



Chlorine triggered de-alloying of AuAg@Carbon nanodots: Towards fabrication of a dual signalling assay combining the plasmonic property of bimetallic alloy nanoparticles and photoluminescence of carbon nanodots



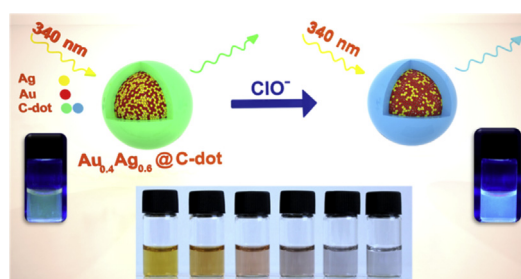
Zahra Mohammadpour, Afsaneh Safavi*, Seyyed Hossein Abdollahi

Department of Chemistry, Faculty of Sciences, Shiraz University, Shiraz, 7194684795, Iran

HIGHLIGHTS

- A new dual signalling assay for hypochlorite ion is introduced.
- Bimetallic Au–Ag nanoparticles are hybridized with fluorescent carbon nanodots.
- It shows amplified colorimetric response with respect to monometallic counterparts.
- This sensor is multifunctional, robust, rapid and sensitive.
- The practical applicability is investigated for environmental monitoring.

GRAPHICAL ABSTRACT



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ABSTRACT

Integration of Au–Ag alloy and fluorescent carbon nanodots (C-dots) into a single platform resulted in a new dual sensing assay for chlorine. Selective etching of Ag from AuAg@C-dots was transformed into: (i) colorimetric signal by surface plasmon resonance (SPR) tuning of the alloy and (ii) fluorimetric signal by perturbation of fluorescence energy transfer between C-dots and alloy nanoparticles. Fast oxidizing of silver atoms incorporated in the bimetallic structure induced by chlorine resulted in selective de-alloying of bimetallic hybrid nanoparticles and an intense visible change of the colloidal dispersion color. On the other hand, the systematic change in Au/Ag ratio strongly affected the emission intensity of C-dots in the hybrid structure leading to an enhancement in the fluorescence signal. Thus, the assay enables the detection of chlorine both under visible and UV lights with high sensitivity. The detection limit (DL) values were calculated as 6.2×10^{-7} M and 5.1×10^{-7} M through colorimetric and fluorimetric pathways, respectively. Most importantly, it was demonstrated to be selective over common cations, anions and some reactive oxygen species (ROS). This assay was successfully applied to the determination of chlorine concentration in bleach solution and tap water. It is robust and is suitable for cost effective chlorine measurement in environmental samples.

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Abbreviations: C-dots, Carbon nanodots; DL, Detection limit; DLS, Dynamic light scattering; EDX, E-dispersive X-ray; IFE, Inner filter effect; NSET, Nanometal surface energy transfer; PL, Photoluminescence; SERS, Surface-enhanced Raman spectroscopy; SPR, Surface plasmon resonance; TBHP, Tert-butyl hydroperoxide; TEM, Transmission electron microscopy; XRD, X-ray diffraction.

* Corresponding author.

E-mail address: safavi@susc.ac.ir (A. Safavi).

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1. Introduction

Strong surface plasmon resonance (SPR) of Ag nanoparticles combined with high chemical stability of Au nanoparticles make bimetallic Au-Ag nanoparticles to be both SPR sensitive and chemically stable in harsh conditions [1]. Nanoscale bimetallic Au-Ag with distinctive optical, electrical and chemical properties offers superior advantages in catalysis, antimicrobial properties, and surface-enhanced Raman spectroscopy (SERS) sensing compared to their monometallic counterparts [2–4]. Synthesis and optical characteristics of bimetallic Au-Ag nanoparticles have been studied extensively in literature [5–7]. They have been prepared by different strategies mostly by co-reduction of metal salts using various reducing agents [3,8–10]. Recently, Essner et al. reported a green approach for preparation of bimetallic alloyed Au-Ag using carbon nanodots (C-dots) both as reducing and stabilizing agents [11]. In another report, Garg et al. investigated the kinetic of oxidative dissolution of silver nanoparticles by chlorine [12]. It was proved that the kinetic of Ag nanoparticles oxidation in the presence of chlorine is much faster than the rate in the presence of hydrogen peroxide or dioxygen [12].

Inspired by these two reports, we synthesized C-dots stabilized Au-Ag alloy with strong and tunable absorption bands across the visible range of the electromagnetic spectrum. The fast response of Ag nanoparticles to chlorine motivated us to use chlorine for selective removal of Ag from $Au_xAg_{1-x}@C$ -dots and design a dual readout sensing system for chlorine. Chlorine is an extensively used disinfectant for water treatment. However, accumulation of this ion in environmental samples is associated with human diseases including neuron degeneration, cancer, arthritis and inflammatory diseases [13–16]. Therefore, developing a fast, selective, sensitive, low cost, visual and portable sensor for measurement of this ion is crucial. To date, several nanoparticle-based probes have been designed for chlorine sensing including carbon nanodots [17], graphene dots [18], quantum dots [19], gold nanoclusters [20], copper nanoclusters [21], gold nanoparticles [22,23] and silver nanoparticles [24,25]. All of these probes are single channel, either colorimetric or fluorimetric. In fluorimetric probes reported so far, the sensing mode is “turn-off” (fluorescence quenching). In this paper, for the first time, we have introduced a dual signalling strategy for both colorimetric and fluorimetric detection of chlorine with widened practical applicability with respect to single channel probes. The turn-on mode (fluorescence enhancement) in the present system takes the advantage of being more sensitive compared with turn-off sensors particularly for use in biological media and cell imaging due to background interference reduction. Moreover, unlike the toxic quantum dots used for chlorine sensing, C-dots used in the present nanohybrid are environmentally friendly. Also, in contrary to gold nanoparticles-based systems, which are subject to aggregation in solutions with high electrolyte concentrations, this nanohybrid is quite stable in strongly saline solutions. Chlorine induced de-alloying of this hybrid bimetallic nanoparticle can be visualized both under visible and UV lights. This assay operates based on a “mix and detect” strategy, is fast, selective, sensitive, simple and robust for environmental monitoring of sodium hypochlorite in bleach and tap water samples.

The overall de-alloying of bimetallic $Au_xAg_{1-x}@C$ -dots mediated by chlorine is depicted in Scheme 1. Selective oxidation of Ag from $Au_xAg_{1-x}@C$ -dots was transduced into colorimetric and fluorimetric responses. De-alloying of $Au_xAg_{1-x}@C$ -dots nanoparticles was achieved using the fast oxidizing capability of chlorine on silver atoms incorporated in the bimetallic structure. The process made an intense visible change of the colloidal dispersion color from yellow to orange, pink, dark pink, gray and finally to colorless. On the other hand, the change in fluorescence signal of C-dots was

used as the second signalling read-out. C-dots by virtue of their great features including water solubility, electron donor/acceptor capability and high photoluminescence (PL) emission intensity have been widely used in different research fields since their first accidental discovery in 2004 [26,27]. C-dots have been hybridized with metallic gold or silver nanoparticles as donor-acceptor energy transfer pairs [28,29]. Also, metal nanoparticles serve as efficient energy acceptors, particularly through the nanometal surface energy transfer (NSET) pathway [30,31]. In this study, fluorescent C-dots are donors while alloyed bimetallic Au-Ag nanoparticles are acceptors. Interestingly, the fine modification of PL signal of C-dots was achieved through the compositional change of alloyed structure by chlorine. Selective removal of Ag from the bimetallic alloy resulted in the red shift of the absorption band of the acceptor. Consequently, signal overlapping between donor-acceptor pairs was reduced, the energy transfer was disrupted and the fluorescence signal was turned on. Based on the fast etching process mediated by chlorine, we demonstrated the use of $Au_xAg_{1-x}@C$ -dots as a new dual signalling platform for quantitative measurement of free chlorine in bleach and tap water samples.

2. Experimental section

2.1. Materials and instrumentation

Sodium hypochlorite (6–14%), anhydrous citric acid, silver nitrate, sodium hydroxide, sodium bicarbonate, hydrogen peroxide 30%, tert-butyl hydroperoxide (TBHP), sodium peroxide, sodium nitrite, and sodium nitrate were purchased from Merck. Peroxynitrite ($ONOO^-$) was synthesized freshly following a literature procedure [32,33]. Briefly, solutions of (i) 0.6 M $NaNO_2$ and (ii) 0.6 M $HCl/0.7 M H_2O_2$ were simultaneously pumped into a T-junction and mixed. Peroxynitrous acid was produced through the acid-catalyzed reaction of nitrous acid and H_2O_2 . Immediately after mixing, the reaction mixture was poured into 3 M of $NaOH$ that was kept in an ice bath and quenched. The yellow reaction product was frozen at $-20^\circ C$ and used within 1 week. The concentration of peroxynitrite was determined spectrophotometrically ($\epsilon_{302 nm} = 1670 M^{-1} cm^{-1}$) [32].

The UV–Vis absorption spectra were measured using a Shimadzu spectrophotometer and a 1-cm path length quartz cuvette. Transmission electron microscopy (TEM) images were acquired on a Hitachi S4160 device. FTIR spectrum was recorded using a Shimadzu FTIR 8000 series. The composition of bimetallic alloy was determined by X-ray diffraction (XRD) using a X'Pert PRO MPD diffractometer (Cu-K α radiation ($\lambda = 1.54060 \text{ \AA}$), step size of 0.02° and 20 s step time for each point). Size distribution measurements were carried out on a Zetasizer Nano ZS from Malvern Company. E-dispersive X-ray (EDX) analysis was performed using a VEGA\\TESCAN-XMU device. A Perkin Elmer PL spectrophotometer (LS45) with a 1-cm quartz cell was used for measuring the PL spectra. Dialysis tubing (D0530) was received from Sigma.

2.2. Synthesis of bimetallic $Au_xAg_{1-x}@C$ -dots

A chemical reduction process proceeded for production of $Au_xAg_{1-x}@C$ -dots [11]. 7 mL of 0.43 mg mL^{-1} of aqueous C-dots solution was heated to boiling under reflux condition for 15 min. $AgNO_3$ and $Au(OH)_4^-$ were used as the metal salts precursors. Different Au:Ag ratios were made by simultaneously addition of aliquots of 10 mM of both metal salts. $Au(OH)_4^-$ was prepared by the addition of X mL of 10 mM of $HAuCl_4$ to 2 mL of 100 mM $NaOH$. (1-X) mL of 10 mM of $AgNO_3$ and the resulting $Au(OH)_4^-$ solution were simultaneously added to the hot C-dot solution. For example, Au:Ag (40:60) was prepared by mixing 0.4 mL of 10 mM $HAuCl_4$ with 2 mL

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