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Novel palladium flower-like nanostructured networks for electrocatalytic oxidation of formic acid

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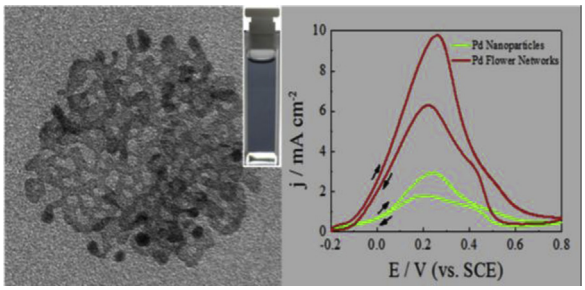
HIGHLIGHTS

- Pd flower-like nanostructured networks was prepared via a novel CO-assistant method.
- The size and morphology of the materials are temperature depended.
- The novel materials indicated enhanced activity for formic acid electrooxidation.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel Pd flower-like nanostructured networks are synthesized via a simple CO-assisted reduction. The morphology and size of the Pd nanostructures are found to strongly depend on the temperature and solvent during the synthesis process. Such Pd flower-like nanostructured networks exhibit a much enhanced activity of about 3 times of that on conventional Pd nanoparticles towards the electrocatalytic oxidation of formic acid. The specific activity of formic acid oxidation on Pd nanostructures is also greatly improved, indicating that the formation of flower-like nanostructured networks is beneficial for the electrooxidation of formic acid. Thus, it could be served as highly active catalyst for formic acid electrooxidation although the stability needs to be greatly improved.

1. Introduction

Recently direct formic acid fuel cells (DFAFCs) have attracted increasing attention due to their high energy density and convenient storage and transport of liquid formic acid, etc [1–5]. To date, as the prevailing catalysts for the electrocatalytic oxidation of formic acid [6,7], Pt and Pd based catalysts have been the research focuses. And, Pd is now deemed as the best choice due to its superior initial electrocatalytic activity and a relatively low cost compared to Pt. However, the activity and durability of Pd-based catalysts towards formic acid oxidation is seriously restricted by $(CO)_{ad}$-like poisoning species and possible dissolution of Pd species in acidic solutions [8,9]. The synthesis of high performance Pd-based catalysts thus turns out to be a hot topic. Preparation of Pd with special morphology has been considered as an effective method to improve the performance for formic acid oxidation [10–14].

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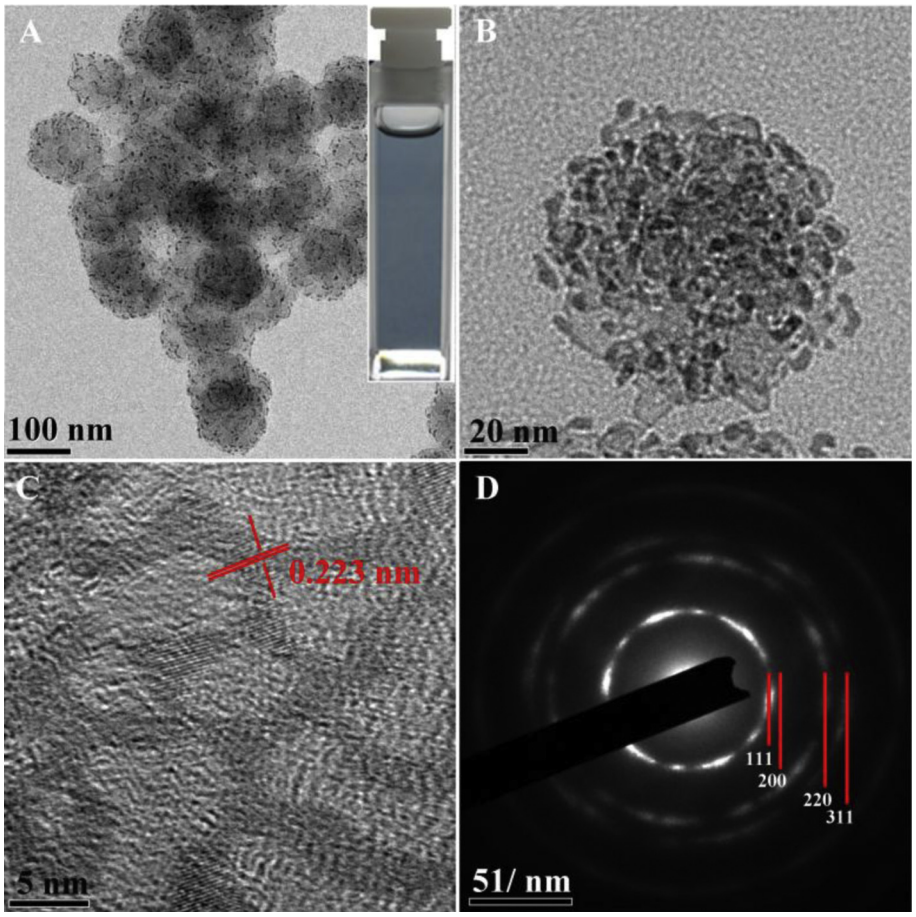

Fig. 1. (A–B) TEM images of Pd FN00 synthesized at 0 °C. Inset in A: photograph of the resultant colloid. (C) HRTEM image of the network. (D) SAED pattern of the network.

Pd has been currently modulated to various nanostructures with well-defined morphologies such as cubes, tetrapods, bipyramidals, freestanding nanosheets, and nanowire networks [10–14]. Among these, highly dispersed and uniform Pd nanowire networks have demonstrated improved electrocatalytic activity for formic acid oxidation depending on the aspect ratio of the nanowires compared to the conventional Pd nanoparticles (NPs) [12,15]. Recent work by Tang et al. has revealed that the use of Pd–Co 3-dimension network catalyst leads to a greatly enhanced catalytic activity and durability towards the oxidation of formic acid owing to their excellent electrochemical self-stability [16]. Herein, we describe a simple CO-assisted synthesis of novel Pd flower-like nanostructured networks (Pd FNs). Such Pd FNs materials can provide much enhanced catalytic activity for the oxidation of formic acid relative to the conventional Pd NPs.

The Pd FNs catalysts were prepared using polyvinyl pyrrolidone (PVP) as a stabilizer and CO as reducing and capping agents in methanol solution at different temperatures. For a comparison, Pd NPs were also prepared with a similar procedure but in an aqueous solution.

2. Experimental section

2.1. Preparation of catalysts

Palladium chloride ($PdCl_2$, AR), sodium chloride (NaCl, AR), PVP (K30, MW = 40,000), methanol (AR), formic acid (AR), and perchloric acid (AR) were purchased from SinoPharm Chemical Reagent Co. Ltd (SCRC). High-purity CO and N_2 were obtained from Air Products and Chemicals, Inc. All the chemicals were used as received.

210 mg PVP and 100 mL of 3.876 mM Na_2PdCl_4/methanol solution was added into a flask. Then, high-purity N_2 was purged into the flask to remove the air in the mixture by stirring violently at a certain temperature (FN00 at 0 °C, FN25 at 25 °C, and FN50 at 50 °C,

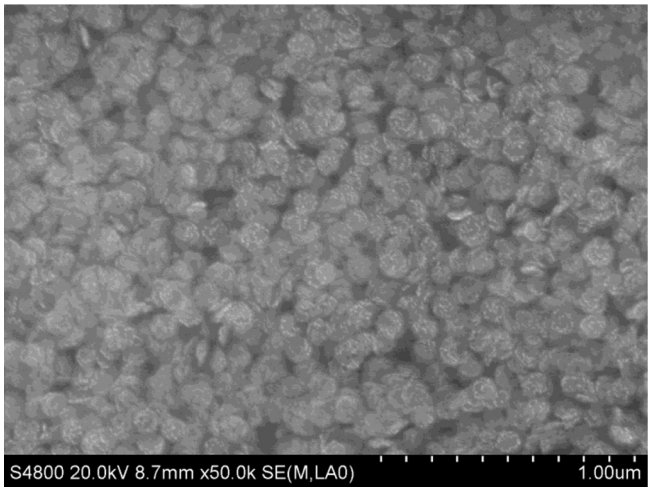

Fig. 2. SEM image of the Pd FN00.