

Article pubs.acs.org/JACS

# Three-in-One: Sensing, Self-Assembly, and Cascade Catalysis of Cyclodextrin Modified Gold Nanoparticles

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Abhijit Nag 06/03/2017

#### Introduction

- Gold nanoparticles (AuNPs) are a continuous research interest in the fields of nanoscience and nanotechnology due to their unique optical/electrical properties and versatile application potentials.
- The extinction coefficient of AuNPs is as high as 10<sup>8</sup>-10<sup>10</sup> M<sup>-1</sup> cm<sup>-1</sup>. So, they are one of the ideal energy acceptors in constructing a fluorescence resonance energy transfer (FRET) system for sensing and biosensing.
- AuNPs exhibit catalytic activity, which makes them a potential candidate for the replacement of expensive Pt in some fields.
- In parallel, macrocyclic supramolecules, such as crown ether, cyclodextrin (CD), and calixarene, possess unique and size tunable cavity structures and exhibit special properties. On the basis of host-guest interactions, they have been well-applied for selfassembly, drug/gene delivery, separation, sensing, etc.
- So, the integration of AuNPs and macrocyclic supramolecules not only provides a kind of hybrid nanomaterial but is expected to bring new properties, functions, and applications.

### In this paper

- In this study, they first demonstrate a three-in-one nanoplatform for sensing, selfassembly, and cascade catalysis enabled by CD modified AuNPs (CD@AuNPs).
- Monodisperse AuNPs 15-20 nm in diameter are fabricated in an eco-friendly way using CD molecules as both reducing agents and stabilizers.
- First, the as-prepared AuNPs are employed as not only scaffolds but energy acceptors for turn-on fluorescent sensing based on guest replacement reaction.
- Then, the macrocyclic supramolecule functionalized AuNPs can be controllably assembled and form well-defined one- and two-dimensional architectures using tetrakis(4carboxyphenyl)- porphyrin as mediator.
- Finally, despite being tens of nanometers in diameter, the AuNPs possess unpredictable catalytic activity and exhibit mimicking properties of both glucose oxidase (GOx) and horseradish peroxidase (HRP) simultaneously.

#### Synthesis of the CD@AuNPs

In 35mL of aqueous solution, 5 mL of PBS (0.1M,pH 7.0), 1 mL of HAuCl<sub>4</sub>(0.01 M) and 10 mL of  $\beta$ -CD(0.01 M) were added and vigorously stirred. Then, the mixture was heated to 100 °C for 60 min. The solution gradually changed from light yellow to light red, purple, wine red, indicating the formation of AuNPs. The same procedures were employed for the fabrication of  $\alpha$ -CD,  $\gamma$ -CD, glucose@AuNPs, only  $\beta$ -CD was replaced by  $\alpha$ -CD,  $\gamma$ -CD, glucose, respectively.



**Figure 1.** As-prepared CD@AuNPs. Three kinds of products made from chloroauric acid and  $\alpha$ -CD (A–D),  $\beta$ -CD (E–H), and  $\gamma$ -CD (I–L), respectively. The four rows show TEM (A, E, I), scanning electron microscopy (SEM) (B, F, J), absorption spectra (C, G, K), and histograms of size distribution (D, H, L) results, respectively.



**Figure 2.** Structural characterizations of the  $\beta$ -CD@AuNPs. (A) High-resolution TEM image of the  $\beta$ -CD@AuNPs. (B) FT-IR spectra of the  $\beta$ -CD@AuNPs (red curve) and  $\beta$ -CD (black curve). High-resolution XPS survey scan of O 1s (C) and C 1s (D) of the  $\beta$ -CD@AuNPs. (E) 1H NMR spectrum (in D2O) of the  $\beta$ -CD@AuNPs. (F) The schematic diagram for the surface chemistry of the  $\beta$ -CD@AuNPs. The cartoon mode in the left of part F only shows the probable structure of the as-prepared  $\beta$ -CD@AuNPs, which does not consider (i) the size proportion between  $\beta$ -CD and the AuNPs, and (ii) the precise amounts of  $\beta$ -CD molecules on each AuNP.



**Figure 3.** Fluorescent sensing of cholesterol using the composite made of the  $\beta$ -CD@AuNP and RB molecules. (A) Fluorescence spectra of RB in the presence of different concentrations of the AuNPs. (B) Plots of RB fluorescence intensities versus the AuNP concentrations. (C) Fluorescence spectra of the ( $\beta$ -CD@AuNP-RB) composite after adding varying amounts of cholesterol. (D) Plots of the ( $\beta$ -CD@AuNP-RB) composite fluorescence intensities versus cholesterol concentrations. (E) Selectivity of the ( $\beta$ -CD@AuNP-RB) composite toward various potential interfering substances. The concentration of cholesterol is 4.0  $\mu$ M; the concentrations of the added various substances (from alanine to lecithin) are 0.3, 0.1, 0.08, 0.12, 0.12, 0.16, 0.2, 0.02, 0.08, 0.26, 0.14, 0.06, 0.08, 0.16, 0.25, 1.0, 0.1, 0.28, 0.16 1.04, 2.5  $\mu$ M, respectively; the concentrations of dopamine, bile acid, bilirubin, progesterone, and HSA (human serum albumin) are 3.0 pM, 4.9 nM, 9.4 nM, 4.5 pg/mL, and 0.035 g/L, respectively. The concentrations of both the analytes and various potential interfering substances correspond to 1000 times dilution of those in serum. (F) DFT models for the interactions of  $\beta$ -CD with tryptophan (I), cholesterol (II), and RB (III), respectively. Also, the chemical structures of the three kinds of guest molecules are displayed. (G) Schematic illustration of fluorescent turn-on detection of cholesterol using the ( $\beta$ -CD@AuNP-RB) composite.

Published in: Yan Zhao; Yucheng Huang; Hui Zhu; Qingqing Zhu; Yunsheng Xia; *J. Am. Chem. Soc.* **2016,** 138, 16645-16654. DOI: 10.1021/jacs.6b07590 Copyright © 2016 American Chemical Society



**Figure 4.** 1D and 2D self-assembly of the  $\beta$ -CD@AuNPs. SEM images of the 1D (A) and 2D (B) assemblies of the  $\beta$ -CD@AuNPs in the presence of 0.1 and 0.3  $\mu$ M TCPP molecules, respectively. (C) The absorption spectra and photo images (inset) of the  $\beta$ -CD@AuNPs in the presence of different concentrations of TCPP molecules, which correspond to parts A and B. (D) Sketch of two  $\beta$ -CD rings connected by a TCPP molecule by para (5,15) host–guest interactions (above, top view; below, side view). TEM images of 1D (E, F) and 2D (G) assemblies of the  $\beta$ -CD@AuNPs in the presence of 0.1 and 0.3  $\mu$ M TCPP molecules, respectively. The different particle–particle distances are highlighted by different colored circles, which are correspond to part H. (H) Histograms for the distances among particle–particle interactions in the 1D assembly (above) and the 2D assembly (below). The two histograms are the results of 150 particle–particle distances, respectively. In the statistics, only the particle–particle distances within 0.5–3.0 nm are counted. (I) Schematic illustration of the 1D/2D self-assembly of the AuNPs based on TCPP concentration modulated by host–guest interactions.

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**Figure S18.**  $\xi$ -potential values of the  $\beta$ -CD@AuNPs containing solution (pH 4.0) in the absence (A) and presence of 0.1 (B) and 0.3 (C)  $\mu$ M TCPP molecules. The concentration of the  $\beta$ -CD@AuNPs is 0.378 nM.



**Figure S19.** The schematic diagrams of  $\beta$ -CD-TCPP host-guest interactions by para- (5,15) (A) and ortho- (5,10) (B1 and B2) position manners.



**Figure 5.** Catalytic properties of the  $\beta$ -CD@AuNPs. (A) Absorption spectra of three TMB related systems. The supernatant came from the CD@AuNPs-glucose system. After catalysis, the AuNPs were separated by centrifugation, and the resulting supernatant was obtained. (B) pH dependent GOx-mimicking property of the AuNPs. (C) Steady-state kinetic assay of GOx-mimicking activity. The velocity (v) of the reaction was measured using 0.605 nM AuNPs. (D) Absorption spectra of three TMB based systems. (E) pH dependent HRP-mimicking property of the AuNPs. (F, G) Steady-state kinetic assay of HRP-mimicking activity. The velocity (v) of the reaction was measured as the concentration of the AuNPs was 0.09 nM. In part F, the concentration of TMB was 0.12 mM. In part G, the concentration of H<sub>2</sub>O<sub>2</sub> was 6 mM. (H) TMB chromogenic reaction systems for H<sub>2</sub>O<sub>2</sub> produced by the catalysis of glucose using  $\beta$ -CD@AuNPs as the catalyst. The pH values of all supernatants had been tuned to 4.5. The "used" AuNPs meant the AuNPs had been used for the first-step GOx-mimicking catalysis. The "fresh" AuNPs meant the AuNPs had not been employed for the catalysis of glucose oxidation. (I) Schematic illustration of the cascade catalysis system using the  $\beta$ -CD@AuNPs as the only catalyst.

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**Figure 6.** Carboxylated  $\beta$ -CD molecules adsorb on Au(111) (A), Au(100) (B), and Au(110) (C) surfaces. Charge density differences of the carboxylated  $\beta$ -CD (D) and carboxylated glucose (E) adsorbed on the Au (110) surface. The light green and light yellow regions represent charge depletion and accumulation, respectively.



Scheme S2. The proposed mechanism for the GOX-mimicking property of the β-CD@AuNPs.<sup>S14</sup>



**Figure S28.** The effects of the AuNPs on the formation of  $\cdot$ OH with terephthalic acid as a fluorescence probe. 10 mM of H<sub>2</sub>O<sub>2</sub>, 0.5 mM of terephthalic acid and different concentrations of the  $\beta$ -CD@AuNPs were incubated in acetate buffer solutions (0.01 M, pH 4.5) and exposed to UV light (365 nm) for 20 min before fluorescence measurement.<sup>S15</sup>

## Conclusion

- In summary, they present an eco-friendly method for one-step fabrication of supramolecule functionalized AuNPs using CD molecules as both stabilizers and reducing agents.
- The AuNPs possess macrocyclic structures on the particle surface, they can be employed as scaffold and energy acceptor for fluorescent sensing.
- Furthermore, the CD@AuNPs act as building blocks for the construction of well-defined nanosuperstructures: 1D/2D architectures are well-obtained by simple modulation of mediator (TCPP) concentrations.
- In addition to conventional host-guest interaction based properties, the CD@AuNPs can achieve unique cascade catalysis.