



A single-step route for large-scale synthesis of core–shell palladium@platinum dendritic nanocrystals/reduced graphene oxide with enhanced electrocatalytic properties



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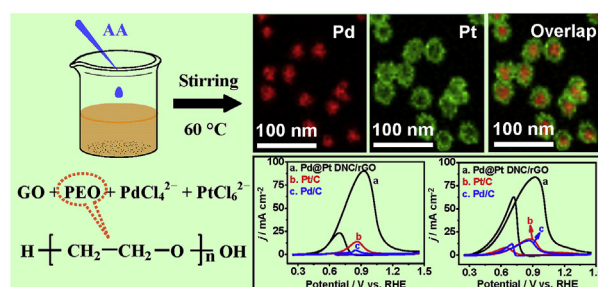
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HIGHLIGHTS

- Pd@Pt DNC/rGO is prepared via a facile and seed-less single-step route.
- PEO is employed as the structure-director and stabilizing agent.
- The nanocomposite has large electrochemically active surface area ($114.15 \text{ m}^2 \text{ g}_{\text{metal}}^{-1}$).
- The nanocomposite exhibits enhanced electrocatalytic performances for MOR and EOR.

GRAPHICAL ABSTRACT



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ABSTRACT

In this report, a facile, seed-less and single-step method is developed for large-scale synthesis of core–shell Pd@Pt dendritic nanocrystals anchored on reduced graphene oxide (Pd@Pt DNC/rGO) under mild conditions. Poly(ethylene oxide) is employed as a structure-directing and stabilizing agent. Compared with commercial Pt/C (20 wt%) and Pd/C (20 wt%) catalysts, the as-obtained nanocomposite has large electrochemically active surface area ($114.15 \text{ m}^2 \text{ g}_{\text{metal}}^{-1}$), and shows superior catalytic activity and stability with the mass activities of 1210.0 and $1128.5 \text{ mA mg}_{\text{metal}}^{-1}$ for methanol and ethanol oxidation, respectively. The improved catalytic activity is mainly the consequence of the synergistic effects between Pd and Pt of the dendritic structures, as well as rGO as a support.

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1. Introduction

Direct alcohol fuel cells (DAFCs) have high energy density, low operating temperature (60–100 °C) and pollutant emission [1,2]. To realize their practical applications, great efforts have been devoted

to search highly active electrocatalysts for increasing oxidation reaction rate and making the process more efficient [3].

Platinum (Pt) is considered as the most efficient catalyst in fuel cells [4,5]. Unfortunately, the practical utilization of Pt is severely limited by its scarcity, sky-rocketing price and easily poisoned by carbon monoxide (CO) [5]. Previous works show that the catalyst displays enhanced catalytic activity and improved CO toleration by alloying Pt with another metal (such as Au, Cu, Ni, and Co), which

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can be explained by the synergistic effects between the two metals [5–7]. Among the second metals, palladium (Pd) itself exhibits high catalytic activity and good CO toleration towards alcohol oxidation, especially in alkaline media [8,9]. Moreover, Pd is much more abundant and less expensive than Pt. To this end, Pd–Pt bimetallic nanomaterials are expected to be promising efficient catalysts in fuel cells [10,11]. By far, numerous methods have been developed to synthesize Pd–Pt nanocrystals with various shapes (e.g. flowers, cubes, tubes, wires and octahedral) [12–15].

Besides, the electrocatalytic activity of bimetallic catalysts is strongly dependent on their shape, size and crystal structure [16]. Recently, shape-controlled synthesis of core–shell nanoparticles is extensively studied owing to their enhanced catalytic activity with low Pt usage [17–19]. For instance, Kim and his workers developed a one-pot reduction method for synthesis of star-like core–shell Pd@Pt nanoparticles anchored on reduced graphene oxide (rGO) with better catalytic performance for methanol oxidation reaction (MOR) than commercial Pt/C, monometallic Pt/rGO, and alloyed PdPt/rGO [20]. However, it is noticed that the core–shell structured catalysts are usually prepared by seed-mediated growth methods, which make the preparation process complicated and time-consuming [21,22]. Additionally, some of them labor under special apparatus, organic agents, and severe reaction conditions [23,24]. Therefore, it is still highly desirable to develop a simple and facile single-step route for production of core–shell structured nanoparticles with good catalytic performance.

From the practical point of view, the stability of a catalyst is important to reduce the cost as well as environmental pollution. However, nanocatalysts usually undergo bad aggregation during the synthetic process and their repeated use in catalysis [25]. It is desired to load the nanocatalysts on a supporting material to prevent them from coarsening and bleaching [25].

Graphene, a single sheet of carbon atoms with hexagonal lattice structure, is an ideal platform for the deposition of nanocatalysts for its extraordinary electronic, thermal and mechanical properties with large specific surface area [26]. For example, Pt–Pd alloy nanoparticles were electrodeposited on rGO-modified electrode and displayed better electrocatalytic capability and stability for ethanol oxidation reaction (EOR) due to the super electron transfer of rGO [27].

Herein, a very simple seed-less method was developed for facile synthesis of reduced graphene oxide supported core–shell Pd@Pt dendritic nanocrystals (Pd@Pt DNC/rGO) in aqueous solution, using poly(ethylene oxide) (PEO) as a structure-directing and stabilizing agent. The electrocatalytic performance of Pd@Pt DNC/rGO was studied using the oxidation of methanol and ethanol as model systems.

2. Experimental

To synthesize Pd@Pt DNC/rGO, the precursors of H_2PdCl_4 and H_2PtCl_6 were subsequently injected into the suspension of graphene oxide (GO) in the presence of PEO under stirring, followed by the drop-wisely addition of ascorbic acid (AA) solution under constant stirring at 60 °C. Their characterizations are determined by transmission electron microscopy (TEM), high-angle annular dark-field scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (HAADF-STEM-EDS), X-ray diffraction (XRD) analysis, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and thermogravimetric analysis (TGA). The details of the experiments were provided in [Supporting Information \(SI\)](#).

3. Results and discussion

3.1. Characterization

To visual the morphology of Pd@Pt DNC/rGO, transmission electron microscopy (TEM) images were recorded firstly. It can be seen from the typical TEM image that many particles are highly dispersed on rGO (Fig. 1A). The particle size ranges from 27 to 47 nm, with an average diameter of 37.7 nm, as illustrated by the size histogram (Fig. 1B). Meanwhile, the associated selected area electron diffraction (SAED) pattern (inset in Fig. 1C) demonstrates the polycrystalline nature of the resulting nanoparticles.

More detailed structural information is provided by high-resolution TEM (HR-TEM) experiments. The HR-TEM images of the architectures (Fig. 1C and D) unambiguously reveal its dendritic structures, which are expected to provide high specific surface area along with abundant active sites and rich corner atoms towards catalytic reactions [28]. The estimated lattice spacing distances of 0.225, 0.228 and 0.232 nm are indexed to the (111) planes of face-centered-cubic (fcc) Pd@Pt crystals and 0.200 nm to (200) planes [29], respectively. Furthermore, several atomic steps emerge on the branched surface, as marked in Fig. 1D. These atomic steps could work as highly catalytic active sites toward MOR and EOR [30].

To gain further insight into the elemental distribution of the nanostructures, high-angle annular dark-field scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (HAADF-STEM-EDS) experiments were manipulated. As can be seen from HAADF-STEM image (Fig. 2A), the typical product contains many solid spheres with dendritic exteriors. The EDS elemental mapping (Fig. 2B–D) images reveal that each nanocrystal contains dendritic Pt exterior and underlying Pd core, demonstrating its core–shell structure. This result is supported strongly by the corresponding EDS line scanning profile (inset in Fig. 2A). As can be seen, Pd is mainly concentrated in the center region while Pt is distributed outside. The atomic ratio of Pd to Pt is close to 1:1 according to EDS analysis (Fig. S1, SI). This ratio is in good accordance with the original Pd/Pt atomic ratio in the precursors, indicating that all of the precursors are completely reduced. Besides, the EDS analysis also confirms the existence of C, O, and Cu elements, which come from rGO, oxygen signal, and copper mesh, respectively.

The crystalline structure of Pd@Pt DNC/rGO was analyzed by X-ray diffraction (XRD, Fig. 3). In the XRD spectrum of Pd@Pt DNC/rGO, the characteristic diffraction peaks at 39.9°, 46.4°, 67.9°, 81.8° and 86.2° are derived from the fcc structure of the metal [31]. These peaks locate between those of pure Pd (JCPDS-46-1043) and Pt (JCPDS-04-0802). In contrast with other core–shell structure, the differences in the XRD patterns for Pt shell and Pd core are not distinct, due to the extremely high lattice match of Pt and Pd (99.23%) [20,32]. Nevertheless, the HAADF-STEM-EDS analysis demonstrates their core–shell structure, rather than the formation of bimetallic alloy (Fig. 2). In addition, in the case of Pd@Pt DNC/rGO, the characteristic diffraction peak of graphene oxide (GO) at 11° disappears, while a new broad peak arises at 23° [33], revealing the effective reduction of GO to rGO.

In order to examine the surface chemical compositions of the products, X-ray photoelectron spectroscopy (XPS) analysis was conducted. As illustrated in the survey spectrum (Fig. 4A), the dominant XPS peaks at 70, 284, 334, and 531 eV come from Pt, C, Pd, and O elements, respectively. Fig. 4B shows the high-resolution C 1s region, which was further separated into four peaks at 287.63, 286.02, 284.89, and 283.54 eV, corresponding to the O–C=O, C=O, C–O, and C–C (sp^2 C) groups, respectively [34]. The weak intensity of the peaks originated from oxygen functionalities confirm the effective reduction of GO.

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