



# One-pot synthesis of ultrafine decahedral platinum crystal decorated graphite nanosheets for the electro-oxidation of formic acid



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## ABSTRACT

Synthesis of five-twinned platinum decahedra is currently a great challenge. Reported herein is a solution synthesis of ultrafine decahedral platinum crystals (average size 5.9 nm) mediated by graphite nanosheets together with poly (dimethyl diallyl ammonium chloride). The graphite nanosheets play a critical role in the formation of Pt decahedra. The obtained Pt decahedral crystals provide a valuable platform for the fundamental study of facet-dependent activity of platinum. The hybrid of Pt decahedral crystal decorated graphite nanosheets shows outstanding activity and durability for the oxidation of formic acid. The hybrid possesses a remarkable current density of  $4.3 \text{ mA cm}^{-2}$ , which is 2 times that of state-of-the-art Pt/C catalyst. The superior catalytic performance is well correlated with the unique structures of decahedral Pt crystals. The synthesis protocol disclosed in this study would pave a new route to fabricate high-performance electrocatalysts for fuel cells.

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## 1. Introduction

The ever-increasing energy consumption and concern on environmental issues have stimulated intense research on sustainable energy conversion and storage [1]. Proton exchange membrane fuel cells (PEMFCs) are considered as a promising device for energy conversion because of the high efficiency and low emission of pollutants [2]. Pt-based electrocatalysts are currently indispensable in PEMFCs. Unfortunately, the scarcity and cost of Pt remains a critical obstacle for the widespread commercialization of PEMFCs. Tremendous effort has been devoted to increasing the utilization efficiency of Pt, thus allowing for decreasing Pt loadings in PEMFCs but without compromising the device performance [3–5]. To this end, one strategy is to increase the proportion of surface atoms by downsizing Pt to the atomic level [6,7]. Admittedly, the surface-to-volume ratio of Pt nanoparticles (NPs) is enormously enhanced when the size is miniaturized to the sub-nanometer scale. However, the production and stabilization of Pt clusters with dozens of atoms are very challenging due to the extremely high surface energy. An alternative strategy is to optimize the activity of Pt NPs by delicately engineering their surface structures through the so-called facet-controlled synthesis [8–11]. It has been estab-

lished that the oxidation of organic fuels and reduction of oxygen in Pt crystals are highly facet-dependent [12–16]. Thanks to the recent advances in materials science, a large number of Pt nanocrystals with well-tailored facets such as, tetrahedral [17], cubic [18], multioctahedral [19], truncated octahedral [20] and high-index tetra-hexahedrons [21] have been studied as electrocatalysts in PEMFCs. Of these reported faceted crystals, twinned Pt NPs have been of particular interest due to the presence of high densities of twins, corners and defects, which show different bond enthalpies, desorption energies, and adsorption geometries in the catalytic reactions [22]. Numerous studies suggest that NPs with twin structures far outperform their single-crystalline counterparts because of the enhanced adsorption of intermediates and/or resistance to adsorbed poisoning species [23–31].

Formic acid is considered to be one of promising fuels in PEMFCs. Compared with methanol, the prominent advantage of formic acid lies in its lower crossover in Nafion<sup>®</sup> membranes, which enables the utilization of high-concentration formic acid in PEMFCs and thus enhances the energy density [32]. Previous studies demonstrated that formic acid oxidation (FAO) was highly dependent on Pt facets [33–36]. It is therefore possible to optimize Pt activity by tailoring the facets of Pt NPs. Herein, we report a simple approach to synthesize graphite nanosheet (GNS) supported Pt decahedra for the FAO. To date, the synthesis of ultrafine multi-twinned Pt NPs is very challenging due to the high internal strain and the occurrence of oxidative etching [37]. To our knowledge,

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the synthesis of single Pt decahedra is rarely reported. In this study, we address this challenge by disclosing a solution synthesis of ultrafine decahedral platinum crystals mediated by GNS together with poly (dimethyl diallyl ammonium chloride) (PDDA). It is found that the GNS plays a key role in the formation of Pt decahedra. Though graphene and its derivatives have been extensively utilized as versatile platforms to fabricate advanced electrocatalysts [38–40], little attention was paid to their structure-directing role in solution-phase synthesis [41]. This work demonstrates that coupling with PDDA, GNS is capable of facilitating the formation of Pt decahedra and that the resulting hybrid shows outstanding performance for the FAO.

## 2. Experimental

### 2.1. Materials

The GNS support was derived from catalytic decomposition of methane and purified by acid leaching and sediment separation as reported in our previous work [43]. The resulting GNS mainly consisted of few-layered graphene (<10 layers) (see Fig. S1) and exhibited a Brunauer-Emmett-Teller (BET) surface area of  $247 \text{ m}^2 \text{ g}^{-1}$ . PDDA solution ( $M_w$ :  $2\text{--}3.5 \times 10^5$  20 wt.%) and  $\text{H}_2\text{PtCl}_6$  solution (8 wt.%) was purchased from Sigma Aldrich. Sodium hydroxide (purity > 99.5%) and ethylene glycol (purity > 99.9%) were purchased from Chemical Reagent Co. (Tianjin, China). All the chemicals were used as received. A commercial Pt/C catalyst (40 wt.%) was supplied by the E-TEK company.

### 2.2. Synthesis of catalysts

The hybrid of decahedral Pt nanocrystal decorated GNS was synthesized via the well-established polyol-assisted reduction method [9]. Typically, 100 mg of GNS support, 2.5 mL of PDDA solution, 2.4 mL of  $\text{H}_2\text{PtCl}_6$  aqueous solution, and 1.2 g of sodium hydroxide were added into 150 mL of ethylene glycol. The mixture was subject to alternate ultrasonication and magnetic stirring to form a stable suspension. The resulting suspension was transferred to a preheated oil bath and refluxed at  $180^\circ\text{C}$  for 30 min under a flow of nitrogen gas (purity > 99.99%). After cooling to ambient temperature, the mixture was separated by centrifuge and thoroughly purified by alternate wash with ethanol and acetone at least for three times until the pH of the supernatant was close to 7. The product was dried at  $80^\circ\text{C}$  overnight and denoted as Pt/GNS-PDDA for convenience.

### 2.3. Structural characterization

The morphology of the samples was observed by transmission electron microscopy (TEM) (JEM-2010F (JEOL)). An energy dispersive X-ray (EDX) analyzer equipped in the TEM was used to analyze the elemental composition of the samples. The actual Pt loading in the electrode was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Varian PE/Sciex ELAN 6100DRC) analysis. X-ray diffraction (XRD) analyses were performed on a high-resolution X-ray diffractometer (Philips X'pert Pro) equipped with  $\text{Cu-K}\alpha$  radiation of  $1.54 \text{ \AA}$ , an X-ray mirror and X'celerator detector for high-speed data collection. The XRD patterns were recorded with a voltage of 40 kV and a current of 30 mA. Prior to test, the instrument was calibrated using a silicon crystal. A thermogravimetric analyzer (DTG-60H, Shimadzu) was used to determine the Pt loading and confirm the purity of the sample. Thermogravimetric analyses were conducted at a temperature range of  $30\text{--}600^\circ\text{C}$  using a heating rate of  $20^\circ\text{C}/\text{min}$  in air flow (flow rate =  $50 \text{ mL}/\text{min}$ ).

### 2.4. Electrochemical measurements

Electrochemical measurements were carried out using a home-made set-up and the details of the experimental procedures were reported in the authors' previous work [44–46]. In brief, a graphite plate (effective area  $1 \times 1 \text{ cm}$ ) coated with a thin layer of catalyst ink was used as working electrode. The loading of the catalyst was ca.  $0.2 \text{ mg cm}^{-2}$ . A saturated calomel electrode (SCE) and Pt gauze were used as reference and counter electrodes, respectively. To determine the electrochemical active surface area (ECSA) of the catalyst, cyclic voltammetry (CV) curves were recorded in 1 M  $\text{H}_2\text{SO}_4$  solution at a scan rate of  $50 \text{ mV s}^{-1}$ . Linear sweeping voltammetry (LSV) tests were conducted in 1 M  $\text{H}_2\text{SO}_4 + 1 \text{ M HCOOH}$  solution at a scan rate of  $5 \text{ mV s}^{-1}$ . Before the test, the electrolyte was bubbled with  $\text{N}_2$  gas for 30 min. The electrochemical measurements were conducted at ambient temperature ( $25 \pm 1^\circ\text{C}$ ) and all potentials in this study were referenced to the SCE.

## 3. Results and discussion

### 3.1. Structural properties

The hybrid of Pt decahedral crystal decorated GNS was synthesized via a one-pot synthesis protocol. The metal precursor, *i.e.*,  $\text{H}_2\text{PtCl}_6$  was reduced in the presence of GNS support and PDDA via the well-established polyol reduction process [42]. The in-situ nucleation, growth and anchoring of Pt NPs to GNS lead to strong coupling between the two components, resulting in enhanced activity [38]. The morphology of the as-prepared Pt/GNS-PDDA was examined by TEM as shown in Fig. 1. Fig. 1a depicts the uniform deposition of Pt NPs into the GNS support (indicated by the arrow). As observed from Fig. 1b, the Pt NPs are nearly monodispersed with few aggregates. A careful inspection reveals that most of these Pt NPs are of a decahedral structure with a few exceptions of single crystallized NPs. Fig. 1c and d presents TEM images of representative decahedral Pt crystals. It reveals that the decahedral Pt NPs exhibit a five-twinned structure, consisting of five adjacent tetrahedrons as illustrated from the inset in the bottom-right corner. As shown in Fig. 1e, a magnified view clearly indicates that the crystal is composed of five single-crystalline domains. The lattice fringes with a spacing value of  $0.23 \text{ nm}$  can be well ascribed to (1 1 1) planes of face-centered cubic Pt crystals. It is also noted from Fig. 1e that numerous defects and dislocations are present in the Pt decahedron. Multiply twinned structures can be also evidenced from the twin boundaries as shown in Fig. 1f. Further statistical analyses indicate that the population of Pt decahedra is dominant in the Pt/GNS-PDDA catalyst based on TEM images. To determine the size of Pt decahedra, at least one hundred NPs were analyzed and the histogram of Pt NPs is shown in Fig. 1g. The average size of Pt NPs in the Pt/GNS-PDDA catalyst is estimated to be  $5.9 \pm 0.8 \text{ nm}$ . The elemental composition of the catalyst was determined by EDX as shown in Fig. 1h. The presence of copper signal in the spectrum is originated from the TEM grid. The catalyst consists of three elements, *i.e.*, platinum, carbon and oxygen, suggesting the complete removal of impurities during the purification process. The actual Pt content in the catalyst is determined to be 32.8 wt.% by ICP-AES, which is close to that of 34.6% as obtained from the EDX analyses.

It is noteworthy that the synthesis of ultrafine multi-twinned nanocrystals is currently challenging [7]. To our knowledge, this study might be the first report to obtain Pt decahedra with sizes of sub-10 nm. To reveal the growth mechanism of Pt decahedra, control experiments were conducted. Another two batches of Pt NPs were synthesized without adding the PDDA surfactant

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