



Peptide templated Au@Pd core-shell structures as efficient bi-functional electrocatalysts for both oxygen reduction and hydrogen evolution reactions



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ABSTRACT

Bimetallic core-shell nanostructures have been gaining considerable research attentions recently, mainly thanks to their versatile applications in many fields, including catalysis, electrocatalysis, electronic, sensing and so on. Herein, we demonstrate a peptide templated Au@Pd core-shell structure for both oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER). By employing peptide sequence FlgA3 as surface capping agent, core-shell structure with Pd nanoparticles coated on the surface of Au nanoparticles were prepared. The Au@Pd core-shell structures demonstrated effective electrocatalytic activities toward both ORR and HER, whereas the catalytic activity was optimized by tuning the Pd-to-Au ratio. Among a series of samples tested, we discovered that the Au@Pd_{1,0} sample exhibited the best ORR activity, superior to that of Pt/C and Pd/C, while its HER activity was also among the finest, close to that of Pt/C and Pd/C. The Au@Pd_{1,0} sample also exhibited remarkable stability beyond Pt/C and Pd/C in both ORR and HER. Such intriguing electrocatalytic performances are attributed to the core-shell structure induced lattice strain. The results offer reliable pathway for designing peptide templated core-shell bimetallic nanostructures as dual or multiple functional electrocatalysts with excellent electrocatalytic activities and longevity.

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1. Introduction

Bi-metallic noble metal nanostructures, including hierarchical heteronanostructures, alloy nanostructures, and especially core-shell structure have been receiving increasing research attentions in the past decade, and can afford to promising applications in many fields including catalysis, electrocatalysis, electronic, sensing and so forth [1–3]. Core-shell structures often display enhanced electrocatalytic properties due to the lattice strain created between the core and shell region as well as the synergistic effects during

the electrocatalytic process. On the other hand, oxygen reduction reaction (ORR), a key reaction occurring at the cathode of fuel cells and metal-air batteries, is a major bottleneck which limits the energy conversion efficiency due to its sluggish reaction kinetics and complicated reaction pathway [4,5]. Meanwhile, hydrogen evolution reaction (HER) has been recognized as the most economically efficient method to massively produce hydrogen, an ideal clean energy source with high energy density and environmental friendly nature [6–8].

Among a good variety of bi-metallic core-shell nanostructures, Au@Pd core-shell nanoparticles with well-defined morphology generally exhibited excellent electrocatalytic activity toward both ORR and HER. Following thrusts reflect the major past research highlights, Shim *et al.* prepared a carbon supported porous Pd layer-coated Au nanoparticles for ORR, and the sample with a Pd/Au ratio of 0.61 showed superior activity with satisfactory stability

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and methanol tolerance under acidic conditions [9]. Geng group developed a general and high-yield displacement approach for fabrication of Au–Pd core-shell structures, while the activities of ORR and methanol oxidation reaction were assessed as a typical example for investigation.[10] With the presence of polyallylamine hydrochloride (PAH) and ethylene glycol (EG), Au@Pd core-shell nanothorns with rough and porous surface were fabricated and remarkably high catalytic activity and durability for ORR in the alkaline media were observed [11].

Despite great progresses achieved on Au@Pd core-shell nanoparticles as electrocatalysts, there are still several problems remained to be resolved for preparing well-defined Au@Pd core-shell structures under chemical less extreme conditions, i.e. to eliminate the employment of organic molecule and solvent like PAH and EG, which are essential for the preparation of the above Au@Pd core-shell nanothorns [11]. Meanwhile, core-shell Au@Ag nanoparticles were first prepared in organic solvent, then the Ag shell was displaced by Pd precursor by galvanic replacement reaction [12,13]. Ag and Cu₂O have been normally chosen as sacrificial templates, which made the preparation process sophisticated, energy consuming and not cost-effective as well. In addition, the employment of organic solvent, harsh reaction conditions are also not environmentally friendly, hence not suitable for sustainable development. A facile approach for preparing Au@Pd core-shell nanostructures as highly efficient electrocatalysts under mild conditions with atomic economy is highly desirable, and this is the primary motivation of our current investigation.

The introduction of bio-molecules such as peptide to direct noble metal nanoparticle formation has demonstrated great promises to fulfill the above aim, as the inherent molecular recognition capabilities of these phage-display isolated peptides can be exploited to achieve desirable particle size, shape and functionalities [14,15]. Furthermore, the preparation of these peptide templated metal nanoparticles is conducted in water under ambient conditions without sacrificial agent. Peptide R5 templated Au, Pd and Pt nanostructures with different morphologies have been prepared for ORR in our previous continuous efforts [16–18]. Recently, we have also successfully showcased the fabrication of peptide A4 templated AuAg alloyed nanoparticle networks, and their oxygen reduction performance in alkaline media was examined [19]. On the basis of our recent peptide FlgA3 templated AuPd alloyed nanoparticles as highly efficient electrocatalyst for ORR [20], herein, we report the peptide FlgA3 templated Au@Pd core-shell nanostructures as dual-functional electrocatalysts for both ORR and HER.

2. Experimental section

2.1. Materials

Peptide FlgA3 (DYKDDDDKPAYSSGAPPMPPF, >98%) was obtained from Top-Peptide (Shanghai, China). Gold chloride trihydrate (HAuCl₄·3H₂O), sodium tetra-chloropalladate (Na₂PdCl₄), and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) were acquired from Energy Chemicals (Shanghai, China). Sodium borohydride (NaBH₄) was purchased from Aladdin Industrial Corporation (Shanghai, China). All the chemicals were purchased from commercial sources and used without further purification. All the solutions were prepared with deionized water (resistivity: 18.3 MΩ cm⁻¹).

2.2. Synthesis of Au@Pd_x nanoparticles

The Au@Pd_x (X is the molar ratio of Pd-to-Au, X = 0.17, 0.50, 1.0 and 1.5) samples were prepared by following a modified procedure documented in previous reports [20,21]. In a typical synthesis, 200

μL FlgA3 (5 mg mL⁻¹) and 324.18 μL HAuCl₄ (0.04 M) were first mixed in 500 μL HEPES (pH = 7.2, 0.1 M) solution in an eppendorf tube and incubated for 2 h. The intermediate products (peptide-coated Au particles) were recovered by centrifugation at 12000 rpm for 5 min and re-dissolved in 500 μL of deionized water. Subsequently, 54.03 μL, 162.09 μL, 324.18 μL, and 486.27 μL of Na₂-PdCl₄ (0.04 M) were added to the above Au nanoparticles, respectively. After incubated for 30 min, the reaction mixture was reduced by NaBH₄ (0.1 M) aqueous solution with a volume of 43.23 μL, 129.69 μL, 259.38 μL, and 389.07 μL accordingly and left undisturbed for 1 h. Finally, the product denoted as Au@Pd_{0.17}, Au@Pd_{0.5}, Au@Pd_{1.0} and Au@Pd_{1.5} were obtained by centrifugation at 12000 rpm for 10 min and dried at ambient temperature.

2.3. Characterizations

The electron microscopic images were acquired by JEM-2100F coupled with high angle annular dark-field (HAADF) scanning transmission electron microscopic (STEM) imaging at an acceleration voltage of 200 kV. High resolution transmission electron microscopy (HR-TEM), bright-field transmission electron microscopy (BF-TEM) and energy dispersive X-ray (EDX) elemental mapping were acquired in a FEI Tecnai F20 machine. X-ray photoelectron spectroscopy (XPS) was conducted with an Escalab 250 photoelectron spectrometer (Thermo fisher scientific, USA).

2.4. Electrochemistry

Electrochemical measurements for ORR were operated on a CHI 750E electrochemical workstation (CH Instruments Inc.) with a conventional three-electrode system at room temperature in an O₂-saturated 0.1 M KOH solution or 0.1 M HClO₄ solution. The as-prepared catalyst-coated glassy carbon disk with gold ring was used as the working electrode. An AgCl/Ag (E_{Ag/AgCl} = E_{RHE} + 0.966 V, RHE = reversible hydrogen electrode) with saturated KCl and a platinum foil were used as the reference and counter electrode, respectively. Slight Pt dissolution might occur during the ORR measurement at the Pt foil counter electrode [22–25], but the ORR performance is not affected. 2 mg of the composite catalysts prepared above were dispersed in 1 mL of 1: 1 (v: v) ethanol/water mixed solvents, and the mixture was sonicated for 30 min to prepare a homogeneous catalyst ink. Then, 10 μL of the catalyst ink was dropcast onto the surface of the working electrode and dried at room temperature. In order to prevent the loss of catalyst in the test, the working electrode with catalyst ink was coated by 10 μL Nafion (20 μL/mL, 5 wt%). The catalyst loading was approximately 101.9 μg cm⁻² for all the samples. The cyclic voltammetric measurements were performed at the scan rate of 10 mV s⁻¹ and linear sweep voltammetric measurements were conducted at different rotation rates (225–2025 rpm) in the potential range from –0.04 V to 1.16 V. The current density was calculated based on the geometrical area (0.196 cm²) of the working electrode. Chronoamperometric tests were conducted in an O₂-saturated 0.1 M KOH solution at +0.5 V for 30,000 s, while accelerated durability tests (ADT) were performed by cycling the catalyst over the potential range of +0.6 V to +1.0 V at 50 mV s⁻¹ in O₂-saturated 0.1 M KOH solution.

HER measurements were also performed with the same electrochemical setup in both 0.5 M H₂SO₄ and 0.1 M KOH aqueous solutions. The as-prepared catalyst-coated glassy carbon electrode (GCE, diameter 3 mm) was used as the working electrode. A Hg/Hg₂Cl₂ electrode and a carbon rod were used as the reference and counter electrode, respectively. 5 mg of the composite catalysts prepared above were dispersed in 1 mL of 1: 1 (v: v) ethanol/water mixed solvents, along with 50 μL of a Nafion solution (5% Nafion in ethanol). After the mixture was sonicated for 30

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