Materials Letters 229 (2018) 316–319

Contents lists available at ScienceDirect

Materials Letters

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

Design of biomimetic surface for fabrication of monodispersed silver nanoparticles with high catalytic activity

Fenfen You, Yan Sun, Lin Zhang *

Department of Biochemical Engineering and Key Laboratory of Systems Bioengineering of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300354, PR China

ARTICLE INFO

Article history:
Received 26 April 2018
Received in revised form 17 June 2018
Accepted 9 July 2018
Available online 10 July 2018

Keywords:
Biomimetic
Nanoparticles
Catalyst
4-Nitrophenol
Catalytic activity

ABSTRACT

A biomimetic surface of protein molecule was synthesized and used as a removable template to fabricate stable and monodispersed silver nanoparticles (Ag NPs). Ag NPs with a diameter of 1.8 ± 0.25 nm were obtained, and exhibited excellent catalytic activity in the reduction of 4-nitrophenol with an average activity parameter of 0.892 $L \cdot mg^{-1} \cdot s^{-1}$. Moreover, the Ag NPs remained stable even after storage at 4 °C for two months, and the activity could be retained up to 88.3%. Therefore, a feasible, straightforward and effective fabrication of stable and monodispersed Ag NPs was achieved herein. It would facilitate the design of functional surface and its application in nano-biomaterials.

1. Introduction

Silver nanoparticles (Ag NPs) have been extensively used in various fields [1,2] beneficial from the unique physicochemical and biological properties. The nanometer size leads to excellent performance of Ag NPs, however, causes high surface energy and irreversible aggregation [3], and thus the limitation on applications. Although various chemical and physical methods [4,5] have been proposed for the synthesis of monodispersed Ag NPs, the assistance of various supports or protective agents is usually necessary. Biosynthesis methods [6,7], especially protein–templated approaches, as an alternative, are promising and have received increasing research interests due to the advantages of nanoscale dimensions, surface functionalities and substrate-specific affinity of natural materials. However, its application was limited by protein instability and the complicated protein surface with various functional groups, which caused uncontrollability of reaction and thus the irreversible aggregation of Ag NPs.

To overcome these obstacles, a biomimetic surface of protein molecule with nano-size and stable homogenous surface containing peptide bond and flexible amino was obtained based on the modification of inorganic nanoparticles, and then used as template for the fabrication of Ag NPs. The catalytic activity of obtained Ag NPs was evaluated in the conversion of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP).

* Corresponding author.
E-mail address: linzhang@tju.edu.cn (L. Zhang).

https://doi.org/10.1016/j.matlet.2018.07.036
0167-577X/

2. Experimental section

Biomimetic surface was synthesized firstly via atom transfer radical polymerization, where silicon dioxide (SiO_2) was used as the modified inorganic nanoparticle because of its facile synthesis, high specific surface area, hydrophilic surface convenient for following chemical modification, and easy recycling by centrifugation. 2-(2-Bromoisobutyryloxy) ethyl methacrylate (BIEM) and acrylamide (AM) were used as monomers (Figs. S1–S3, Table S1), where BIEM contributed to the formation of hyperbranched structure, and AM provided peptide bond and flexible amino to mimic the functional groups in protein molecules. The molecular weight of the obtained polymer was 735 Da (Fig. S4). Then, biomimetic surface was used as a removable template to fabricate Ag NPs with silver nitrate ($AgNO_3$) as donor of silver ions and sodium borohydride ($NaBH_4$) as reducing agent. The biomimetic surface was not a raw material but was synthesized and used based on the polymer properties. Finally, reduction of 4-NP to 4-AP was employed to evaluate the catalytic activity of Ag NPs [8]. *For more detailed information, please look into SI.*

3. Results and discussion

3.1. Fabrication of Ag NPs

TEM image of Ag NPs synthesized with the assistance of biomimetic surface was obtained (Fig. 1b). Monodispersed and spherical

dots were observed, most of which distributed uniformly in solution while the left attached on the biomimetic surface. The obtained solution was milky due to the existence of biomimetic surface. It changed to colorless and transparent once the biomimetic surface were removed by centrifugation, as shown in the inset of Fig. 1c. The diameter of Ag NPs in solution was determined as 1.8 ± 0.25 nm from TEM image. The crystalline structure of Ag NPs was further determined in HRTEM image (Fig. 1d). The interplanar spacing for the lattice planes was measured as 0.23 ± 0.02 nm, corresponding to the (1 1 1) crystal plane of silver (JCPDS No. 4-783), which confirmed the successful synthesis of Ag NPs in the crystalline state [9]. The size of Ag NPs was then characterized using DLS. Unimodal size distribution of Ag NPs with an average diameter of 7 nm was observed (Fig. 1e), confirming the monodispersed distribution. Moreover, no obvious peak corresponding to Ag NPs in the UV–Vis spectra (Fig. 1f) or signal of Ag element (absorption at 3 keV) in EDS spectrum (Fig. 1g) was observed, confirming the diameter of Ag NPs was 2 nm or smaller size [10]. The signals corresponding to C, O, and Si in EDS spectrum (Fig. 1g) indicated the existence of biomimetic surface, while the signal corresponding to Cu could be attributed to the net copper grid used in the preparation of TEM samples.

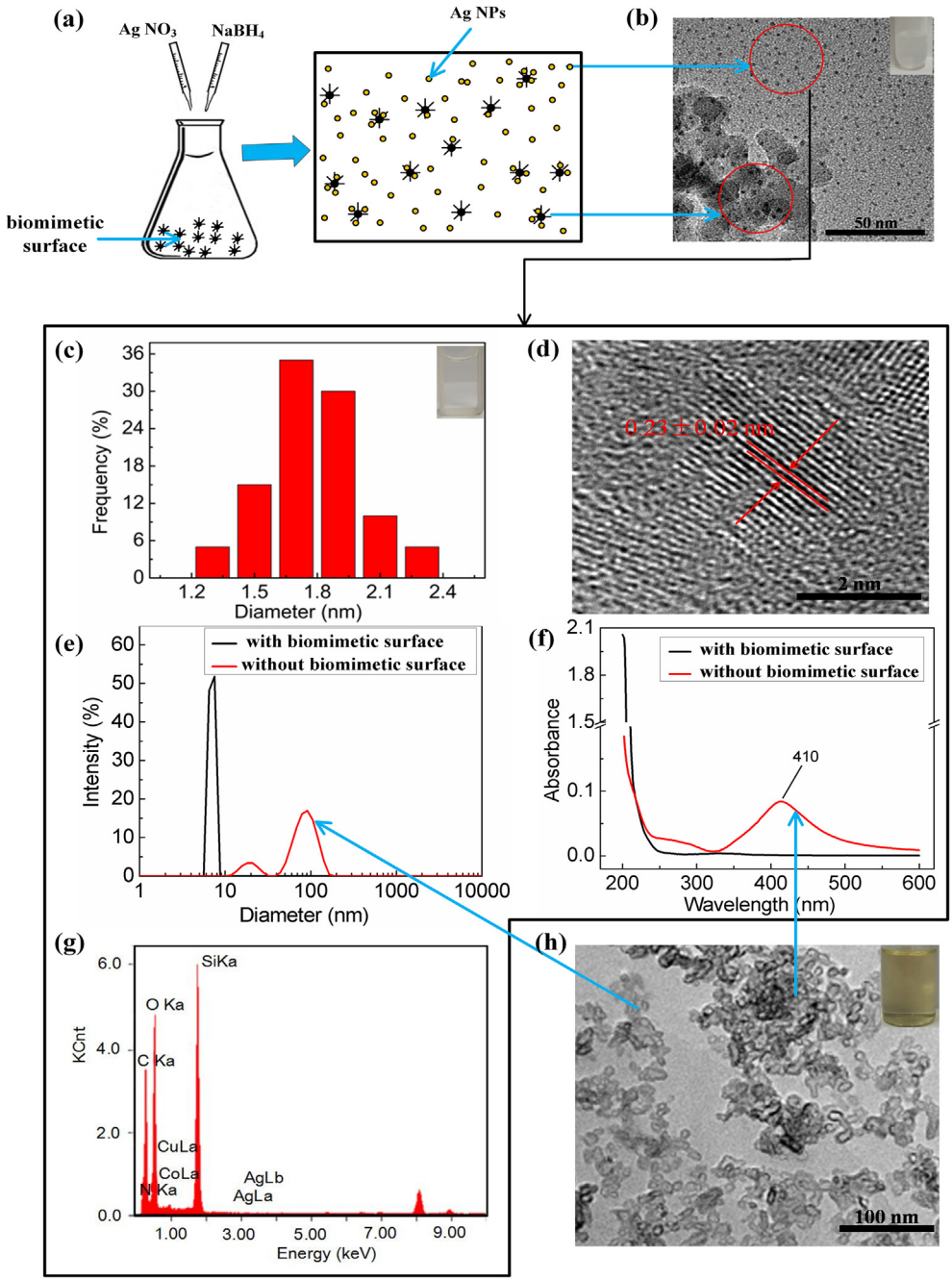

Fig. 1. Characterization of Ag NPs synthesized with the assistance of biomimetic surface. A schematic diagram is shown in (a). TEM image of Ag NPs is shown in (b). Size distribution of Ag NPs in solution is shown in (c), and the HRTEM image is shown in (d). Size distribution of Ag NPs in solution synthesized with (black) or without (red) biomimetic surface is shown in (e), and corresponding UV–Vis spectra are shown in (f). EDS spectrum of Ag NPs in solution is shown in (g). TEM image of Ag NPs synthesized without biomimetic surface is shown in (h). In (b), (c) and (h), the typical photographs are shown in the insets. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)