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Mesoporous silica-encapsulated gold nanoparticles as artificial enzymes for self-activated cascade catalysis

Youhui Lin, Zhenhua Li, Zhaowei Chen, Jinsong Ren*, Xiaogang Qu*

State Key laboratory of Rare Earth Resources Utilization and Laboratory of Chemical Biology, Changchun Institute of Applied Chemistry, Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Changchun, Jilin 130022, China

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ABSTRACT

A significant challenge in chemistry is to create synthetic structures that mimic the complexity and function of natural systems. Here, a self-activated, enzyme-mimetic catalytic cascade has been realized by utilizing expanded mesoporous silica-encapsulated gold nanoparticles (EMSN-AuNPs) as both glucose oxidase- and peroxidase-like artificial enzymes. Specifically, EMSN helps the formation of a high degree of very small and well-dispersed AuNPs, which exhibit an extraordinarily stability and dual enzyme-like activities. Inspired by these unique and attractive properties, we further piece them together into a self-organized artificial cascade reaction, which is usually completed by the oxidase-peroxidase coupled enzyme system. Our finding may pave the way to use matrix as the structural component for the design and development of biomimetic catalysts and to apply enzyme mimics for realizing higher functions.

1. Introduction

Creating artificial enzymes that mimic the complexity and function of natural systems have been a great challenge for the past two decades [1–4]. Natural enzymes possess high activity and high substrate specificity under mild reaction conditions. However, the practical application of enzymes is often hampered by their intrinsic drawbacks, such as sensitivity of catalytic activity to environmental conditions, the difficulties in recovery and recycling, high costs in preparation and purification, and low operational stability (denaturation and deactivation) [5,6]. Therefore, the discovery and development of enzyme mimics is highly desired [2,4,7,8].

Recently, nanoscale materials, such as magnetic nanoparticles, graphene oxide, cerium oxide nanoparticles, metal-hybrid nanostructures and single wall-carbon nanotubes etc. have been discovered to possess unique enzyme-mimic catalytic activities and shown promising potential in environmental detection and biomedical applications [4,5,9–15]. However, a major challenge in biomimetic catalysis is the possibility of piecing these synthetic nanocomponents together into organized functional systems (artificial enzymatic cascade systems), a phenomenon common in nature [16–18], but much more difficult to achieve with synthetic building blocks. Importantly, when they are scaled up for assembling a cascade system, an effective method to eliminate the incompatibility of different reactions should be adopted. Until now, there are no published reports on the nanomaterials-based enzyme-mimetic catalytic cascade. Very recently, gold nanoparticles (AuNPs) with different surface modifications have been synthesized and found to exhibit glucose oxidase(GOx)- or peroxidase-like activity separately, a property not revealed in bulk gold [19–23]. For instance, cysteamine-capped AuNPs show peroxidase-like activity, whereas citrate-capped AuNPs have GOx-like activity. However, their potential as enzyme mimics is limited by low catalytic activity and stability mainly due to their heterogeneous distribution and aggregation [21]. Moreover, single-component AuNPs with dual enzyme-like functionalities active could not be realized (Scheme 1). Firstly, enzyme-like activities of AuNPs are extremely sensitive to surface properties. The unsupported AuNPs with different surface modifications only keep one of enzyme-like functionalities active, while the other catalytic activity can be completely blocked. For example, cysteamine-capped AuNP cannot catalyze the glucose oxidation reaction, whereas the citrate-capped AuNPs cannot possess peroxidase-like activity [22,23]. In addition, the low stability of unsupported NPs under different conditions causes a serious decline in their performance during catalytic operation. More importantly, it is extremely difficult to scale them up for assembling an enzymatic cascade system owing to the incompatibility of various reactions operating under different conditions. Recently, the emergence and recent advance of

* Corresponding authors. Tel./fax: +86 431 85262625.
E-mail addresses: jren@ciac.jl.cn (J. Ren), xqu@ciac.jl.cn (X. Qu).

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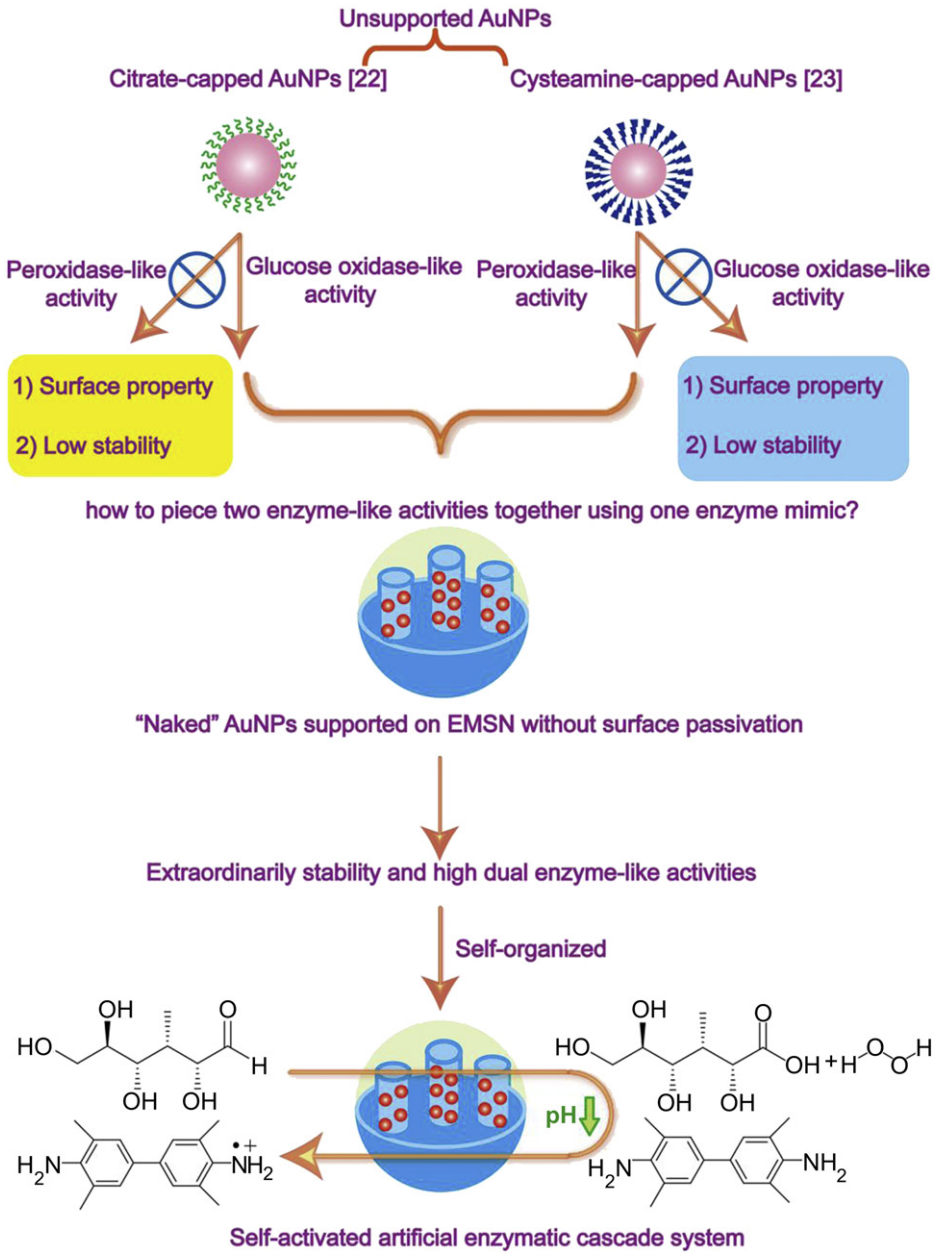

Scheme 1. Rational design of EMSN-AuNPs as intelligent enzyme mimics for realizing higher functions (self-organized artificial catalytic cascade).

nanotechnology opens new opportunities for the development of nanoparticles with stable and high catalytic activity [24–28]. Therefore, the rapid progress in solid-supported catalysts prompted us to evaluate whether matrices will improve the performance of AuNPs-based artificial enzyme for realizing higher functions. Especially, metal nanoparticles embedded in mesoporous host matrices have attracted sustained interest owing to their unusual catalytic, electronic and optical properties [26,27]. Thus, mesoporous matrix was used as a model system to provide the "proof-of-principle" verification of the concept.

Herein, we describe a rational approach of the construction of the "naked" AuNPs supported on expanded mesoporous silica support (EMSN), which can be served as dual artificial enzymes. Meanwhile, we offer an effective way to eliminate the incompatibility of different reactions through self-activated process, and investigate this dual activity in an one pot system for realizing artificial enzymatic cascade reaction.

2. Materials and methods

2.1. Materials

Tetraethylorthosilicate (TEOS), sodium hydroxide and 1,3,5-trimethylbenzene were purchased from Sigma–Aldrich. Glucose and hydrogen tetrachloroaurate (III) ($HAuCl_4 \cdot 3H_2O$) were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). Hydroxylamine, 3-aminopropyltriethoxysilane (APTES), N-cetyltrimethylammonium bromide (CTAB), and sodium borohydride ($NaBH_4$) were obtained from Alfa Aesar. 3,3,5,5-Tetramethylbenzidine (TMB) was purchased from BBI (Ontario, Canada). H_2O_2 was obtained from Beijing Chemicals (Beijing, China). All other reagents were of analytical reagent grade, and used as received. Ultrapure water (18.2 MΩ; Millpore Co., USA) was used throughout the experiment.

2.2. Measurements and characterizations

The pH measurements were performed with a PHS-3C portable pH meter (Shanghai Precision & Scientific Instrument Co., China). The UV–Vis absorption spectra were recorded using a Jasco V550 UV/Visible spectrophotometer (JASCO International Co., LTD., Tokyo, Japan). A field emission scanning electron microscope