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Microorganism-assisted synthesis of Au/Pd/Ag nanowires

Xiaoer Chen [a,b], Jing Wang [a,b], Tareque Odoom-Wubah [a,b], Xiaolian Jing [a,b], Jiale Huang [a,b], Qingbiao Li [a,b,c,d], Yanmei Zheng [a,b,*]

[a] Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China
[b] National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, Xiamen University, Xiamen 361005, PR China
[c] Key Lab for Chemical Biology of Fujian Province, Xiamen University, Xiamen 361005, PR China
[d] The Key Lab for Synthetic Biotechnology of Xiamen City, Xiamen University, Xiamen 361005, PR China

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ABSTRACT

Well-defined Au/Pd/Ag nanowires (NWs) that are difficult to synthesize via pure chemical reduction method are fabricated using a facile one-pot microorganism-mediated method in the presence of hexadecyltrimethylammonium bromide (CTAB). The result showed that the formation of Au/Pd/Ag NWs were strongly dependent on the mass of *Pichia pastoris cells* (PPCs) and CTAB concentration of the reaction solution. The PPCs acted as templates in the formation of Au/Pd/Ag NWs, and an appropriate concentration of CTAB was favor of anisotropic growth during the NWs formation procedure. This work exhibits a novel method to fabricate multi-metallic nanostructures by combining a surfactant and microorganisms.

1. Introduction

Nanoparticles have attracted intensive research in recent years for their novel optical, electronic, and chemical properties [1–3]. Multi-metallic nanostructures containing noble metals, such as Pt, Au, Ag, Pd, *etc.*, with controllable properties have become a research hot spot because of their enhanced performance in catalysis, sensing, microelectronics, electrochemistry, optics [4]. Multi-metallic nanostructures such as AuPd nanoflowers [5,6], Au@Ag core-shell nanopolyhedrons [7], PdAg nanodendrities [8] can be synthesized by a variety of chemical, physical and biological methods. Various templates have been used to fabricate or immobilize nanoparticles in a controlled manner. Bio-templates (bacterium [9], viruses [10], fungus [11], plants [12], DNA [13] *etc.*) have the advantages of nanoscale dimensions, versatility and specificity. Bio-templates contain many functional groups such as hydroxyl, amino and carboxyl with the ability to adsorb a variety of metal ions to form specific structures. Sen et al. synthesized silver nanoparticles using glucan isolated from a mushroom *Pleurotus florida* blue variant [14]. Wang et al. synthesized unique Au nanohorns that are difficult to synthesize through pure chemical reduction are facilely synthesized using PPCs as templates [15]. In this work, we report a facile, one-pot way using PPCs as surface support to synthesize Au/Pd/Ag NWs in the presence of CTAB. The NWs were characterized by SEM, EDS and TEM. The surface composition of Au/Pd/Ag NWs/PPCs composites was analyzed by XPS. To the best of our knowledge, the biosynthesized of Au/Pd/Ag NWs has not been reported yet. Basically, such tri-metallic NWs can be synthesized through galvanic replacement reactions between pre-synthesized Ag NWs with Au and Pd precursors, which poses the problem of Ag leaching. Moreover, the Ag NWs should be synthesized at harsh conditions.

2. Experiment and methods

2.1. Materials

Pichia pastoris GS115 was bought from Invitrogen Corporation, USA. $HAuCl_4$, $PdCl_2$, $AgNO_3$, CTAB and ascorbic acid (AA) were all purchased from Sinopharm Chemical Reagent Co., Ltd. China. Deionized (DI) water was used throughout the procedure.

2.2. Cultivation of PPCs

Pichia pastoris GS115 yeast were incubated in nutrient broth containing yeast (10 g L^{-1}), glucose (20 g L^{-1}), and soya peptone (20 g L^{-1}) for 48 h at 30 °C and 200 rpm. Then the yeast cells were collected via centrifugation at ambient temperature and dried at

* Corresponding author at: Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China.
E-mail address: zym@xmu.edu.cn (Y. Zheng).

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60 °C for 12 h. Finally, the dried cells were crushed into powder and were stored in a desiccator.

2.3. Preparation of Au/Pd/Ag NWs/PPCs composites

In a typical biosynthesized of Au/Pd/Ag NWs, the dried cells (0–40 mg) were resuspended in 20 mL DI water containing CTAB (0–8.0 mM), $PdCl_2$ (0.62 mM) and $HAuCl_4$ (0.37 mM). The solution was hosted in a 50 mL round flask (containing a teflon-coated magnetic stirring bar). The Pd(II) and Au(III) ions were first adsorbed by cells at 60 °C for 50 min under stirring. Then 400 μL AA (0.1 M) was quickly added into the above solution, while 5 mL $AgNO_3$ (0.40 mM) were slowly injected into suspension using a syringe pump. At last, the solution was kept at 60 °C for 3 h. After reaction, the Au/Pd/Ag NWs/PPCs composites were collected via centrifugation, and were washed with DI water for several times, and dried in a vacuum oven at 40 °C.

2.4. Material characterization

The morphologies of the Au/Pd/Ag NWs/PPCs composites were detected on a SEM (Zeiss Sigma, Germany). EDS and elemental mapping analysis were conducted on the same SEM. HR-TEM observations were performed on a Tecnai F30 microscope. XPS was carried out on a Quantum 2000 spectrometer using Al-Kα line as the excitation source.

3. Results and discussion

3.1. Characterization of Au/Pd/Ag NWs/PPCs composites

The SEM image of the Au/Pd/Ag NWs (Fig. 1a) showed that the produced nanowires were of uniform morphology and the nanowires possess large length–diameter ratio. The EDS pattern from the SEM (Fig. 1b) confirms that the NWs were composed of Au, Pd and Ag. HR-TEM observation (Fig. 1c) reveals that nanowires were single crystal structures with the lattice distances along the direction of a single nanowire calculated to be 0.243 nm. The elemental mapping images show that Au (Fig. 1d), Pd (Fig. 1e) and Ag (Fig. 1f) were evenly distributed all over the nanowires, which proves that the biosynthesized Au/Pd/Ag NWs were alloy in nature, which is consistent with the EDS results.

The surface composition and chemical state of the Au/Pd/Ag NWs/PPCs composites were investigated by XPS. The XPS spectra peaks of O 1s and C 1s located at 530.8 and 282.8 eV (Fig. 2a) are stem from PPCs. Fig. 2b shows the peak of Au(0) $4f_{7/2}$ and $4f_{5/2}$ located at 84.95 and 88.6 eV. Fig. 2c shows that the Pd(0) $3d_{5/2}$ peak is located at 335.1 eV. The peak shifted to 340.35 eV corresponding to Pd(0) $3d_{3/2}$ peak. Ag(0) $3d_{3/2}$ and Ag(0) $3d_{5/2}$ peaks are located at 374.1 and 368.1 eV, respectively. The weak Pd(II) 3d peaks (Fig. 2c) and Ag(I) 3d peaks(Fig. 2d) were also shown because of the slight oxidation of some Pd atoms and Ag atoms on the cells surfaces by air. The formed tri-metallic nanostructures are responsible for the shift of Au 4f, Pd(0) 3d and Ag(0) 3d peaks to higher binding energy [16].

3.2. Effect of the synthetic conditions

The Au/Pd/Ag NWs formation and morphologies are found strongly dependent on the mass of added PPCs and CTAB concentration in the reaction solution. In the absence of PPCs, only nanoparticles with random shapes were obtained rather than nanowires (Fig. S1a). When the mass of PPCs is doubled the branches of the nanowires obtained (Fig. S1b) were reduced compared to nanowires produced with 20 mg PPCs (Fig. 1a). The reason is that PPCs act as templates and the increase of PPCs provides more templates for nanowires to form which also reduces the chances of mutual interference during the process of formation. It is obvious that the role of PPCs is indispensable in the procedure of nanowires evolution. The effect of CTAB in controlling the nanostructures was also investigated. In the absence of

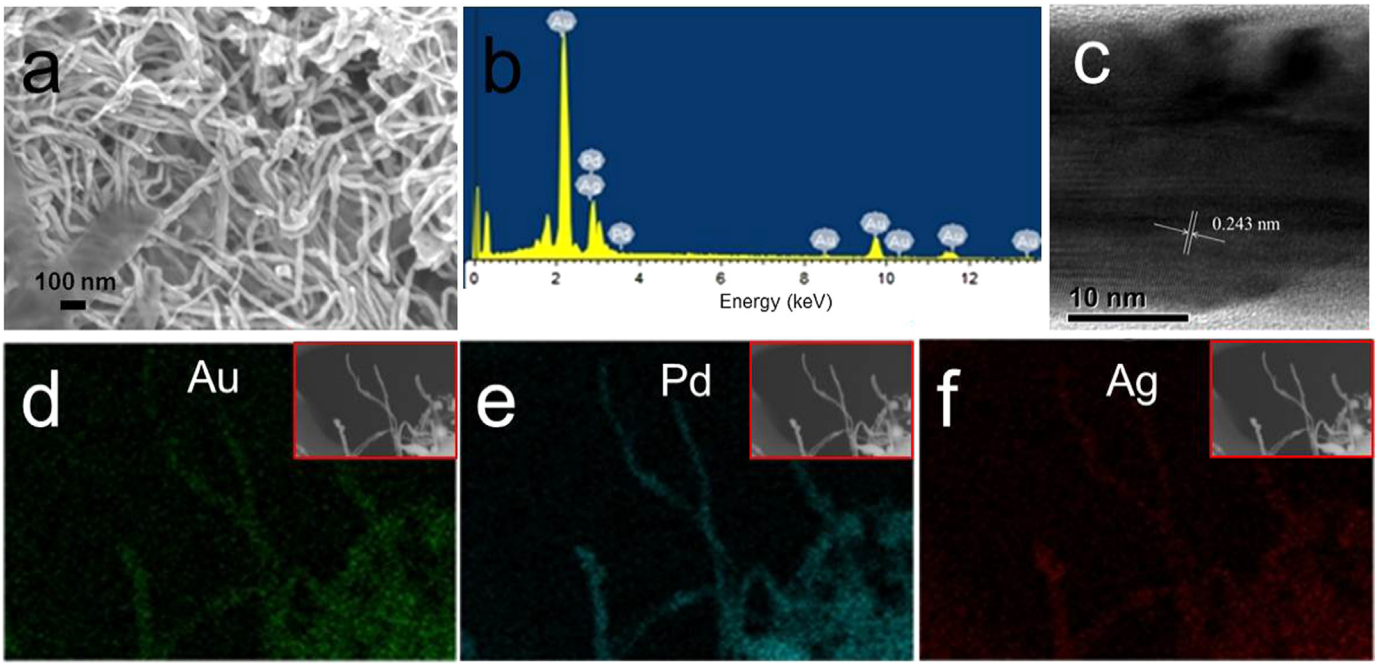

Fig. 1. SEM image (a), EDS image (b), HR-TEM image (c), elemental mapping images from SEM of Au (d), Pd (e) and Ag (f) of the biosynthesized Au/Pd/Ag NWs/PPCs composites with reaction condition of AA (1.6 mM) at 60 °C at the CTAB concentration of 4.0 mM in the presence of 20 mg PPCs.