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Facile and green fabrication of small, mono-disperse and size-controlled noble metal nanoparticles embedded in water-stable polyvinyl alcohol nanofibers: High sensitive, flexible and reliable materials for biosensors

Han Zhu [b], MingLiang Du [a,b,*], Ming Zhang [a,b], Pan Wang [b], ShiYong Bao [b], YaQin Fu [a,b], JuMing Yao [a,b]

[a] Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Zhejiang Sci-Tech University, Ministry of Education, Hangzhou 310018, PR China
[b] Department of Materials Engineering, College of Materials and Textile, Zhejiang Sci-Tech University, Hangzhou 310018, PR China

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ABSTRACT

A facile and green approach has been demonstrated for the fabrication of highly uniform and monodisperse noble metal (Ag, Au, Pt) nanoparticles (NMNPs) in polyvinyl alcohol (PVA) nanofibers by combining an in situ reduction and electrospinning technique, which are used as efficient biosensor for the detection of H_2O_2. The small and stable NMNPs can be easily obtained in aqueous solution using EGCG as both reductant and stabilizer. Through electrospinning technique, uniform and smooth nanofibers can be obtained and the NMNPs with narrow size distributions are well dispersed in PVA nanofibers. The investigation indicates that the viscosity of the PVA solution play an important role in controlling the size of NMNPs. The fabricated AgNPs/PVA nanofibers functionalized electrodes exhibits remarkable increased electrochemical catalysis toward H_2O_2 and excellent stability and reusability. The biosensor allows the highly sensitive detection of H_2O_2 with a broad linear range span of the concentration of H_2O_2 from 10 μM to 560 μM. The rapid electrode response to the change of the H_2O_2 concentration is attributed to the fast diffusion of the H_2O_2 onto the surface of small AgNPs through the porous nanofibers structures.

1. Introduction

Noble metal nanostructures have received intensive research interests in recent decades due to their unique structure-dependent properties and potential applications in numerous fundamental and applied fields, such as catalysis, sensors, energy conversion, antibacterial, biology and biomedicine [1–4]. Recent years have witnessed tremendous efforts devoted to the design and synthesis of noble metal nanoparticles (NMNPs) in the application of electrochemical biosensors [5–7]. Electrochemical biosensors, a subclass of chemical sensors, possess high specificity of biological recognition processes [8,9]. These devices contain a biological recognition element (enzymes, proteins, antibodies, nucleic acids, cells, tissues or receptors) that selectively reacts with the target analyte and produces an electrical signal that is related to the concentration of the analyte [9,10]. Electrochemical detection of biomolecules using nanomaterials can often achieve high sensitivity because nanomaterials are extremely sensitive to electronic perturbations in the surrounding environment [11,12]. For example, Mao et al. prepared reduced graphene oxide sheet decorated with gold nanoparticles using as biosensors for the detection of protein, suggesting a lower detection limit and rapid current response [6].

It is well-known that the electrocatalytic activity of metal nanoparticles is extremely sensitive to their sizes, sharp and dispersion [13–16]. Small size usually can dramatically affect their physical and chemical properties arised from their large surface-area-to-volume ratio and the spatial confinement of electrons, phonons, and electric fields in and around these particles [17–20]. However, along with the exciting properties caused by the small size, significant challenges still remain for the preparation and isolation of nanoparticles with controlled polydispersity, toxicity, and aggregation, which are due to the high surface energy and large surface curvature of nanoparticles.

A high dispersion of NMNPs is basically important to present high catalytic activity, and unfortunately, the associated tendency of NMNPs to aggregate would lower their catalytic activity and reuse life-time [21–23]. Therefore, how to design and prepare NMNPs with long-term dispersion stability and high catalytic efficiency is a primary challenge for the widely applications. Recently, one-dimensional (1-D) nanostructures such as nanowires, nanobelts and nanotubes were used as supports to protect NMNPs against aggregating and facilitate their recovery [24,25]. Chauhan et al. fabricated Au nanoparticles/multiwalled carbon nanotubes/polymers modified Au electrodes used as lysine

* Corresponding author at: Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Zhejiang Sci-Tech University, Ministry of Education, Hangzhou 310018, PR China. Tel.: +86 571 86843255.
E-mail addresses: du@zstu.edu.cn, psduml@gmail.com (M. Du).

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biosensors, demonstrating an improved analytical performance with higher stability and low limit of detection and response time [26]. However, conventional deposition precipitation method is unlikely to produce highly dispersed NPs.

Organic polymer nanofibers have been recently recognized as a new kind of 1-D supports and besides the stabilizing and protecting effects for NMNPs, polymers can offer unique possibilities for modifying both the environment around NMNPs and access to the catalytic sites [21,22]. Through electrospinning technique, various morphologies nanofibrous mats with high specific surface area, porosity, flexibility and stability can be easily achieved [27–30]. Polyvinyl alcohol (PVA) is a water soluble polymer with good biocompatibility. Combining the flexibility, good biocompatibility and porous structures of PVA nanofibers, we use the PVA solution to prepare the uniform, well-dispersion and small size of NMNPs.

In modern life, from the viewpoint of practical applications, it would be of great value to explore a facile and green approach for the synthesis of NMNPs in nanoscience [21,31]. In our previous reports, a green reductant, tea polyphenols (TP) was used to synthesis small and uniform Au nanoparticles (AuNPs) and the TP can also act as a stabilizer for protecting the AuNPs from aggregations [31–34]. In this paper, a group of water-soluble polyphenols richly deposited in plants, epigallocatechin gallate (EGCG), was used as reductant for the synthesis of NMNPs in PVA and aqueous solution via an in situ reduction. It is easy to achieve small, highly dispersion, reliable, stable, and uniform NMNPs using this method. Through electrospinning technique, uniform and smooth nanofibers can be obtained and the NMNPs with narrow size distributions are well dispersed in PVA nanofibers. The size of AgNPs embedded in PVA nanofibers and the morphology and diameter of the nanofibers can be adjusted by changing the concentration of PVA. In order to obtain AgNPs/PVA nanofibrous mats with performance porous structures and water stability, GA vapor was used to crosslink the nanofibers. After the immersion in water for 12, 24, 48 h, respectively, the porous nanofibers structure was still well preserved, suggesting the successful crosslinkage. The functional AgNPs/PVA nanofibrous mats were used as electrochemical biosensors for the detection of H_2O_2.

2. Experiment

2.1. Materials

Silver nitrate ($AgNO_3$) was acquired from Changzhou GuoYu Environmental S&T Co., Ltd. Chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, 99.9%) and chloroautic acid ($HAuCl_4{\cdot}4H_2O$, 99.9%) were acquired from Shanghai Civi Chemical Technology Co., Ltd. Polyvinyl alcohol (88% hydrolyzed, Mw = 88 000), horseradish peroxidase (HRP, RZ ~ 3, activity ≥ 300 units mg^{-1}), hydroquinone (HQ) and H_2O_2 (30 wt%) were obtained from Aladdin Chemistry Co., Ltd. Epigallocatechin gallate (EGCG) was purchased from Xuancheng Baicao Plant Industry and Trade Co., Ltd. Glutaraldehyde (GA) aqueous solution (30 wt%) and phosphate buffer (PB) were obtained from Hangzhou Gaojing Fine Chemical Co., Ltd. Nafion aqueous solution (5 wt%) was obtained by Aldrich Chemistry Co., Ltd. All the chemicals were used as received without further purification. Deionized water (DIW) was used for all solution preparations.

2.2. Green synthesis of noble metal (Ag, Au, Pt) nanoparticles (NMNPs) in aqueous solution using EGCG as reductant

For the synthesis of NMNPs, 2 mL Ag (I) solution (5 mmol L^{-1}), 2 mL Au (III) solution (5.0 mmol L^{-1}) and 3 mL Pt (VI) solution (10.0 mmol L^{-1}) were firstly dissolved in 25 mL DIW under moderate stirring to get a homogeneous solution. Then, the mixture were injected into a 3-neck flask (fitted with a reflux condenser and a Teflon-coated stir bar) and heated to 65 °C with vigorously stirring by magnetic force. After a few minutes, 0.0125 g, 0.0125 g, and 0.025 g EGCG dissolved in 5 mL DIW, were injected into the above Ag (I), Au (III), and Pt (VI) solution, respectively. Samples were taken over a period time and then refrigerated at 4 °C for the following characterizations. The reaction times of each sample were 1 min, 5 min, 15 min, 30 min, 60 min, 120 and 180 min, respectively. The diameters and distribution of the NMNPs were measured by Image-Pro Plus6.2 software (200 particles of NMNPs were randomly selected for the measurement).

2.3. Preparation of NMNPs in PVA electrospun precursor solution using EGCG as reductant

5 g PVA powder was dissolved in 45 mL DIW to get a concentration of 10 wt% solution and was stirred at 80 °C for 5 h to obtain a transparent homogeneous solution. The solution was then cooled to room temperature and 10 mL 10 wt% PVA solution were injected into three 3-neck flask, respectively. The calculated amounts of $AgNO_3$ (0.0375 g), $HAuCl_4{\cdot}3H_2O$ (0.0462 g) and $H_2PtCl_6{\cdot}6H_2O$ (0.0642 g) were added into the flasks, respectively. 0.025 g EGCG dissolved in 2 mL DIW was injected into the above solutions, respectively. The solutions were kept at 65 °C under vigorously stirring for 3 h to ensure the complete reduction. After that, the precursor solutions for electrospinning were refrigerated at 4 °C for the further characterizations.

2.4. Electrospinning of NMNPs embedded in PVA nanofibers

Each of the noble-metal-PVA electrospun precursor solution was collected in a 10 ml syringe equipped with a 24 gauge stainless steel needle tip. The syringe was fixed on an electric syringe pump set to maintain a constant feed rate of 0.01 mL min^{-1}. The high voltage power supplier was connected to the needle by a high-voltage insulating wire with two clamps at the end. A grounded metal plate covered with aluminum foil served as the collector. The voltage used for electrospinning was 12 kV. The distance between the needle tip and the collector was 12 cm. All experiments were performed at room temperature. Finally, after 4 h, the NMNPs/PVA nanofibrous mats were peeled off from the aluminum foil and kept in polyethylene sealing bags. The diameters and distribution of the NMNPs and nanofibers were measured by Image-Pro Plus6.2 software (200 particles of NMNPs were randomly selected for the measurement).

2.5. Preparation of size-controlled AgNPs embedded in PVA nanofibers

1.2, 1.5 and 1.8 g PVA powder were dissolved in 13.8 13.5 and 13.2 mL DIW to get a series concentration of 8, 10, and 12 wt%, respectively. 0.0375 g $AgNO_3$ was added into the PVA solutions, respectively, and the solutions were vigorously stirred at 65 °C for 0.5 h to obtain a homogeneous solution. Then, 0.025 g EGCG dissolved in 2 mL DIW was injected into the above solutions, respectively. The solutions were kept at 65 °C under vigorously stirring for 3 h to ensure the complete reduction. After that, the precursor AgNPs/PVA solutions were used to prepare a non-woven mat via electrospinning technique. The electrospun time of the precursor solutions are 3 h and then, the AgNPs/PVA nanofiber mats were peeled off from the aluminum foil and kept in polyethylene sealing bags. The diameters and distribution of the nanofibers were measured by Image-Pro Plus6.2 software (200 nanofibers were randomly selected for the measurement).