Catalysis-reduction strategy for sensing inorganic and organic mercury based on gold nanoparticles

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ABSTRACT

In view of the high biotoxicity and trace concentration of mercury (Hg) in environmental water, developing simple, ultra-sensitive and highly selective method capable of simultaneous determination of various Hg species has attracted wide attention. Here, we present a novel catalysis-reduction strategy for sensing inorganic and organic mercury in aqueous solution through the cooperative effect of AuNP-catalyzed properties and the formation of gold amalgam. For the first time, a new AuNP-catalyzed-organic reaction has been discovered and directly used for sensing Hg^{2+}, Hg_2^{2+} and CH_3Hg^+ according to the change of the amount of the catalytic product induced by the deposition of Hg atoms on the surface of AuNPs. The detection limit of Hg species is 5.0 pM (1 ppt), which is 3 orders of magnitude lower than the U.S. Environmental Protection Agency (EPA) limit value of Hg for drinking water (2 ppb). The high selectivity can be exceptionally achieved by the specific formation of gold amalgam. Moreover, the application for detecting tap water samples further demonstrates that this AuNP-based assay can be an excellent method used for sensing mercury at very low content in the environment.

1. Introduction

Mercury (Hg) has been widely recognized as one of the most hazardous pollutant and highly dangerous element because of its accumulative and toxic properties in the ecological system (Schrope, 2001). Mercury presents a variety of combined forms in environment, including inorganic mercury (Hg^{2+} and Hg_2^{2+}) and organic mercury (such as CH_3HgX, $X=Cl^-$, Br^-, AcO^-, etc.) (Nolan and Lippard, 2008). Although Hg^{2+} is the main existing form in natural water, all inorganic mercury released into the ecosystem can be eventually converted to organic forms by microorganisms or microalgae in aquatic environments (Lehnherr et al., 2011). And organic mercury has much higher toxicity than inorganic forms due to their high liposolubility in the food chain (Jensen and Jermelov, 1969; Boening, 2000). Therefore, an important and challenging task in the scientific community is to design and develop ultrasensitive detection methods for Hg species in water samples to reduce or avoid the threat of Hg to human health (Nolan and Lippard, 2008).

In principle, the conventional approaches, such as atomic absorption spectroscopy (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS) (Yan et al., 2003; Gao et al., 2012; Hong et al., 2011),

can measure the total Hg content with a satisfying sensitivity. However, the disadvantages of these methods are obvious that they require complicated, multistep sample preparation and sophisticated instruments, which all limit the applications of these methods for Hg detection.

In order to conveniently and efficiently sense Hg species, various detection strategies have been developed, in which, optical methods (Kim et al., 2012), such as fluorescence (Ding et al., 2016; Bera et al., 2014), chemosensors (Zapata et al., 2009; Cai et al., 2011), and colorimetric assays (Chen et al., 2014a, 2014b; Lee et al., 2007), have been regarded as the most attractive tools due to the simplicity and high sensitivity. The detecting mechanisms of these methods are almost to use the receptors to recognize the targeted metal ions based on the principles of traditional coordination or host-guest chemistry, which makes the optical methods have two universal drawbacks for sensing Hg: 1) Most methods aim at one of the Hg species (Hg^{2+} or organic mercury), and no method is used for Hg_2^{2+} detection maybe because it is difficult to obtain appropriate receptors to effectively interact with Hg_2^{2+}. Thus the detection results only represent partial Hg content rather than total Hg content in samples, which is a potential hazardous issue. 2) Most methods are not sensitive enough to apply in

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real water samples, although the detection limits of these assays are from nM to μM range. In view of low concentration but high toxicity of Hg in aquatic environment, the U.S Environmental Protection Agency (EPA) has set the maximum allowable level of Hg in drinking water at 10 nM (2 ppb) (EPA, 2001). Therefore, the detection methods with detection limits in the pM (ppt) to low-nM (ppb) range are highly desirable to analyze Hg species. Although there are some reports that can detect Hg^{2+} with ultra-sensitivity (Bera et al., 2014), or simultaneously detect both Hg^{2+} and organomercury (Shu et al., 2015; Chen et al., 2010; Santra et al., 2009). However, to our knowledge, the optical method for simultaneously detecting various Hg species with a pM magnitude in aqueous solution has not been previously reported.

Gold nanoparticles (AuNPs), as one of optical probes, have been widely used to detect metal ions due to their attractive optical properties (Wang and Ma, 2009; Du et al., 2013; Lee and Mirkin, 2008; Xue et al., 2008; Huang and Chang, 2007; Liu and Lu, 2003; Zhou et al., 2008; Li et al., 2010). However, most of these assays based on functionalized AuNPs face with the same drawbacks as other optical methods. In fact, from the perspective of nanoparticle applications, the attempt of exploring the inherent properties of AuNPs e.g. their surface properties, instead of using the properties of functional molecules on their surface for detecting analytes, may bring breakthrough in sensing methodology and mechanism for Hg species.

AuNP catalysis, using the surface properties of AuNPs, has attracted continuous interests because of its potential applications in many organic reactions (Arcadi, 2008; Zhang et al., 2012; Panigrahi et al., 2007; Comotti et al., 2004). The previous research demonstrates the catalytic efficiency is extremely sensitive to the surface properties of AuNPs (Arcadi, 2008). A little surface morphology change may significantly affect the catalytic performance of AuNPs. In addition, in an Au-Hg mixed system, the Hg° exhibits a strong affinity to clean AuNP surface due to forming Au amalgam, which can be used to distinguish Hg species from other general metal ions to ensure the specificity based on AuNPs. Therefore, combining AuNP-catalyzed properties with Au amalgam for sensing Hg species with a desired performance is greatly possible. In fact, some articles have reported that the peroxidase-like catalytic activities of AuNPs could be used to detect metal ions (Lien et al., 2014; Wang et al., 2012; Tseng et al., 2012). In these cases, however, the detection sensitivities are also not satisfactory (only at nM range), possibly because the reductant (citrates were generally used in these cases) is too weak to reduce Hg species below nM concentration in samples. In addition, some active reagents such as H_2O_2 and $NaBH_4$ in the detection system could influence the stability of AuNPs, which lowers the detection accuracy.

In the present work, we describe a novel strategy for simultaneously detecting inorganic and organic mercury with ultra-sensitivity and excellent selectivity in aqueous solution based on the cooperative effect of AuNP catalysis and Au amalgam. To realize the highly sensitive detection for Hg species, a piperazine derivative, HEPPSO i.e. N-(2-Hydroxyethyl) piperazine-N′-(2-hydroxypro-panesulfonic acid), has been specially selected and introduced to AuNPs to construct a catalysis-reduction assay for Hg species. A new AuNP-catalyzed-organic reaction is first discovered: AuNPs can catalyze HEPPSO into the catalytic product with an obvious absorption peak at about 340 nm which is used as the signal reporter for detecting Hg. HEPPSO presents a suitable reduction capacity for Hg species (such as Hg^{2+}, Hg_2^{2+} and $(CH_3)Hg^+$) to Hg°. The formation of Au amalgam by depositing Hg° atoms on AuNP surface influences the AuNP-catalyzed activities, which changes the amount of the catalytic product accompanying with the change of its absorption peak intensity at 340 nm. By using this catalysis-reduction strategy based on AuNPs, various Hg species have been simultaneously recognized at pM (ppt) range in water solution.

2. Experimental methods

2.1. Preparation of the AuNPs

The citrate-stabilized gold nanoparticles (AuNPs) with 13 nm in diameter were synthesized according to the modified Turkevich-Frens method (Turkevich et al., 1951; Frens, 1973). The citrate-stabilized AuNPs with approximate 30 nm in diameter were obtained by decreasing the amount of sodium citrate in the synthetic process of AuNPs. The morphology and size of the AuNPs were verified through transmission electron microscope (TEM) analysis. The 3101PC UV–VIS–NIR scanning spectrophotometer was used to measure the UV–Visible (UV–Vis) absorption spectra. The absorption peak of the AuNPs with the diameter at 13 and 30 nm are 519 and 525 nm, respectively. The carbonate stabilized AuNPs in diameter of approximate 6 nm were obtained by the following procedure. 1.5 mL 1% $HAuCl_4$ aqueous solution and 500 μL 0.2 M K_2CO_3 were dissolved in 100 mL water which was cooled in ice-water bath with stirring. $NaBH_4$ was dissolved in 5 mL water at a concentration of 0.5 mg/mL. 5×1 mL aliquots of fresh $NaBH_4$ solution were added to above mixture solution under the vigorous stirring. A color change from blueish-purple to raddish-orange can be observed. After stirring for 5 min in ice-water bath, AuNPs with approximate 6 nm in diameter were obtained.

2.2. Preparation of the HO-AuNPs and PH-AuNPs

To prepare the HO-AuNPs, the citrate-stabilized AuNPs in diameter of 13 nm were centrifuged twice to remove superfluous ligands, and then the stock solution of HEPPSO (25 mM, pH 7.5) was added to obtain the HO-AuNPs in water. All experiments were carried out at room temperature. Other experimental conditions, such as the solution pH, the concentration of HEPPSO or AuNPs, the AuNP size, and incubation time of HO-AuNPs, were determined by different experimental requirements. To prepare the PH-AuNPs, HO-AuNPs were added by a certain amount of Hg species in advance. Generally, after a series of optimization tests, PH-AuNPs were obtained by incubating HO-AuNPs (25 mM HEPPSO, 2.5 nM AuNPs and pH 7.5) with 0.6 μm Hg species. After incubation for 1 h, the mixture was then centrifuged and the precipitates were redissolved in the HEPPSO buffer (25 mM, pH 7.5). The freshly prepared PH-AuNPs were used to study the interaction between PH-AuNPs and Hg species or other metal ions, and the sensing sensitivity and selectivity.

2.3. The interaction of HO-AuNPs/PH-AuNPs and metal ions

To study the interaction between HO-AuNPs and mercury species, a series of 180 μL HO-AuNP solutions (2.5 nM AuNPs and 25 mM HEPPSO) with an appropriate pH (pH 7.0 or 7.5) were equilibrated at room temperature for 5 min 20 μL stock solutions of individual or mixed Hg species were then added to each of these mixtures to give the desired total Hg content (1 pM–100 μM). After incubation for 4 h, UV–Vis absorption spectra of detection solutions or their supernatants after centrifugation were recorded. For detecting Hg species, the freshly prepared PH-AuNP solutions (2.5 nM AuNPs, 25 mM HEPPSO and pH 7.5) were added to various concentrations of Hg species (1 pM–100 μM), and above experimental procedures were repeated. For studying the interactions between the freshly prepared PH-AuNPs and other metal ions (the concentration of each metal ion is 1 μM), the UV–Vis absorption spectra were recorded by the same procedures as described above. Moreover, for all quantitative experiments, before measurements the AuNPs in HO-AuNP or PH-AuNP solution were removed by centrifugation to eliminate the interference from the AuNP absorption.