Journal of Colloid and Interface Science 505 (2017) 421–429

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

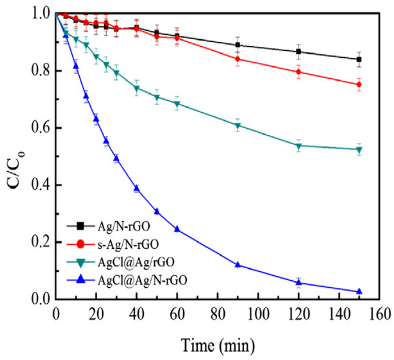
Regular Article

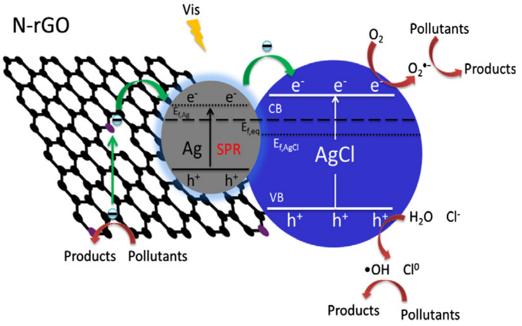
Silver chloride enwrapped silver grafted on nitrogen-doped reduced graphene oxide as a highly efficient visible-light-driven photocatalyst

Liang Wang [a,b], Yilun Shi [a,b], Tianfu Wang [c], Lili Zhang [d,*]

[a] State Key Laboratory of Separation Membranes and Membrane Processes, Tianjin Polytechnic University, Tianjin 300387, China
[b] School of Environmental and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300387, China
[c] Tsinghua University High School, Beijing 100085, China
[d] Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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 ·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.

---

* Corresponding author.
E-mail address: llzhang@rcees.ac.cn (L. Zhang).

http://dx.doi.org/10.1016/j.jcis.2017.06.037
0021-9797/© 2017 Elsevier Inc. All rights reserved.

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, X = Br, 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 g-C_3N_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 Ag@AgCl/RGO through a precipitation reaction followed by photoreduction, which exhibited an excellent photocatalytic activity. Wei et al. [25] prepared nitrogen-doped grapheme-modified AgX@Ag (NG-AgX@Ag, X = Br, 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 ($FeCl_3 \cdot 6H_2O$) 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 Ag/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 NH_3 H_2O) 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, Ag/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 Ag/N-rGO without adding $AgNO_3$, and Ag/rGO was prepared without adding NH_3 H_2O.

The AgCl@Ag/N-rGO nanocomposite was prepared by an *in situ* oxidation reaction from Ag/N-rGO and $FeCl_3$ at room temperature. Typically, 0.5 g Ag/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 AgCl@Ag/N-rGO (*x* wt%, y), where y indicates the volume of $FeCl_3$ added in the preparation process. The AgCl@Ag/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-Ag/N-rGO (3 wt%) was prepared, as described above, with $Fe(NO_3)_3$ added instead of $FeCl_3$. AgCl@Ag/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 Cu Kα radiation (k = 1.540598 Å) at 40 kV and 40 mA. The X-ray photoelectron spectroscopy (XPS) data were taken on a Kratos Axis-Ultra instrument with monochromatic Al Kα 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-