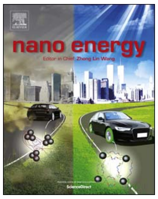
Nano Energy xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Nano Energy

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



Full paper

NiO-induced synthesis of PdNi bimetallic hollow nanocrystals with enhanced electrocatalytic activities toward ethanol and formic acid oxidation

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ARTICLE INFO

Keywords:
PdNi alloy
Hollow nanocrystals
Galvanic replacement
Morphology control
Ethanol oxidation
Formic acid oxidation

ABSTRACT

Noble-metal hollow nanocrystals possess numerous unique advantages such as high surface-to-volume ratio and high utilization of noble metals, which make them a promising electrocatalyst for electro-oxidation of small molecules in fuel cells. Herein, we prepared bimetallic PdNi hollow nanocrystals (PdNi-HNCs) by taking advantage of the galvanic replacement reaction in an aqueous solution and developed a facile NiO-induced strategy for the controlled synthesis of PdNi-HNCs with dendritic or smooth outer shell architectures. A very short oxidation time of an amorphous Ni template is demonstrated to be the key factor to successful fabrication of the dendritic morphology. The results of electrochemical testing indicate that the electrocatalytic activities of PdNi-HNCs are highly dependent on their morphologies. The PdNi-HNCs with a rough and dendritic shell exhibit a mass activity of 1201.5 and 768.0 mA mg_{Pd}^{-1} toward ethanol oxidation reaction (EOR) and formic acid oxidation reaction (FAOR), respectively, much greater than those of the commercial Pd black catalyst (502.6 and 266.3 mA mg_{Pd}^{-1}, respectivlely). In particular, the 1500 cyclic voltammetry cycles in alkaline solution and the 30,000 s chronoamperometry tests in acid solution suggest an enhanced long-term durability of PdNi-HNCs with dendritic nanoarchitectures. We ascribe the better catalytic activity to the hollow feature, higher specific electrochemical surface area, more abundant active sites and more appropriate electronic structure of the PdNi-HNCs with a rough and dendritic shell.

1. Introduction

Currently, liquid fuel cells are expected to be one of the most promising renewable and environmentally friendly energy sources to substitute for traditional fossil-fuel energies [1–3]. It is well known that platinum (Pt) is commonly used as an anode and cathode catalyst in liquid fuel cells. However, the traditional Pt-based catalysts suffer from high cost and scarcity, which greatly restrict their large-scale application. To the best of our knowledge, palladium (Pd) is considered as the most possible and economical substitute for Pt because Pd and Pt have analogous crystal structures (only a 0.77% lattice constant mismatch) and Pd is more abundant [3].

Many studies have shown that Pd-based nanocrystals (NCs) represent comparable or even higher catalytic activity for liquid fuel oxidation or oxygen reduction reactions, and greater resistance to CO poisoning than that of Pt [4–9]. Nevertheless, Pd remains a relatively expensive metal compared to other types of non-Pt catalysts. Therefore, further expanding the utilization of Pd is especially important.

The past few years have witnessed great progress in the fabrication of highly active Pd-based NCs with multifarious nanoarchitectures from zero to three dimensions [9–13]. Among them, hollow NCs (HNCs) have sparked tremendous research attention owing to their cost-saving feature [14–18]. Owing to its high utilization of noble metals, high surface-to-volume ratio, void interior and high porosity, Pd-based NCs with hollow features present great potential as efficient catalysts in fuel cell technologies [19–21].

In general, three synthetic strategies—the use of sacrificing templates, taking advantage of the Kirkendall effect and galvanic replacement—have been developed to synthesize HNCs [22–31]. Among these strategies, the galvanic replacement reaction, involving a standard reduction potential difference between two redox pair, has been widely employed to generate noble-metal HNCs that would meet the demand for cost effective electrocatalysts. For example, Wang's group [32,33] has synthesized NiPt nanospheres with smooth outer shells and

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https://doi.org/10.1016/j.nanoen.2017.11.033
Received 18 September 2017; Received in revised form 5 November 2017; Accepted 14 November 2017
2211-2855/

Please cite this article as: Chen, Z., Nano Energy (2017), https://doi.org/10.1016/j.nanoen.2017.11.033

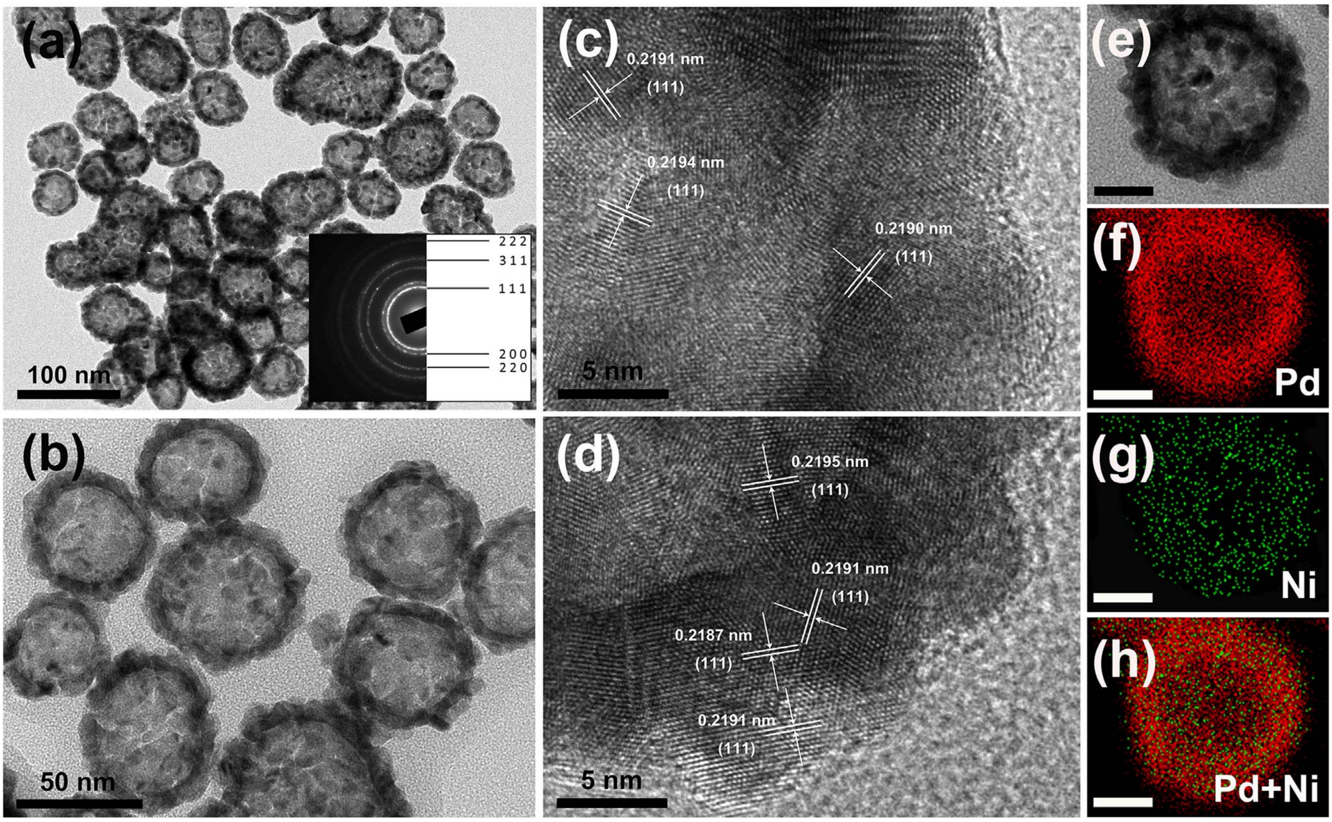

Fig. 1. (a), (b) Low-magnification TEM images of PdNi-HNCs-R (inset: the selected area electron diffraction (SAED) pattern); (c), (d) High-magnification TEM images; (e to h) EDS elemental mapping images of Pd and Ni. (Scale bars: 20 nm).

various compositions, sizes, and shapes by a facile wet chemical route through galvanic replacement. The as-prepared hollow products have shown enhanced electrocatalytic performance for methanol and ethylene glycol oxidation compared with commercially available Pt/C. Recently, Dubau and co-workers [34,35] revealed the effect of structural defects of hollow PtNi/C nanoparticles with identical chemical compositions and elemental distributions but different nanostructures, crystallite sizes, and lattice strains, on catalytic performance. They proved that strain and ensemble effects, as well as structural defects (grain boundaries and vacancies), contribute to catalytic enhancement.

In addition, in a series of previous works it has been demonstrated that the rough dendritic architecture highly favors desirable high mass-activity of noble-metal NCs [36–43]. It would be greatly advantageous to prepare dendritic NCs with hollow interiors because of the expected utilization of noble metals and more abundant active sites and structural defects that dendritic structures may possess. For instance, Hong and co-workers [44] generated hollow Pt-Pd alloy NCs by manipulating the degree of galvanic replacement of Pd with Pt. The dendritic hollow NCs exhibited considerably enhanced oxygen reduction electrocatalytic activity. In addition, Yamauchi's group [45] reported a synthesis of PdPt bimetallic dendritic nanocages by a selective chemical etching of Pd cores from dendritic Pt-on-Pd NCs. The hollow interiors and dendritic shells were demonstrated to provide abundant catalytic sites, leading to a very high electrocatalytic activity for the methanol oxidation reaction [45].

However, it is still a significant challenge to design and readily synthesize Pd-based HNCs with controllable outer nanoarchitectures without any post-treatment. In the present work, we designed a new NiO-induced route to facilely generate PdNi bimetallic HNCs with controllable outer morphology. We discovered that the morphology of the final PdNi-HNCs would be affected by oxygen employed before the process of galvanic replacement reaction. The NiO on the surface of a Ni nanosphere template plays a crucial role in the formation of the dendritic HNCs. The morphology of PdNi-HNCs is strongly influenced by the surface oxidation degree of the Ni templates, resulting in PdNi-HNCs with smooth or rough morphology which are denoted PdNi-HNCs-S and PdNi-HNCs-R, respectively. The as-prepared PdNi-HNCs with different morphologies were further applied to electrochemical catalysis for ethanol oxidation reaction (EOR) and formic acid oxidation reaction (FAOR). Their electrocatalytic activities are highly dependent on their morphologies.

2. Experimental section

2.1. Chemicals

Nickel (II) chloride anhydrous ($NiCl_2$, 98%) and palladium (II) chloride ($PdCl_2$) were purchased from Alfa Aesar. Poly(vinylpyrrolidone) (PVP; MW = 30,000 g/mol) and sodium borohydride ($NaBH_4$, 98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Vulcan XC-72R carbon was obtained from E-TEK. All reagents were used without further purification. The deionized water (18.2 MΩ cm) used was prepared using an ultrapure water system (Millipore).

2.2. Synthesis

The PdNi-HNCs with dendritic or smooth shells were fabricated by taking advantage of galvanic replacement between Ni nanosphere templates and H_2PdCl_4 aqueous solution in the presence of PVP. In typical synthesis, $NiCl_2$ (9.3 mg) and PVP (100 mg) were dissolved in 42 mL DI water, and ultrasounded for 15 min at room temperature. After deoxygenation with N_2 for 30 min, 10 mL of freshly prepared $NaBH_4$ (10 mg) solution was introduced into the above solution with vigorous stirring. The color of the solution immediately turned dark brown after employing BH_4^-, indicating the formation of Ni nanoparticles. Subsequently, oxygen was bubbled into the Ni suspension for