX and the recombination of plasmon-induced electron-hole pairs before arriving at the surface lead to a loss of plasmonic photoactivity [13]. Therefore, it is meaningful to synthesize a new hybrid material that can enhance the photocatalytic activity and stability through increasing the surface of area and promoting the charge transfer.

Reduced graphene oxide (rGO), a unique sp^2 hybrid carbon network material, has received considerable attention owing to its extremely high surface area, high thermal and chemical stability, and excellent charge carrier mobility [14]. To enhance the specific capacity of graphene, chemical doping of graphene, such as B [15], N [16] and organic molecules [17], has been investigated. Among them, N-doped reduced graphene oxide (N-rGO) was found to aid in tailoring its electronic properties and improving its photocatalytic efficiency [18]. Three typical N-bonds quaternary N, pyridinic N and pyrrolic N, in N-rGO have been widely reported and their effects on the photocatalytic performance have also been investigated [19]. Compared with pristine graphene, N-doped graphene has more activated regions, which can anchor metals [20] or metal oxides [21] on the reduced graphene materials. For example, Marcilla et al. [22] reported NiCoMnO_4 nanoparticles anchored on nitrogen-doped graphene nanosheets as highly efficient bifunctional electrocatalysts for oxygen reduction evolution reactions. Niu et al. [23] constructed AgBr nanoparticles supported on a $\text{g-C}_3\text{N}_4$ -decorated nitrogen-doped graphene nanocomposite, which demonstrated a high efficiency for organic contaminant degradation and CO_2 reduction under visible light. Therefore, plasmonic photocatalysts anchored on nitrogen-doped graphene nanosheets could be more efficient and stable for wastewater treatment. Moreover, Quan et al. [24] synthesized a plasmonic photocatalyst $\text{Ag}/\text{AgCl}/\text{RGO}$ through a precipitation reaction followed by photoreduction, which exhibited an excellent photocatalytic activity. Wei et al. [25] prepared nitrogen-doped graphene-modified AgX/Ag ($\text{NG-AgX}/\text{Ag}$, $\text{X} = \text{Br}, \text{Cl}$) by a co-precipitation method, which showed a greatly improved photocatalytic activity compared to AgX/Ag . These photocatalysts were constructed by compositing individual components. Due to close interfacial interactions that efficiently promote charge transfer [26], it is necessary to develop an *in situ* convenient way to prepare the effective composite photocatalysts.

In this study, we anchored AgCl/Ag on N-rGO by a facile hydrothermal-*in situ* oxidation method. The obtained composites

showed distinctly enhanced photocatalytic activities and stabilities for the degradation of pollutants, including 2-chlorophenol (2-CP), bisphenol A (BPA), phenol, and 2,4-dichlorophenoxyacetic acid (2,4-D) under visible light irradiation, resulting from the SPR of the Ag NPs and the anchoring effect between the Ag NPs and the N-rGO. The possible mechanism for the photocatalytic system was investigated.

2. Experiment

2.1. Chemicals

Silver nitrate (AgNO_3), Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and phenol were purchased from Sinopharm Chemical Reagent Co., Ltd. BPA, 2,4-D, diphenhydramine (DP), and phenytoin (PHT) were obtained from Acros (Geel, Belgium). 2-CP was purchased from Sigma-Aldrich (St Louis, United States). 5-*tert*-Butoxy carbonyl-5-methyl-1-pyrroline-N-oxide (BMPO) was supplied by the Bioanalytical Lab (Sarasota, FL). All chemicals were at least analytical grade. The molecular structures of 2-CP, phenol, BPA, 2,4-D, DP and PHT are shown in Fig. S1. Deionized water was used throughout this study.

2.2. Preparation

A graphene oxide (GO) dispersion in water was prepared by sonication of graphite oxide that was obtained via a chemical exfoliation of natural graphite following the modified Hummers method [27]. An $\text{Ag}/\text{N-rGO}$ nanocomposite was synthesized by a hydrothermal method. Typically, 60 mL GO solution (0.05 wt%) and 100 mL silver ammonia solution (0.1 M AgNO_3 in 3 M $\text{NH}_3 \cdot \text{H}_2\text{O}$) were mixed and hydrothermally treated at 130 °C for 3 h. After cooling down to room temperature, the resulting samples were centrifuged, washed and dried in vacuum at 60 °C for 5 h. Following this procedure, $\text{Ag}/\text{N-rGO}$ (x wt%) was obtained, where x represents the weight ratios of GO to Ag in the preparation process. N-rGO was synthesized through the same steps used for making $\text{Ag}/\text{N-rGO}$ without adding AgNO_3 , and Ag/rGO was prepared without adding $\text{NH}_3 \cdot \text{H}_2\text{O}$.

The $\text{AgCl}/\text{Ag}/\text{N-rGO}$ nanocomposite was prepared by an *in situ* oxidation reaction from $\text{Ag}/\text{N-rGO}$ and FeCl_3 at room temperature. Typically, 0.5 g $\text{Ag}/\text{N-rGO}$ (x wt%) was added into 40 mL of a 0.1 M FeCl_3 aqueous solution and stirred for 30 min. Then, the solid sample was quickly centrifuged, washed and dried in vacuum at 60 °C for 5 h. The synthesized samples were designated as $\text{AgCl}/\text{Ag}/\text{N-rGO}$ (x wt%, y), where y indicates the volume of FeCl_3 added in the preparation process. The $\text{AgCl}/\text{Ag}/\text{N-rGO}$ (3 wt%, 40) photocatalyst exhibited the highest photocatalytic activity, stability and crystallinity, as shown in Figs. S2–S5 and Table S1. This catalyst was used for all of the subsequent experiments unless otherwise specified. As references, s- $\text{Ag}/\text{N-rGO}$ (3 wt%) was prepared, as described above, with $\text{Fe}(\text{NO}_3)_3$ added instead of FeCl_3 . $\text{AgCl}/\text{Ag}/\text{rGO}$ (3 wt%, 40) was prepared by an *in situ* oxidation reaction from Ag/rGO and FeCl_3 at room temperature, as described above.

2.3. Characterization

The powder X-ray diffraction (XRD) patterns of the samples were recorded on a Scintag-XDS-2000 diffractometer with $\text{Cu K}\alpha$ radiation ($k = 1.540598 \text{ \AA}$) at 40 kV and 40 mA. The X-ray photoelectron spectroscopy (XPS) data were taken on a Kratos Axis-Ultra instrument with monochromatic $\text{Al K}\alpha$ radiation (225 W, 15 mA, 15 kV). The C1s photoelectron binding energy was set at 284.8 eV and used as reference for calibrating other peak positions. The UV–vis diffuse reflectance spectra (UV–vis DRS) were con-

ducted on a Hitachi U-3900 spectrophotometer with an integrating sphere attachment. Fourier transform-infrared (FTIR) spectra were acquired using a Bruker FTIR. Raman spectra were recorded on a LabRAM HR Evolution (HORIBA, France) equipped with a CCD detector using a laser source at an excitation line of 532 nm. The field emission scanning electron microscope (FESEM) and energy dispersive X-ray spectrometer (EDS) were performed using an SU8020 FESEM instrument (Hitachi), which was operated at the accelerating voltage of 20 kV and a detector current of 10 mA. The electron spin resonance (ESR) spectra were obtained with a Bruker A300-10/12 ESR spectrometer using BMPO as a spin trap agent to detect reactive oxygen species. The photoelectrochemical measurements were performed on a CHI 660D electrochemical workstation with a standard three-electrode system. The prepared photocatalyst electrode was employed as the working electrode, a Pt wire and saturated calomel electrode (SCE) served as the counter electrode and reference electrode, and a 0.1 M Na₂SO₄ solution was used as the electrolyte.

2.4. Photocatalytic activity

The photocatalytic activity of the AgCl@Ag/N-rGO was evaluated by the degradation of 2-CP, BPA, phenol, 2,4-D, DP and PHT under visible light irradiation. A 150 W Xe arc lamp with a 400-nm cutoff glass filter was used as the light source. The incident visible light intensity was measured with a radiometer (Photoelectric Instrument Factory Beijing Normal University), and the intensity was 3.5 mW cm⁻². Prior to illumination, 60 mL of a suspension containing 1.6 g L⁻¹ photocatalysts and 10 mg L⁻¹ pollutant solution was vigorously stirred in the dark for 30 min to establish the adsorption-desorption equilibrium. During irradiation, the suspension samples were withdrawn at given time intervals and filtered to remove the catalyst powders for analysis. The concentrations of the organic pollutants were measured using a high-performance liquid chromatograph (Agilent 1200 series, U.S.A.) equipped with a UV detector and a Zorbax SB-Aq column (5 μ m, 4.6 $\times$ 250 mm; Agilent). The mobile phase consisted of a mixture of methanol/water or a mixture of acetonitrile/water (with 0.08% phosphoric acid) at a flow rate of 1.0 mL min⁻¹. The total organic carbon (TOC) of the solution was analyzed using a TOC-V_{CPH} analyzer (Shimadzu). The released metallic ions from the catalysts in the reaction process were determined by ICP-OES on an OPTIMA 2000 (Perkin Elmer Co., USA). To test the stability and recyclability of AgCl@Ag/N-rGO, the catalyst was filtered, washed and dried at 60 °C in vacuum. The catalyst used again in the second cycle. This process was repeated several times.

All the reported data were the average of the triplicates with a standard deviation of less than 5%.

3. Results and discussion

3.1. Materials characterization

Fig. 1A and B show the FESEM image of N-rGO and AgCl@Ag/N-rGO, respectively. N-rGO showed a transparent, thin and wrinkled morphology, which displayed the typical graphene structure. It is clear that the AgCl@Ag particles were enwrapped by N-rGO, indicating that the AgCl@Ag particles attached onto the N-rGO sheets [28]. Meanwhile, the EDS analysis (inset in Fig. 1B) and elemental mapping (Fig. 1C) indicate the existence of C, N, Cl and Ag in AgCl@Ag/N-rGO. The concentrations of the nitrogen, silver and chlorine were 8.71 at.%, 25.05 at.% and 20.17 at.% from the EDS analysis. The atomic ratio of silver and chlorine was approximately 1.24.

The typical XRD patterns of GO, N-rGO, Ag/N-rGO and AgCl@Ag/N-rGO are shown in Fig. 2. GO showed a sharp peak at $2\theta = 12.1^\circ$, corresponding to an interlayer d-spacing of 0.73 nm between the stacked graphite oxide sheets [29]. After the reduction with the ammonia solution by a hydrothermal method, the sharp diffraction peak of GO disappeared while a weak and broad diffraction peak at $2\theta = 23.9^\circ$ with an interlayer d-spacing of 0.37 nm appeared in N-rGO, indicating the efficient reduction of GO [29]. The reduction of GO is further demonstrated by the FTIR spectra in Fig. 3. The broad peak at 3371 cm⁻¹ ascribed to the strong absorption of hydroxyl groups on the GO surface after the reduction with ammonia solution the hydroxyl groups almost disappeared in the spectra of N-rGO, Ag/N-rGO and AgCl@Ag/N-rGO. The same is true for the oxygen-containing functional groups at 1728 cm⁻¹ (C=O), 1225 cm⁻¹ (C–OH) and 1053 cm⁻¹ (C–O) [30]. However, for the spectra of Ag/rGO and AgCl@Ag/rGO, the oxygen-containing functional groups decreased, but still existed, indicating that the ammonia solution could promote the reduction of GO. On the XRD diffractogram of Ag/N-rGO (Fig. 2), five characteristic peaks at approximately 38°, 44°, 64°, 77° and 84° represented the (111), (200), (220), (311) and (222) planes of metallic Ag (JCPDS 65-2871). For AgCl@Ag/N-rGO, the diffraction peaks corresponding to the AgCl phase (JCPDS 85-1355) could be clearly observed, and the corresponding diffraction peaks of metallic Ag decreased significantly. Due to the relatively low content of N-rGO in the Ag/N-rGO and AgCl@Ag/N-rGO, negligible diffraction peaks ascribed to N-rGO could be detected by XRD. Compared to the XRD pattern of AgCl@Ag/N-rGO, AgCl@Ag/rGO showed relatively low diffraction intensity (Fig. S6). That was due to the much smaller crystallite sizes and higher crystallinity of AgCl@Ag/N-rGO. The Raman spectra of the different samples are shown in Fig. 4. Two characteristic peaks at approximately 1355 cm⁻¹ and 1600 cm⁻¹ corresponding to the D band and G band were observed in Ag/N-rGO. The D band is attributed to the vibrations of carbon atoms with dangling bonds in disordered graphite planes and the defects [31]. The G band corresponds to the E_{2g} vibration mode arising from the in-plane bond stretching of the C–C sp² bond [32]. The intensity ratio of the D band to the G band refers to the degree of defects (or the defect density) in the carbon materials [33]. The ratio of the D band and G band intensities (I_D/I_G) of Ag/N-rGO (1.26) was significantly higher than that of GO (0.81) and slightly higher than that of N-rGO (1.09), indicating the reduction of oxygen-containing groups in GO and the existence of more defects in the N-rGO of Ag/N-rGO [34]. After *in situ* oxidation, the I_D/I_G of AgCl@Ag/N-rGO (1.00) decreased compared to that of Ag/N-rGO, indicating the partial re-oxidation of the defects by Fe³⁺ ions [35]; meanwhile, it was still higher than that of GO, indicating some of the defects in N-rGO were well maintained [36].

To further verify the structure of AgCl@Ag/N-rGO, the surface chemical composition and chemical states were characterized by XPS (Fig. 5). As shown in the inset of Fig. 5, the N1s spectrum could be deconvoluted into two components: the pyridinic nitrogen (N-6) at 399 eV and the pyrrolic nitrogen (N-5) at 400 eV. Specifically, pyridinic N (N-6) bonded with two carbon atoms at the edges or defects of graphene and donated one p electron to the π system; meanwhile, pyrrolic N (N-5) connected with two carbon atoms and contributed two electrons to the system [37]. The results confirm that nitrogen atoms were introduced. The N-groups on rGO could serve as favorable nucleation and anchor sites for Ag NPs owing to the coordination with Ag⁺ [21]; thus, a strong coupling between Ag and N-rGO existed in AgCl@Ag/N-rGO. The two peaks located at approximately 367.4 eV and approximately 373.4 eV in the Ag 3d spectra (Fig. S7A) were ascribed to the Ag 3d_{5/2} and Ag 3d_{3/2} binding energies, respectively. Furthermore, the peaks of Ag 3d_{5/2} and 3d_{3/2} could be deconvoluted into peaks at 367.4,

Fig. 1. FESEM images of: (A) N-rGO, (B) AgCl@Ag/N-rGO. (The inset shows the EDS spectrum of AgCl@Ag/N-rGO) and (C) the elemental mappings of AgCl@Ag/N-rGO.

Fig. 2. XRD patterns of (A): (a) GO and (b) N-rGO. (B): (a) Ag/N-rGO and (b) AgCl@Ag/N-rGO. (♦) Ag.

Fig. 3. FTIR spectra of (a) GO, (b) N-rGO, (c) Ag/rGO, (d) AgCl@Ag/rGO, (e) Ag/N-rGO and (f) AgCl@Ag/N-rGO.

Fig. 4. Raman spectra of (a) GO, (b) N-rGO, (c) Ag/N-rGO and (d) AgCl@Ag/N-rGO.

Fig. 5. An XPS spectrum of the AgCl@Ag/N-rGO photocatalyst. The inset shows a high-resolution N 1s spectrum with the peak deconvoluted into the pyridinic and pyrrolic N peaks.

368.1 eV, 373.4 and 374.1 eV, respectively. The peaks at 367.4 and 373.4 eV were for the Ag^+ of AgCl, whereas the peaks at 368.1 and 374.1 eV were attributed to metallic Ag^0 [38]. As shown in Fig. S7B, on the basis of the calculation of the auger parameter ($=\text{BE}(\text{Ag}3d_{5/2}) - \text{Auger}(\text{M4VV}) + 1486.71$ (characteristic energy, eV)), the auger parameters of AgCl@Ag/N-rGO and Ag/N-rGO were 723.6 eV and 725.0 eV, respectively, which could be assumed to be Ag^+ and Ag^0 [39]. Moreover, a little shoulder at approximately 725 eV in Ag MVV-Auger (Fig. S7B, spectrum a) indicates the presence of Ag^0 [40]. The XPS results indicate that the Ag^0 NPs were mainly surrounded by AgCl.

Fig. 6 show the typical UV–visible spectra of GO, Ag/N-rGO and AgCl@Ag/N-rGO. GO displayed a broad absorption band maximum between 270 nm and 390 nm, which was accompanied by a tail absorption between 400 and 800 nm. In contrast, Ag/N-rGO exhibited a strong absorption at 320 nm, which is likely due to the electrons directly bonded to the silver atoms that acted as bulk silver [41]. Compared with GO and Ag/N-rGO, AgCl@Ag/N-rGO exhibited the strongest absorption in the visible region ($\lambda > 400$ nm), and a broad absorption peak could be seen at approximately 500 nm, which was caused by the surface plasmon resonance (SPR) of the residual Ag NPs after the oxidation of FeCl_3 .

Fig. 6. UV–vis diffuse reflectance spectra of (a) GO, (b) Ag/N-rGO and (c) AgCl@Ag/N-rGO.

3.2. Photocatalytic performance

The photocatalytic activity of different catalysts was evaluated by the photodegradation of 2-CP under visible light irradiation ($\lambda \geq 400$ nm) in Fig. 7. Ag/N-rGO, s-Ag/N-rGO and AgCl@Ag/rGO could only degrade approximately 16%, 25% and 48% of 2-CP within 150 min, respectively. In contrast, the AgCl@Ag/N-rGO photocatalyst exhibited the highest photocatalytic activity, and degraded approximately 97% of 2-CP under identical experimental conditions. Correspondingly, the TOC removal of AgCl@Ag/rGO was only 1.9%; however, approximately 75.6% of the TOC was removed in the AgCl@Ag/N-rGO suspension, which was due to pyridinic N serving as highly active sites and increasing the activity of the catalyst [22]. Remarkably, the superior photocatalytic activity of AgCl@Ag/N-rGO outperformed that of N-doped TiO_2 (56.1% of 2-CP degradation and 24.7% of TOC removal), which is considered the standard example of the visible-light photocatalyst [42]. The photocatalytic activities of the related photocatalysts in previous literature, such as Ag@AgCl/RGO [24] and NG-AgCl@Ag [25], were also tested under the same conditions (Fig. S8). AgCl@Ag/N-rGO exhibited a 2-CP substrate degradation activity similar to those of Ag@AgCl/RGO and NG-AgCl@Ag. The TOC removal of Ag@AgCl/RGO and NG-AgCl@Ag was 67.8% and 72.1%, respectively, lower than that of AgCl@Ag/N-rGO (75.6%). Moreover, during the 2-CP degradation, the Ag^+ leaching concentration of AgCl@Ag/N-rGO was only 0.22 mg L^{-1} , which is relatively low compared to those of Ag@AgCl/RGO (0.34 mg L^{-1}) and NG-AgCl@Ag (0.49 mg L^{-1}) (Table S1). In addition, after five 2-CP photodegradation cycling runs, the photoactivity of AgCl@Ag/N-rGO demonstrated no significant loss, as shown in Fig. 8. The XRD patterns of AgCl@Ag/N-rGO were also unchanged after the photoreaction (Fig. S9). The results suggest that AgCl@Ag/N-rGO was an effective and stable visible-light-driven photocatalyst due to the enhanced electron transfer resulting from the close interfacial contact between the Ag and N-rGO and the *in situ* formation of AgCl around Ag.

Industrial effluents may be basic or acidic, and thus, the effects of the initial solution pH on the photodegradation efficiency of 2-CP were studied (Fig. S10). At the natural pH of 2-CP (pH = 6.0), AgCl@Ag/N-rGO exhibited the highest photocatalytic activity. When adjusting the pH to 4.0 and 8.0 using dilute HNO_3 and NaOH, the photocatalytic activity of 2-CP decreased. The pH value of the 2-CP solution influenced the photocatalytic process for many reasons, including the surface charge state of AgCl@Ag/N-rGO and the dissociation of 2-CP. When the pH decreased, the active hydro-

Fig. 7. The degradation of 2-CP (10 mg L^{-1}) in different photocatalyst suspensions (1.6 g L^{-1}) under visible light ($\lambda \geq 400$ nm): (a) AgCl@Ag/N-rGO, (b) AgCl@Ag/rGO, (c) s-Ag/N-rGO and (d) Ag/N-rGO. (The data were the average of the triplicates with a standard deviation of less than 5%).

Fig. 8. Cycling runs in the photodegradation of 2-CP (10 mg L^{-1}) in an AgCl@Ag/N-rGO aqueous dispersion (1.6 g L^{-1}) under visible light ($\lambda \geq 400 \text{ nm}$).

xyl groups on the catalyst surface decreased accordingly, resulting in a decrease in the generated $\cdot\text{OH}$ and causing slowed reaction rate for the 2-CP degradation [43]. When the pH increased to 8.0, 2-CP ($\text{pK}_a = 8.56$) was probably dissociated into chlorophenoxide ions, which would compete for the reactive sites with the hydroxyl groups and reduce the $\cdot\text{OH}$ radicals. Meanwhile, the repulsion between the negatively charged surface of AgCl@Ag/N-rGO (the pH of the point of zero charge, $\text{pH}_{\text{pzc}} = 1.70$, Fig. S10) and chlorophenoxide ions at high pH could also decrease the photocatalytic degradation rate of 2-CP.

In addition, three other aromatic pollutants (i.e., BPA, phenol and 2,4-D) were degraded more than 82%, 82% and 60%, respectively, at 150 min and the corresponding TOC removals were 52.3%, 51.8% and 25.9% (Fig. 9). However, only 25% of DP with N-containing side-chains could be removed, and the TOC removal was only 4.9%. More specially, PHT with N-containing heterocyclic ring could not be degraded by AgCl@Ag/N-rGO after a 150-min reaction under visible light. In fact, the N functional groups in N-rGO are Lewis-base sites [44] that repel the pollutants with N-containing side-chains or heterocyclic rings in which the N heteroatoms can serve as Lewis bases [45]. Therefore, the photoactivity of AgCl@Ag/N-rGO was related to the structure of the organic substances, and the interaction between N-rGO and pollutants was probably partly responsible for the removal of pollutants.

3.3. Photocatalytic mechanism

To investigate the active species in the photocatalytic process of AgCl@Ag/N-rGO under visible light irradiation, the effects of various radical scavengers on the degradation of 2-CP were shown in Fig. 10. The degradation of 2-CP was markedly depressed by *p*-benzoquinone (*p*-BQ, 1 mM), indicating that the superoxide anion radicals ($\text{O}_2^{\cdot-}$) were the main reactive oxygen species in the reaction. In the presence of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$, 5 mM), the rate decreased by 30%, illustrating that the photogenerated holes (h^+) were partly responsible for the removal of 2-CP. In addition, the degradation of 2-CP was depressed to some extent with the addition of NaHCO_3 (100 mM), but little change was noted with the addition of *tert*-butanol (TBA, 100 mM) in the AgCl@Ag/N-rGO suspension, suggesting the existence of surface-adsorbed $\cdot\text{OH}$ in the reaction [42].

The ESR technique with BMPO was employed to further explore the reactive species. As shown in Fig. 11A, the characteristic peaks of BMPO- $\cdot\text{OH}$ in AgCl@Ag/N-rGO were obviously visible. However, no such signals were detected in the Ag/N-rGO suspension under visible light ($\lambda \geq 400 \text{ nm}$) irradiation. The result was consistent with the active species trapping experiment. In Fig. 11B, the similar

Fig. 10. Plotted degradation kinetics of 2-CP (10 mg L^{-1}) in the AgCl@Ag/N-rGO suspension (1.6 g L^{-1}) under visible light ($\lambda \geq 400 \text{ nm}$) with (a) no scavenger added, (b) TBA (100 mM), (c) NaHCO_3 (100 mM), (d) $\text{Na}_2\text{C}_2\text{O}_4$ (5 mM) and (e) *p*-BQ (1 mM). (The data were the average of the triplicates with a standard deviation of less than 5%).

Fig. 9. (A) The photodegradation and (B) TOC removal of different organic pollutants (10 mg L^{-1}) in an AgCl@Ag/N-rGO suspension (1.6 g L^{-1}) under visible light ($\lambda \geq 400 \text{ nm}$): (a) 2-CP, (b) BPA, (c) Phenol, (d) 2,4-D, (e) DP and (f) PHT. (The data were the average of the triplicates with a standard deviation of less than 5%).

Fig. 11. BMPO spin trapping ESR spectra recorded for the Ag/N-rGO and AgCl@Ag/N-rGO samples under visible light ($\lambda \geq 400$ nm) in an aqueous dispersion for BMPO·OH (A) and in a methanol dispersion for BMPO- $O_2^{\cdot-}$ (B).

signals of BMPO- $O_2^{\cdot-}$ were observed under air and N_2 -saturated conditions, indicating that the photogenerated electrons could reduce the adsorbed O_2 on the catalyst surface to form $O_2^{\cdot-}$. Compared with Ag/N-rGO, AgCl@Ag/N-rGO could produce more $O_2^{\cdot-}$, indicating that the SPR of the Ag NPs and the AgCl at the surface could promote the electron transfer to the catalyst surface, resulting in the generation of more $O_2^{\cdot-}$.

To illustrate the charge-transfer processes, cyclic voltammetry analyses were performed under air-saturated and N_2 -saturated conditions, shown in Fig. 12. No peaks appeared for the Ag/N-rGO catalyst before and after light irradiation under N_2 -saturated

condition (Fig. 12A). The Ag/N-rGO sample exhibited a pair of well-defined redox peaks corresponding to the oxidation and reduction of Ag in dark and air-saturated conditions (Fig. 12B), but the peaks disappeared under light irradiation with the tested wavelengths, indicating that Ag could be oxidized by oxygen in the solution in the dark. Meanwhile, N-rGO as an electron donor could transfer electrons to Ag after light irradiation. Under N_2 -saturated conditions, a weak oxidation peak for Ag was detected at the AgCl@Ag/N-rGO photoanode in the dark (Fig. 12C). When the AgCl@Ag/N-rGO was irradiated by light with the wavelengths $\lambda \geq 800$ and $\lambda \geq 600$ nm, no oxidation peak for Ag appeared, fur-

Fig. 12. Photocurrent changes at the Ag/N-rGO (A, B) and AgCl@Ag/N-rGO (C, D) photoanodes in N_2 -saturated (A, C) and air-saturated (B, D) 0.1 M Na_2SO_4 aqueous solutions.

Fig. 13. The photocatalytic mechanism for AgCl@Ag/N-rGO composite photocatalyst.

ther indicating that N-rGO could transfer electrons to Ag after light irradiation. Furthermore, a weak peak could be seen under light irradiation with the wavelengths $\lambda \geq 510$ to $\lambda \geq 400$ nm, which could be assigned to the plasmon-induced charge separation of Ag NPs. A similar phenomenon was observed in air at the AgCl@Ag/N-rGO photoanode (Fig. 12D). In contrast, the oxidation peak of Ag NPs was observed even in the dark due to the presence of oxygen and showed the strongest intensity. Under visible-light irradiation, the electrons from the plasmon-induced Ag NPs transferred to the conduction band of AgCl and were then trapped by oxygen to form $O_2^{\cdot-}$. Meanwhile, electrons from N-rGO could be transferred to the Ag NPs to reduce the oxidized silver. Therefore, the oxidation peak of Ag NPs became weaker after light irradiation than before in air.

Herein, based on the above results, the photocatalysis mechanism was illustrated in Fig. 13. Under visible light irradiation, photogenerated electron-hole pairs could be formed in the Ag NPs due to the SPR. Meanwhile, some electron-hole pairs existed in the AgCl due to the self-photosensitivity [10]. The increased electron density caused the Fermi level disequilibrium. Thus, the electrons were transferred into the conduction band of the AgCl until the Fermi level of the system achieved equilibrium, resulting in the formation of $O_2^{\cdot-}$ on the surface of the AgCl [46]. Based on the cyclic voltammetry analyses, the other electron transfer occurred from N-rGO to the Ag NPs, which could decrease the Ag^+ leaching to keep the system stable. Meanwhile, pollutants could lose electrons to N-rGO by the interaction between pollutants and N-rGO, and then were oxidized. On the other hand, the holes on the valence band of AgCl could oxidize H_2O to form $\cdot OH$ [47], which was also confirmed by the ESR result. Moreover, the generated holes at the valence band of the AgCl could oxidize the Cl^- ions to Cl^0 atoms [48], which could also degrade and mineralize the organic pollutants. Therefore, the high photoactivity and photostability of AgCl@Ag/N-rGO could be obtained by the fast charge separation and transfer to form $O_2^{\cdot-}$, excited h^+ , and $\cdot OH$ and Cl^0 radicals on the catalyst surface for removing pollutants.

4. Conclusions

A plasmonic photocatalyst AgCl@Ag/N-rGO with close interfacial contact was synthesized by a hydrothermal-in situ oxidation method. The AgCl@Ag/N-rGO photocatalyst was highly efficient and stable for the degradation and mineralization of various pollu-

ants under visible light, such as 2-CP, BPA, phenol and 2,4-D. Compared to AgCl@Ag/rGO and other related photocatalysts, AgCl@Ag/N-rGO demonstrated optimal performance properties. The strengthened photocatalytic performance could be attributed to the SPR effects of the Ag NPs and the close interfacial contact in AgCl@Ag/N-rGO, promoting the separation and migration of photo-generated electrons and holes. Two electron transfer processes were verified from Ag to AgCl and from N-rGO to Ag, and pollutants could lose electrons to N-rGO through this interaction. Additionally, the active species ($O_2^{\cdot-}$, h^+ and surface-adsorbed $\cdot OH$) were formed to degrade organic pollutants in the photoreaction system of AgCl@Ag/N-rGO. This study provides a new perspective in the development of visible-light-driven photocatalysts for water pollution purification and solar energy conversion.

Acknowledgment

This work was supported by National Key Research and Development Plan [2016YFA0203204] and the National Natural Science Foundation of China [Grant Numbers 51538013, 21407165, 51278527, 51638011].

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2017.06.037>.

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