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Gold nanoparticles decorated Ag(Cl,Br) micro-necklaces for efficient and stable SERS detection and visible-light photocatalytic degradation of Sudan I

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ABSTRACT

In this paper, we report an air-exposed and room-temperature immersion reaction for synthesis of novel Au nanoparticles decorated Ag(Cl,Br) [Ag(Cl,Br)–Au] micro-necklaces from the AgBr template for efficient and stable photocatalytic degradation and SERS detection of food contaminant Sudan I (SDI) molecules. Amazingly, as the photocatalyst, the partial substitution of bromine atoms by chlorine in crystalline lattices and decoration of Au nanoparticles on the surface have synergistically ensured these Ag(Cl,Br)–Au micro-necklaces of enhanced degradation efficiency of SDI from 65.1% achieved by AgBr to 100% after 18 min of visible light irradiation, along with significantly promoted efficiency maintenance after 12 cycles of the photocatalytic reaction. Meanwhile, due to the designed decoration of Au nanoparticles on surfaces of semiconducting micro-necklaces, these Ag(Cl,Br)–Au micro-necklaces also exhibited the ability to offer sensitive SERS signals for trace detection of SDI molecules with the limit of detection as low as 10^{-10} M being achieved. Hence, in consideration of the novel structures, facile preparation as well as attractive applications in both SERS detection and photocatalytic degradation of SDI dye of these Ag(Cl,Br)–Au micro-necklaces, it is believable that such bifunctional substrate materials hold great potential for various environmental and health-related applications.

1. Introduction

The food contamination scandals occurred worldwide in the past decade have forced people to put intense focus on Sudan I (SDI, 1-phenylazo-2-naphthol) dye as a potential carcinogen which may cause DNA damage and cancer [1–3]. Researchers therefore have made a great effort to develop efficient approaches for trace detection of SDI. Till now, a number of analytical techniques, including the optical sensing (fluorescence [4] and surface plasmon resonance [5,6]), high-performance liquid chromatography, [7–10] enzyme-linked immunosorbent assay, [11–15] electrochemical methods [16–20] and so on, have been developed for molecular detection of SDI, among which the surface-enhanced Raman scattering (SERS) spectroscopy [21–30] might be the most promising one. As an extremely sensitive and surface-selective technique, SERS spectra can be tailored on substrate materials to provide rapid detections of organics down to single-molecule level [31–33]. A booming trend in the research of trace determination of food contamination and other organic pollutants by SERS spectroscopy is to introduce the process of photocatalysis simultaneously into the same substrate systems to achieve in-situ degradation of such organics as well. The combination and integration of SERS substrates with photocatalytic materials have so far triggered several promising applications like photocatalytic degradation induced self-cleaning SERS platforms [34–37], or inversely, the in-situ SERS monitoring and even quantitative probing of surface plasmon-promoted catalytic reactions [38–45]. Nevertheless, in spite of few reports on Sudan III and IV degradation [46–48], neither the photocatalytic degradation of SDI molecules itself, nor the simultaneous SERS detection and photocatalytic degradation for SDI received adequate research [24,49].

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Silver halide compounds, for example the silver bromide (AgBr) and silver chloride (AgCl), are important light-sensitive materials and plasmonic photocatalysts. However, their optical instability as well as feasibility of decomposition have inhibited them to be high-performance single-component photocatalysts. The grains of silver halide materials are photosensitive due to their point ionic defects and electron traps by silver ions of high mobility [50,51]. Hence for application, these silver halides are usually coupled with noble metals [52–56] and other semiconductor materials [57–59] to promote charge separation by metallic electron sinks or semiconductor *p-n* junctions, and thus inhibit the combination between photoelectrons and either silver ions or photoholes at interfaces, so that they can finally become plasmonic photocatalysts with considerable structural stability and high efficiency under visible light irradiation. The properties of Ag(Cl,Br) are similar to other silver halides like AgBr and AgCl while it has been seldom studied before [60]. Just like the case of AgBr and AgCl, only if the photoelectrons are prevented effectively from combining with silver ions and photoholes, such Ag(Cl,Br) materials can be novel and stable photocatalysts. So far, only Huang et al. have once prepared the Ag@Ag(Cl,Br) powder successfully for visible-light-driven plasmonic photocatalyst [60].

Here in this work, we obtained gold nanoparticles decorated Ag(Cl,Br) [Ag(Cl,Br)–Au] micro-necklaces for the first time via an air-exposed and room-temperature immersion reaction accompanied with a mild annealing process from AgBr micro-necklaces facilely grown on pristine silver foils. As a result, these Ag(Cl,Br)–Au micro-necklaces have demonstrated stable performance for both photocatalytic degradation and sensitive SERS detection of SDI molecules. Specifically on the one hand, as novel photocatalyst, the partial substitution of bromine by chlorine element and decoration of gold nanoparticles on the surface have synergistically endowed the Ag(Cl,Br)–Au micro-necklaces with enhanced degradation efficiency of SDI from 65.1% achieved by AgBr to nearly 100% after 18 min of visible light irradiation. One the other hand, the introduction of gold nanoparticles also enabled the composite micro-necklaces to provide appreciable SERS sensitivity owing to which the limit of detection (LOD) for SDI of as low as 10^{-10} M was finally achieved. Overall, it is believed that the Ag(Cl,Br)–Au micro-necklaces presented in this work, with their novel structures, facile preparation as well as attractive applications as bifunctional SERS and photocatalytic substrates toward SDI dye, suggest many opportunities of developing novel multifunctional devices for environmental and health monitoring and management.

2. Experimental section

2.1. Materials and chemicals

Silver foils (Ag, 3N, 0.1 mm thick), polyvinylpyrrolidone (PVP, K-30), iron(III) nitrate nonahydrate ($Fe(NO_3)_3·9H_2O$, AR), potassium bromide (KBr, SP), chloroauric acid tetrahydrate ($HAuCl_4·4H_2O$, AR), sodium hydroxide (NaOH, AR), nitric acid (HNO_3, AR), Sudan I (SDI, BS), absolute ethanol (GR) and acetone (AR) were all purchased from Sinopharm Chemical Reagent Company. All chemicals were used just as received without further purification, and for all experiments, deionized water (DI water, Millipore) with the resistivity greater than 18.0 MΩ·cm was used.

2.2. Preparation of the Ag(Cl,Br)–Au micro-necklaces

As-purchased silver foils were first cut into pieces ($3 \times 0.5\ cm^2$) and cleaned by dilute nitric acid solution and acetone, respectively. Briefly, a piece of Ag foil was first immersed into the mixture aqueous solution (50 mL) of $Fe(NO_3)_3·9H_2O$ (0.5 M), KBr (0.5 M) and PVP (0.15 M) in air at room temperature for about 8 h to form AgBr micro-necklaces on the surface according to a literature report [61]. Afterward, the piece of foil was taken out of the mixture solution carefully and rinsed with ethanol and DI water thoroughly. Next, the foil was once again immersed into the aqueous solution containing 0.01 M $HAuCl_4$ (with the pH value tuned to 7.0 by addition of 0.2 M NaOH solution drop by drop) and maintained for about 3 h. After the foil was again taken out and rinsed by DI water thoroughly, it was dried in air and annealed in air at 300 °C for 2 h (with the heating rate set at 5 °C/min). The whole process finished when the finally obtained brown gray foil cooled down naturally in air.

2.3. Characterization

Scanning electron microscope (SEM) images and energy dispersive X-ray spectra (EDS) were recorded using a field-emission SEM (FE-SEM, S4800, Hitachi, Japan) equipped with an energy dispersive spectrometer (XFlash 5030, Bruker, Germany). High-resolution transmission electron microscopy (HRTEM) analysis was conducted on a field-emission TEM (FE-TEM, JEOL JEM-2100F, Japan) equipped with a post-column Gatan imaging filter system (GIF, Tridium 863, United States) working at 200 kV of the acceleration voltage. The TEM samples were prepared by ultramicrotome cutting of the fragments of as-synthesized Ag(Cl,Br)–Au micro-necklaces obtained by continuous sonification. X-ray diffraction (XRD) measurement was carried out on a powder X-ray diffractometer (D8 Advance, Bruker, Germany) working with Cu-Kα radiation (1.5406 Å) at 40 mA and 40 kV. The UV–vis absorbance spectra of SDI solutions and UV–vis-NIR diffuse reflectance spectra (DRS) of the samples were obtained on a Shimadzu UV-3600 (Japan) and a JASCO V-670 (Japan) UV–vis-NIR spectrophotometer, respectively. The Raman and SERS spectra were collected on a laser confocal Raman micro-spectrometer (in*Via* reflex, Renishaw, UK) equipped with an integrated optical microscope (DM-2500, Leica, Germany).

2.4. Details for SERS measurements

Dilute SDI solutions in mixed solvent of ethanol and water (volume ratio = 1:1) were first prepared at different concentrations. A piece of as-obtained sample foil was immersed into the solution at room temperature and kept for 12 h in the dark so that the SDI molecules could fully absorbed onto the surfaces of the Ag(Cl,Br)–Au micro-necklaces. The piece of foil was afterward taken out and dried by an infrared lamp for final measurement. Particularly in all measurements, the excitation source of a 632.8 nm He–Ne laser, grating of 1800 1/mm, laser power of 1.7 mW (10% × 17 mW), exposure time of 10.0 s, accumulation of five times and objective lens of 50 ×/0.50 were applied. During the recyclability test, the used Ag(Cl,Br)–Au foil was recycled and rinsed by absolute ethanol and DI water thoroughly before entering each new cycle. The intensities of selected bands in the SERS spectrum recorded in the first cycle was regarded as the reference (100%).

2.5. Details for photocatalytic measurements

The photocatalytic degradation reaction of SDI was carried out in a quartz cuvette ($1 \times 1 \times 4\ cm^3$, Jingke Optical Instrument, Yixing). Typically, a piece of AgBr or Ag(Cl,Br)–Au foil was vertically put into fresh solutions of SDI (3 mL, 10^{-6} M with 1:1 vol ratio of ethanol and water as the solvent) within the quartz cuvette. The cuvette was afterward irradiated by a Xe lamp ($\lambda \geq 420$ nm, 300 W, Labsolar-IIIAG, Perfect-Light Company, Beijing) at room temperature. Meanwhile, the UV–vis absorbance spectra of the reaction solutions were quickly recorded at two minutes interval. Just similar to the SERS measurement, the used foils were recycled and