Applied Surface Science 402 (2017) 469–477

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Modulation of surface structure and catalytic properties of cerium oxide nanoparticles by thermal and microwave synthesis techniques

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ARTICLE INFO

Article history:
Received 7 December 2016
Received in revised form 8 January 2017
Accepted 16 January 2017
Available online 17 January 2017

Keywords:
Cerium oxide nanoparticles
Convective heating
Microwave irradiation
Reactive oxygen species
Superoxide dismutase

ABSTRACT

Cerium oxide nanoparticles (CNPs) have been intensively explored for biomedical applications in recent few years due to the versatile enzyme mimetic activities of the nanoparticles. However, the control of CNPs quality through the optimization of synthesis conditions remains largely unexplored as most of the previous studies only focus on utilizing the catalytic activities of the nanoparticles. In the present study, CNPs with size about 5 nm were synthesized by thermal decomposition method using traditional convective heating and recently developed microwave irradiation as heating source. The quality of CNPs synthesized by the two heating manner was evaluated. The CNPs synthesized by convective heating were slightly smaller than that synthesized by microwave irradiation heating. The cores of the CNPs synthesized by the two heating manner have similar crystal structure. While the surface subtle structures of the CNPs synthesized by two heating manner were different. The CNPs synthesized by microwave irradiation have more surface reactive hot spot than that synthesized by convective heating as the nanoparticles responded more actively to the redox environment variation. This difference resulted in the higher superoxide dismutase (SOD) mimetic activity of CNPs synthesized by microwave irradiation heating than that of the convective heating. Preliminary experiments indicated that the CNPs synthesized by microwave irradiation heating could better protect cells from oxidative stress due to the higher SOD mimetic activity of the nanoparticles.

1. Introduction

CNPs have found versatile enzyme mimetic activities including SOD, oxidase, catalase, peroxidase and phosphatase [1–5]. These catalytic properties have driven the intensive study of CNPs in bio-applications such as anti-irradiation, bio-detection, cancer therapy and tissue engineering [6–10]. Because the nanoparticles used in bio-applications usually have to be hydrophilic, previously used CNPs were mostly synthesized by water based wet chemistry method [11–13]. In such CNPs synthesis procedure, precipitation reagent like $NH_3{\cdot}H_2O$ or H_2O_2 is added into the cerium salt solution with or without stabilizer under agitation, and the CNPs were immediately formed after the addition of precipitation reagent [14,15]. Although this method could easily obtain hydrophilic CNPs, the reaction between the cerium and the precipitation reagent is too fast to be well controlled. As a result, the nanoparticles synthesized by this method usually have poor crystallinity, morphology and size distribution. These defects could affect the practical application of CNPs since previous studies have proved that nanoparticle morphology and size distribution have significant effect on the bio-application of nanoparticles.

In the past few decades, thermal decomposition method has been well explored for inorganic nanoparticles synthesis [16–20]. In a general thermal decomposition synthesis procedure, the precursor containing the elements necessary to build up the nanoparticles is dissolved in organic solvent added with stabilizer and heated to the decomposition temperature. The decomposed metal precursor form the nucleus of the nanoparticles and the stabilizer was bound to the nucleus to prevent the aggregation of the nanoparticles. Comparing with water based wet chemistry method, thermal decomposition method could achieve higher crystallinity, better morphology and narrower size distribution of inorganic nanoparticles. Although the nanoparticles synthesized by thermal decomposition method are usually dispersed in organic solvent, the lateral surface modification using inorganic material affinitive compounds such as dopamine, alendronate, and polyacrylic acid

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http://dx.doi.org/10.1016/j.apsusc.2017.01.149
0169-4332/

could easily transfer the nanoparticles into water [21–24]. Therefore, thermal decomposition method could be developed as a better way to get high quality CNPs than water based wet chemistry method.

In the thermal decomposition synthesis procedure, the precursor, stabilizer, solvent and heating manner, including reaction temperature and heating programs, are the main factors that control the quality of the nanoparticles. As for the heating manner, the traditional heating form is convective heating where the energy is generated by heating device and transfer to the reaction solution through convective currents. Because the energy has to penetrate the reaction vessel before reaching the central of the reaction solution, the heat distribution in the reaction system is not uniform especially at the early stage of the reaction [25]. This could lead to broad nanoparticle size distribution, low reaction yield and the generation of by-products. To avoid these problems, the reaction system has to be well designed. For example, the reaction temperature and heating program need to be nicely controlled, the solvent and stabilizer used in the reaction need to be carefully selected [26–28]. Although high quality of nanoparticles could be achieved after optimizing the above-mentioned reaction conditions, these additional operations could complicate the nanoparticle synthesis procedure.

In the past few years, microwave irradiation has been explored as a new heating source for thermal decomposition nanoparticle synthesis [29]. Unlike the traditional convective heating that generate heat through convective currents and thermal conductivity, microwave irradiation directly couple microwave energy to the solvent, precursor and stabilizer of the nanoparticle synthesis system. The main advantage of this heating manner is that the reaction mixture could be quickly and uniformly heated to a given temperature leading to a higher synthesis yield, shorter reaction time, lower reaction temperature, less by-products and better size distribution [25,30–32].

To take advantage of the above-mentioned superiorities, microwave irradiation has also been tried on CNPs synthesis in previous studies [33–37]. Undoubtedly, the microwave irradiation heating could promote the CNPs synthesis yield. However, the other superiorities of microwave assisted CNPs synthesis have not been well exhibited in the previous studies. Firstly, the morphology and size distribution of the CNPs synthesized by previous microwave assisted methods have not been nicely controlled. Secondly, the differences of crystal structure and catalytic activity of CNPs synthesized by traditional convective heating and microwave irradiation heating methods have not been evaluated. To well explore and utilize the superiorities of microwave irradiation for future CNPs synthesis, we investigated the differences of CNPs synthesized by traditional convective heating and microwave irradiation heating methods. The synthesis conditions, subtle structure, catalytic activity and biocompatibility of the synthesized CNPs were carefully evaluated.

2. Materials and methods

2.1. Synthesis of CNPs by traditional convective heating

The CNPs were synthesized according to a previous study with modification [19]. In general, 434 mg cerium (III) nitrate hexahydrate was dissolved in 1 mL oleylamine and 5 mL 1-octadecene (ODE). The mixture was heated to 80 °C for 30 min under vacuum and then heated to designed temperature using electric thermal heating mantle as heating source. After cooling to room temperature, the nanoparticles were washed by 1:1 tetrahydrofuran and acetone until the supernate was clear. Finally, the nanoparticles were dispersed in tetrahydrofuran and stored at −20 °C.

2.2. Synthesis of CNPs by microwave irradiation heating

In a typical reaction, 434 mg cerium (III) nitrate hexahydrate was dissolved in 1 mL oleylamine and 5 mL ODE. The mixture was heated to 80 °C for 30 min under vacuum and then heated to 180 °C using a CEM Discover SP instrument operated at 300W. After cooling to room temperature, the nanoparticles were washed by 1:1 tetrahydrofuran and acetone until the supernate was clear. Finally, the nanoparticles were dispersed in tetrahydrofuran and stored at −20 °C.

2.3. Surface modification of CNPs

The CNPs were transferred from tetrahydrofuran into water by coating the nanoparticles with polyethylene glycol (PEG, MW = 600) using alendronate as anchor according to our previous method [22]. In a typical surface modification reaction, 110 mg PEG diacid, 35 mg *N*-(3-Dimethylaminopropyl)-*N*-ethylcarbodiimide (EDC) and 21 mg N-Hydroxysuccinimide (NHS) were mixed in 2 mL dichloromethane for 12 h. The solvent was removed by rotate evaporation, and the activated PEG diacid was added with 20 mg alendronate and 50 mg Na_2CO_3 dissolved in 4 mL water. The mixture was stirred for 12 h. After that, 6 mL tetrahydrofuran and 2 mL of the synthesized CNPs were added into the mixture. The reaction was carried out at 80 °C for 12 h under magnetic stir. After cooling to room temperature, the water layer containing PEG coated CNPs was separated by centrifugation. The nanoparticles were washed by 20 mL acetone and dialyzed in water for 24 h. The PEG coated CNPs were freeze dried for 48 h. The surface PEG coating was characterized by thermo gravimetric analysis (TGA) using a TA Q50 analyzer with temperature increase rate of 20 °C/min. The graphs were analyzed by the TA Universal Analysis software.

2.4. Characterization of CNPs

The CNPs size was measured by transmission electron microscope (TEM). One drop of CNPs dispersed in hexane was casted onto a carbon coated copper grid. The sizes of the nanoparticles were recorded on a Tecnai G2 F20 S-TWIN TEM operating at 200KV. The images were analyzed by Gatan Digital Micrograph software. X-ray diffraction (XRD) analysis was performed on a PERSEE XD2 instrument equipped with a Cu Kα radiation source (λ = 0.15406 nm) operated at 36 kV and 30 mA with a scanning speed of 2°/min. The graphs were analyzed by MDI Jade software.

2.5. Ce^{3+}/Ce^{4+} ratio characterization

The nanoparticles were freeze dried for 48 h. The XPS spectra were recorded on a SCIENTIFIC ESCALAB 250 multipurpose surface analysis system. The photoelectron spectra were excited by an Al Ka (1486.6 eV) anode operated at 100W. The base pressure during XPS analysis was maintained at less than10^{-9} mbar, and the binding energy scale was calibrated from the C1 s peak at 284.8 eV. The 3d peak positions of cerium were fitted using XPSPEAK41 software with binding energy from 875 to 920ev. The binding energy of 880.0, 885.0, 899.2 and 903.4 are the characteristic peaks of Ce^{3+}, and the binding energy of 882.1, 888.1, 897.9, 900.8, 906.8 and 916.35 are the characteristic peaks of Ce^{4+} [38].

2.6. SOD mimetic activity analysis

The SOD mimetic activity of CNPs was determined by the inhibition of superoxide free radical which was generated by the riboflavin under light illumination [22]. The reaction system contains the detection solution and the CNPs solution. The detection solution was prepared by mixing 200 μL EDTA (0.1 mol/L), 75 μL