Biosensors and Bioelectronics 72 (2015) 306–312

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

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

Visual determination of aliphatic diamines based on host–guest recognition of calix[4]arene derivatives capped gold nanoparticles

Yangyang Chen [a,1], Jiangjiang Zhang [a,1], Yanmin Gao [a], Jaebeom Lee [b], Hongxia Chen [a,*], Yongmei Yin [c,**]

[a] Laboratory of Biosensing Technology, School of Life Sciences, Shanghai University, Shanghai 200444, China
[b] Department of Applied Nanoscience, Pusan National University, Miryang 627-706, Korea
[c] Department of Oncology, The First Affiliated Hospital of Nanjing Medical University, Nanjing 210029, PR China

ARTICLE INFO

Article history:
Received 14 January 2015
Received in revised form
1 April 2015
Accepted 13 April 2015
Available online 14 April 2015

Keywords:
Diamines
Spermines
Calix[4]arenes
Gold nanoparticles
Biosensors
Host–guest recognitions

ABSTRACT

Since amine compounds have been widespread pollutants in nature and they are extensively used in pharmaceutical industeries and dye manufacturing, it is highly desirable to develop simple, effective and naked-eye available analytical methods for such aliphatic diamines determination. Calixarenes as macrocycles have drawn intensive interests for fields such as biomedicine, supramolecular chemistry and smart materials. Here, instead of the normal complicated modification strategy, a facile and efficient method for one-pot synthesis of calix[4]arene crown ether (CCE4) capped gold nanoparticles (AuNPs) is proposed. The as-prepared CCE4–AuNPs are not only high water dispersity and stability even after storage for 3 months, but also capable of host–guest recognition of diamines in aqueous systems. Size-selective encapsulation of amine group between CCE4 and diamines carry out the aggregation of CCE4–AuNPs. The determination of diamines such as hexamethylenediamine or spermine can be realized by the UV–vis absorbance change and visual color difference.

1. Introduction

Toxic compounds such as amines have been widespread pollutants in nature, since they are extensively used in pharmaceutical industries and dye manufacturing (Reinert and Mohr, 2008). Various biogenic amines such as spermine, spermidine, cadaverine and putrescine are aliphatic diamines, which produced by the enzymatic decarboxylation of amino acids (Önal, 2007). They are of endogenous origin at low concentrations and play important role on the physiological metabolisms. For example, the spermine which exists in various eukaryotic cells and is involved in synthesis of DNAs, RNAs and proteins, is known to play a critical role in process of the cell growth, proliferation and differentiation, as well as in stabilizing membrane and cytoskeletal structures (Wang et al., 2012). Besides, spermine can be an indicative maker of malignant tumors, and is proposed as a tool for early diagnosis and to evaluate the effectiveness of cancer therapy (Yao et al., 2014). Therefore, it is highly desirable to develop simple, effective and naked-eye available analytical methods for such aliphatic diamines determination.

Macrocycles, as most promising materials including cyclodextrins (Chen and Jiang, 2011; Mellet et al., 2011), crown ethers (Gokel et al., 2004), cucurbiturils (Kim et al., 2007; Masson et al., 2012) and calixarenes (Acharya et al., 2012; Kim et al., 2012) have been broadly studied to explore the self-assembly process and host–guest interaction system due to their various recognitions properties. Recently, macrocycle decorated inorganic nanoparticles have drawn particular interests in optical, electronic, thermal and catalytic performances because of their unique integration between physicochemical prosperities of nanoparticles and molecular recognition of macrocycles (Boudebbouze et al., 2013; Kuang et al., 2011; Li et al., 2013; Tarn et al., 2014). It was reported that calix[4]arene crown ether (CCE4) can recognize amino group with high specificity through the macrocyclic cave mediated host–guest interactions (Chen et al., 2011; Oh et al., 2005). Therefore, as shown in Fig. 1, we proposed that visual determination of diamines can be achieved through the – recognition between amine groups and CCE4 mediated aggregation of CCE4 capped gold nanoparticles (CCE4–AuNPs).

However, a bottleneck problem occurs in synthesis of CCE4–AuNPs, since CCE4 is extremely poor soluble in aqueous. An involved strategy has been reported for the immobilization of calix[4]arenes onto AuNPs (Ciesa et al., 2010; Pulkkinen et al., 2014). The employed method consists of three main steps: (i) phase transfer of Au (III) from aqueous to toluene phase in the presence

* Corresponding author.
** Corresponding author.
E-mail addresses: hxchen@shu.edu.cn (H. Chen), ym.yin@hotmail.com (Y. Yin).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.bios.2015.04.036
0956-5663/

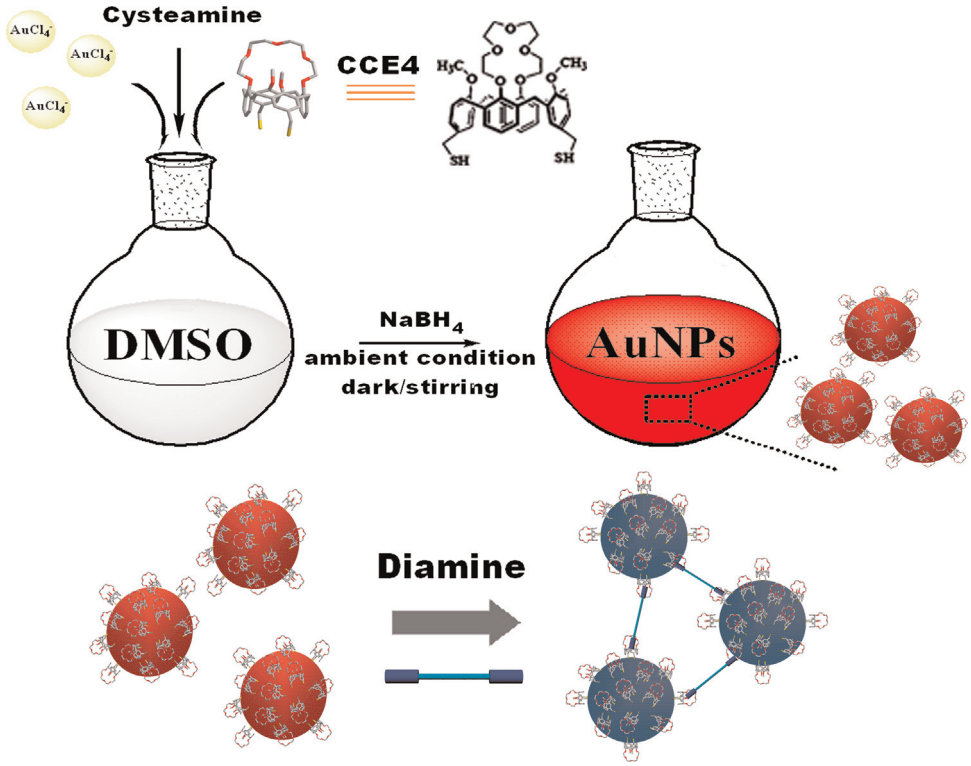

Fig. 1. Schematic demonstration of synthesis approach and the sensing process of diamine mediated aggregation of the CCE4–AuNPs. For clarity, cysteamines as the stabilizer co-capped on the surface of AuNPs are not illustrated.

of tetraoctylammonium bromide (TOAB) for 7 days; (ii) AuNP formation via $NaBH_4$ reduction in toluene phase; (iii) ligand exchange between calix[4]arenes and TOAB. This strategy suffers sophisticated and time-consuming in phase transfer procedures from aqueous to the toluene phase. Therefore, great efforts are still required to explore facile and efficient methods for decorating macrocycles onto AuNPs. Herein, we develop a facile one-pot synthesis method to fabricate CCE4–AuNPs which are well stabilized and dispersed in aqueous. And the prepared CCE4–AuNPs, which as the biosensor, has been successfully employed to visually determine diamines such as hexamethylenediamine or spermine.

2. Experimental section

2.1. Materials and reagents

All chemicals were used as received, if not mentioned otherwise. Gold (III) choloride hydrate, sodium borodeuteride, cysteamine, hexamethylenediamine, spermidine, cadaverine dihydrochloride and each kind of L-amino acids were purchased from Sigma-Aldrich (St. Louis, MO, USA). Spermine and putrescine dihydrochloride were obtained from Aladdin (Shanghai, China). Calix[4]arene crown ether was purchased from Proteogen (Seoul, Korea). Milli-Q water ($>18\ M\Omega$) was used. The reagents were dissolved in water, if not mentioned otherwise. All the glassware used in synthesis of AuNPs were immersed into aqua regia for 30 min and washed over 10 times then dried before use.

2.2. Apparatus

The UV–vis spectra data were obtained by a Shimadzu UV-2450 PC UV–vis spectrophotometer, using a quartz cuvette of 50 μL in volume and 10 mm in path length. TEM, HRTEM and the selected area electron diffraction (SAED) pattern images were recorded on a JEM-2010F instrument with an operating accelerating voltage of 200 kV. Energy-dispersive X-ray (EDX) Spectrum was also examined by JEM-2010F instrument. The sample was prepared by centrifuged twice then drop-casted on a carbon coated copper grid, and dried under an infrared lamp. X-ray photoelectron spectroscopy (XPS) was performed with a Thermo Scientific Escalab 250Xi system that is equipped with a monochromatic Al Kα X-ray source ($h\nu = 1486.6$ eV; spot size = 500 μm; power = 15 kV × 200 W). The sample was prepared by centrifuged twice then drop-casted on the copper grid, and dried under an infrared lamp. Zeta-potential and dynamic light scattering (DLS) data were acquired on a Malvin Zetasizer3000HS system. All of the optical pictures were taken by a Panasonic DMC-LX5 portable camera.

2.3. Preparation of CCE4–AuNPs

Briefly, 10 mL DMSO solution was poured into a 25 mL glass beaker. Then, 100 μL cysteamine solution (16 mg/mL), 100 μL CCE4 solution (200 μM, dissolved in DMSO) and 500 μL Au (III) solution (10 mg/mL) were pipetted into with vigorous stirring at room temperature under dark. After a few minutes, the color changes from bright yellow to colorless, then freshly prepared sodium borodeuteride solution (1 mM, 500 μL) was sequentially and rapidly pipetted into the mixture solution. During which, a procedural color change from colorless to light brown and brownish red was observed. Then appropriate volume of water was added into with additional stirring for an aging time of 30 min. The resulting solution was deep red and stored at 4 °C in amber botter and ready for use.

2.4. Synthesis of cysteamine capped AuNPs

The only cysteamine capped gold nanoparticles (CS–AuNPs) were prepared according to the method previously reported with appropriate modification (Jv et al., 2010; Lee et al., 2011).