



# Development of silver/gold nanocages onto indium tin oxide glass as a reagentless plasmonic mercury sensor



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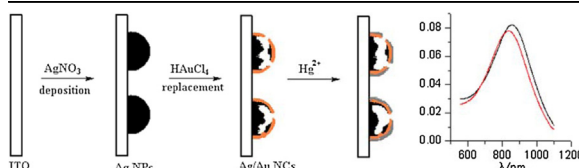
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## HIGHLIGHTS

- A reagentless, sensitive and selective optical sensor for detection of Hg(II) was developed.
- Silver–gold nanocages were prepared on the transparent indium tin oxide coated glass surface.
- The nanomaterials could act as optical sensing probe as well as reducing agent.
- The plasmonic sensor could be used to detect mercury ions in field analysis.

## GRAPHICAL ABSTRACT



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## ABSTRACT

We demonstrate the utilization of silver/gold nanocages (Ag/Au NCs) deposited onto transparent indium tin oxide (ITO) film glass as the basis of a reagentless, simple and inexpensive mercury probe. The localized surface plasmon resonance (LSPR) peak wavelength was located at  $\sim 800$  nm. By utilizing the redox reaction between  $\text{Hg}^{2+}$  ions and Ag atoms that existed in Ag/Au NCs, the LSPR peak of Ag/Au NCs was blue-shifted. Thus, we develop an optical sensing probe for the detection of  $\text{Hg}^{2+}$  ions. The LSPR peak changes were linearly proportional to the concentration of  $\text{Hg}^{2+}$  ions over the range from 10 ppb to 0.5 ppm. The detection limit was  $\sim 5$  ppb. This plasmonic probe shows good selectivity and high sensitivity. The proposed optical probe is successfully applied to the sensing of  $\text{Hg}^{2+}$  in real samples.

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## 1. Introduction

Gold and silver nanoparticles exhibit unique localized surface plasmon resonance (LSPR) properties, which have attracted great

attention from the bioanalytical field [1–6]. In the recent years, great progress has been achieved in the development of LSPR-based biosensors, such as *Staphylococcus aureus* enterotoxin B [7], phosphopeptides [8], Alzheimer's tau protein [9], hepatitis B virus [10], and salbutamol [11]. Moreover, the LSPR spectroscopy can be monitored using a basic UV–vis spectrophotometer. Thus, LSPR-based biosensors have been developed as a fast, simple, and low cost technology.

Herein, we further extended the scope of LSPR-based sensors to detect mercury ions. Mercury is regarded as a highly toxic and widely dispersed in the environment, which can lead to damage of

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brain, nervous system, kidneys, and immune system. Plasmonic metal nanoparticles-based colorimetric detection is a highly attractive approach for the development of on-field analysis or rapid screening [12]. For the detection of Hg(II) ions, there are two major sensing mechanisms for metallic nanoparticles: (1) aggregation-dependent shifts in plasmon peak wavelength. Many gold nanoparticle probes for the colorimetric determination of Hg(II) have been developed, which is based on oligonucleotides [13,14], oligopeptides [15,16], and other functional molecules [17–19]. (2) Local refractive index-dependent shifts in plasmon peak wavelength. For example, mercury ions can be reduced by reducing agents (mostly sodium borohydride) to deposit it onto the surface of metal nanoparticles. Mercury adsorption would induce a blue shift of the LSPR peak of metal nanoparticles. This changes in the LSPR band can be used for the detection of Hg(II) concentration [20–24]. Guo et al. developed a test strip for Hg<sup>2+</sup> detection based on DNA-functionalized gold nanoparticles. However, DNA is expensive and instable during storage. Recently, silver nanoparticles were used as both sensing platform and reducing agent for the detection of Hg(II) [25–27]. This method has good selectivity, high sensitivity and requires no additional reagents. However, it is well known that silver nanoparticles are not very stable for storage, which is limited in the application.

It has been reported that bimetallic nanostructures of Ag/Au either in alloy or multilayer form can tune the electronic, optical and chemical properties [28,29]. For example, a charge compensation mechanism leads to increase electron density within the Ag layer yielding a negative oxidation state. Thus the oxidation resistivity is enhanced and the chemical stability is improved [29]. In this paper, we first deposited silver nanoparticles on transparent indium tin oxide (ITO) glass by electrochemical method. Subsequently, these nanoparticles are used as templates to grow thin gold shells with holes due to the diffusion of the dissolution of Ag across the shells. Stopping the replacement reaction between silver and gold salt at intermediate stage, a bimetallic gold–silver nanoshell with several pinholes and a partial hollow centre was produced, which was defined as Ag/Au nanocage (Ag/Au NC). Herein, we demonstrate the analytical potential of Ag/Au NCs for detecting Hg(II) ions. This method holds high selectivity, good sensitivity, and requires no additional reagents.

## 2. Experimental

### 2.1. Chemical and materials

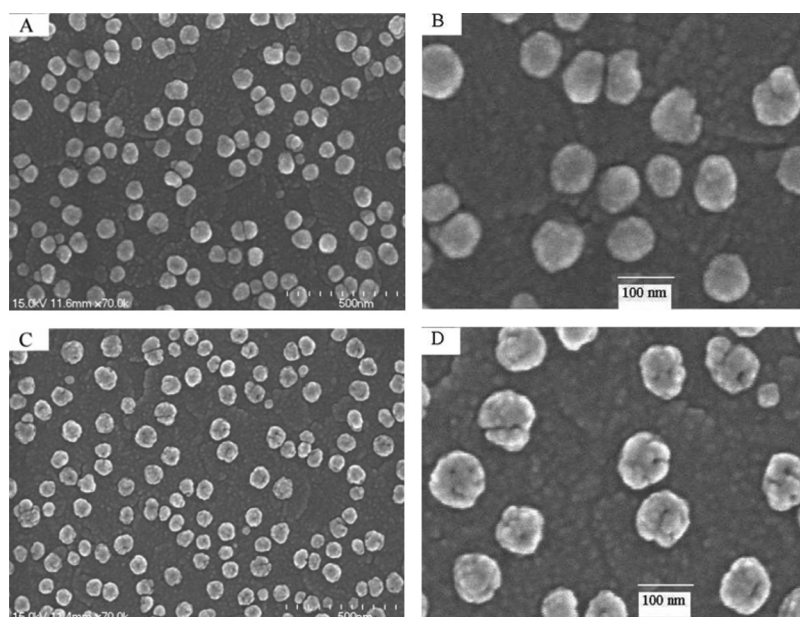
Indium tin oxide film coated glass (1.1 mm of thickness, less than 100 Ω) was purchased from Suzhou NSG Electronics Co., Ltd. (Suzhou, China). Tetrachloroauric acid (HAuCl<sub>4</sub>·4H<sub>2</sub>O), silver nitrate (AgNO<sub>3</sub>), KNO<sub>3</sub>, Hg(NO<sub>3</sub>)<sub>2</sub>, Na<sub>2</sub>HPO<sub>4</sub>, and citric acid were obtained from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals were of analytical grade and used without further purification. 0.1 mol L<sup>-1</sup> phosphate–citric acid buffer solution (pH 2.0) was prepared by mixing stock standard solution of Na<sub>2</sub>HPO<sub>4</sub> and citric acid. All solutions were made up with Millipore water.

### 2.2. Apparatus

The deposition of silver nanoparticles on ITO substrate surface and cyclic voltammograms were performed using CHI 830 electrochemical workstation (CH Instruments, Shanghai, China). UV-visible absorption spectra were recorded with a TU-2810 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.). Scanning electron microscopy (SEM) was obtained using S-4700 scanning electron microscope (Hitachi, Japan). The topography images of these nanoparticles in solution were obtained with transmission electron microscopy (TEM) (FEI Company Tecnai G<sup>2</sup> 20, Holand). X-ray diffraction (XRD) analysis was recorded by X'Pert-Pro MPD (Panalytical, Holland).

### 2.3. Fabrication of Au/Ag NCs

The ITO electrode (0.6 × 3.0 cm<sup>2</sup>) was cleaned using NH<sub>3</sub>–H<sub>2</sub>O (1:20), ethanol, and distilled water for 10 min sequentially in an ultrasonic bath. Then the electrode immersed in the 0.2 mmol L<sup>-1</sup> AgNO<sub>3</sub> and 0.3 mol L<sup>-1</sup> KNO<sub>3</sub> solutions. Prior to electrolysis the electrolyte was deoxygenated by bubbling highly pure N<sub>2</sub> for about 15 min and maintained under N<sub>2</sub> atmosphere during experiment. Silver nanoparticles were electrodeposited by applying a cyclic voltammogram (CV) in the potential range –0.2 to –0.5 V at 0.05 V s<sup>-1</sup> for 100 cycles at 30 °C. After rinsed with water, the Au/Ag



**Fig. 1.** SEM image of silver nanoparticles deposited onto ITO substrate (A) with its high resolution image (B) and SEM image of Ag/Au NCs formed by reacting these silver nanoparticles with an HAuCl<sub>4</sub> solution (C) with its high resolution image (D).

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