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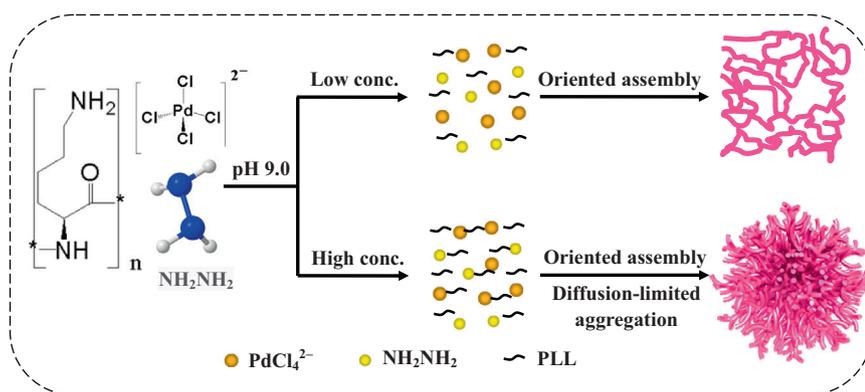
Poly-L-lysine mediated synthesis of palladium nanochain networks and nanodendrites as highly efficient electrocatalysts for formic acid oxidation and hydrogen evolution



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GRAPHICAL ABSTRACT



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ABSTRACT

The morphology- and size-tunable synthesis of nanocatalysts has attracted substantial research interest especially in catalysis. In this work, we synthesized free-standing Pd nanochain networks (Pd NCNs) and Pd nanodendrites (Pd NDs) through a direct poly-L-lysine (PLL)-mediated one-pot aqueous method. The presence of PLL and its concentrations were critical in this regard, showing PLL as the structure-directing and capping agents during the nucleation and crystal growth procedures. The synthesized architectures exhibited improved catalytic activity and enhanced durability towards formic acid oxidation and hydrogen evolution reactions relative to commercial Pd black catalyst. Moreover, the electrochemical active surface area and the electrocatalytic performance of Pd NCNs were dramatically enhanced in comparison to Pd NDs mainly owing to the unique network-like structure of Pd NCNs.

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1. Introduction

Developing reproducible and green energy sources is a major topic due to the dramatic consumption of fossil fuels and the

severity of environmental pollution [1]. Particularly, formic acid fuel cells are a kind of valuable energy sources [2]. Meanwhile, hydrogen energy is an environmentally friendly and renewable energy carrier produced by water electrolysis [3]. Notably, novel electrocatalysts are always researched for formic acid oxidation reaction (FAOR) and hydrogen evolution reaction (HER) [4,5].

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To date, Pt nanocatalysts are extensively studied because of their high catalytic characters in environmental and energy applications [6]. However, the high cost and limited reserve are the main barriers, which seriously hinder their commercial applications [7,8]. To solve these problems, some strategies have been explored, including alloying Pt with transition metals [9], modifying the structures and morphologies of the catalysts [10], and substituting Pt catalysts with other metal counterparts [11].

Among these methods, great research interest is focused on adopting Pd nanocatalysts to replace Pt counterparts because Pd is less expensive and more abundant in earth than Pt [12]. More importantly, the catalytic properties of Pd are comparable to Pt, mainly due to their similar face centered cubic (*fcc*) crystal structure and atomic size [13]. Previous researches demonstrate that Pd nanocatalysts have the similar catalytic features, together with the reduced cost and the relatively abundant reserves [14].

Recently, it is a hot topic for the scalable synthesis of Pd nanocatalysts with different shapes and sizes especially in catalysis, since their catalytic characters greatly rely on their morphologies [15,16]. Hitherto, many Pd nanomaterials with different morphologies have been prepared, such as Pd spheres [15], Pd rods [17], Pd wires [18], Pd sheets [19], Pd dendrites (NDs) [20] and network-like structures consisting of numerous chains/wires [21].

Importantly, the three-dimensional (3D) Pd architectures have sparked remarkable interest because of their enlarged surface areas and high mass transfer efficiency [21]. For example, Tang and co-workers fabricated Pd nanochain networks (NCNs) by a one-pot hydrothermal method [21]. In another example, Sun's group synthesized Pd NDs by a seed mediated growth method [22]. Nevertheless, the aforementioned strategies are usually suffered from time-consuming and complicated synthetic procedures, thereby developing a simple, general and efficient method is urgent for construction of novel hierarchical Pd nanostructures.

As it is known, capping agent can effectively regulate the morphology and size of metallic nanocatalysts, and eventually influence the subsequent catalytic behaviors [23]. Poly-L-lysine (PLL, Fig. S1, Supporting Information, SI) is a kind of biocompatible homopolymers with many hydrophilic amino- and imino-groups, which is commonly used as an attachment factor for improving cell adherence, and widely employed for food preservative and drug delivery [24]. Their strong chelating ability and electrostatic interactions with the metal precursors can efficiently modulate the morphology and structure of the sequential-generated metal nanocrystals [25].

Herein, we report the synthesis of 3D free-standing Pd NCNs and Pd NDs by precisely adjusting the PLL concentrations. The respective electrocatalytic properties were investigated by employing FAOR and HER as the representative models.

2. Experimental

2.1. Synthesis of Pd NCNs and Pd NDs

In a typical synthesis of Pd NCNs, 1.00 mL of H_2PdCl_4 (100 mM) was put into 8.75 mL of water containing 32.0 mg of PLL (25 mM) under stirring in a water-bath (35 °C). Immediately, the freshly-prepared NaOH solution (1.0 M) was put into the mixture to adjust the solution pH to 9.0, followed by the addition of 0.25 mL of the hydrazine solution, and continuously reacting for 5 h under stirring. Then, the reaction system was kept static for 3 h at ambient temperature. Eventually, PLL was absolutely removed from the reaction system by centrifugation, washing sufficiently with water because of their excellent water solubility, followed by drying at 60 °C in vacuum.

Similarly, the Pd NDs were prepared by changing the PLL concentration to 100 mM by the same way, while the other experimental conditions were remained identical.

2.2. Construction of Pd NCNs and Pd NDs modified electrodes

For the construction of the Pd NCNs and Pd NDs modified electrodes, 2.0 mg of the as-prepared samples were well dispersed in 1.00 mL of water under ultrasonication for 30 min to gain the homogeneous catalyst ink (2.0 mg mL^{-1}). Subsequently, 6 μL of the suspension was placed onto the glassy carbon electrode (GCE, $\Phi = 3 \text{ mm}$) or glassy carbon rotating disk electrode (RDE, $\Phi = 3 \text{ mm}$), dried in air, and coated with another layer of Nafion (4 μL , 0.05 wt.%) to tight the samples.

In control experiments, traditional Pd black catalyst modified electrode was prepared by the similar way. More details of the materials and characterization were displayed in SI.

3. Results and discussion

3.1. Characterization of Pd NCNs and Pd NDs

The morphology and structure of Pd NCNs and Pd NDs were characterized by transmission electron microscopy (TEM) images. Fig. 1 displays the TEM images of the product prepared at 25 mM PLL. The sample contains rich and interconnected chain-like networks (Fig. 1A and B). The correlative high-resolution TEM (HRTEM) images (Fig. 1C) show the clear lattice fringe spacing of 0.234 nm, which is indexed to the (1 1 1) crystal planes of single Pd [26]. Furthermore, the Pd NCNs contains highly branched surfaces with the wave-like structures (marked in Fig. 1C). Besides, the wave-like borders are enclosed by the {1 1 0} and {3 3 1} crystal facets, which would provide enriched active sites accessible for reactants [27,28]. These facets are composed of the (1 1 1) terraces and (1 1 0) steps. As displayed by the atomic models of the facets (Fig. S2), $n = 2$ and 3 are assigned to the (1 1 0) and (3 3 1) crystal planes, respectively [29]. In addition, the selected area electron diffraction (SAED) pattern exhibits a set of bright concentric rings (Fig. 1D), which correspond to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) crystal planes of Pd NCNs, confirming their highly crystalline nature [30].

By increasing the concentration of PLL up to 100 mM, there are many well-defined dendrite-like Pd nanoparticles (NPs) with numerous highly-branched surfaces, as displayed by the low- and medium-magnification TEM images (Fig. 2A and B). The particles have narrow size distribution, and the correlative average diameter is roughly 54.87 nm (inset in Fig. 2A).

The HRTEM images (Fig. 2C) exhibit the lattice fringe distance of 0.232 nm, which is well ascribed to the (1 1 1) planes of single Pd [26], in good accordance with the prepared Pd NCNs. The borders of Pd NDs display wave-like structures, and the product possesses atomic steps and some crystal facets, such as {1 1 0} and {3 3 1} (Fig. S2), which would offer high density of active sites for catalysis [31]. This assumption coincides well with the above case of Pd NCNs. In addition, their polycrystalline nature is manifested by the SAED pattern with several concentric rings (Fig. 2D) [30].

The surface elemental species and valence states of Pd NCNs and Pd NDs were determined by X-ray photoelectron spectroscopy (XPS). Clearly, the high-resolution Pd 3d XPS spectrum can be deconvoluted into two couples of peaks (Fig. 3). For Pd NCNs, the peak intensities of Pd^0 (340.50 and 335.26 eV) are much stronger than those of Pd^{2+} species (342.92 and 335.26 eV), indicating the effective reduction of the Pd precursor (Fig. 3A) [21]. Meanwhile, the strong peaks at 340.30 and 335.00 eV are ascribed to Pd $3d_{3/2}$ and Pd $3d_{5/2}$ for Pd NDs (Fig. 3B), revealing that Pd^0 is the main species in Pd NDs, which coincides well with the case of Pd NCNs

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