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# Ascorbic acid assisted bio-synthesis of Pd-Pt nanoflowers with enhanced electrochemical properties.

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ABSTRACT

Bimetallic Pd-Pt nanoflowers (Pd-Pt NFs) of varying sizes (20–60 nm) were synthesized through the concurrent reduction of $Pd(NO_3)_2$ and $K_2PtCl_4$ using *Cinnamomum camphora* (*C. camphora*) leaf extract assisted by ascorbic acid (AA). *C.Camphora* acted as both a co-reducing agent and a green template in the synthesis protocol providing a fast, simple, green and cost-effective means of producing the Pd-Pt NFs. Characterization techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) were used to confirm the Pd-Pt NFs formation. FT-IR analysis showed that biomolecules such as polyphenols and flavonoids were responsible for the reduction while stretching vibration bands from C—H, —C=C—, O—H, and —C—O— O acted as capping agents. The as-formed Pd-Pt NFs showed excellent performance and stability in the electro-oxidation of ethanol in alkaline media. Electro-catalytic performance increased with Pt content, while addition of Pd increased stability. The $PdPt_3$ NFs presented the best performance with a mass activity of 1.43 A $mg^{-1}_{metal}$, 5.72, 4.93, 2.27, 1.27, 11 and 4.6% higher than the Pd, Pt, $Pd_3Pt$, and PdPt NFs, and commercial Pt and Pd-black respectively. However, it was more prone to poisoning, with an $I_f/I_r$ value of 0.78 compared to 1.37 for $Pd_3Pt$ NFs.



## 1. Introduction

Electro-oxidation of alcohols has received significant attention in the past decades since they are anodic reactions in direct alcohol fuel cells (DAFCs) [1–3]. Pt-based materials are more active than others toward ethanol oxidation reaction (EOR) in acidic solutions [4]. They however, show low activity than Pd in alkaline media [5]. Previous studies demonstrated that by alloying with Pd, the EOR activity in alkaline media could be improved and higher than Pd or Pt alone [6–8]. For example, Yang et al. synthesized Pd-Pt alloy nanostructures supported on carbon nanotubes using ultrasound-assisted strategy. The as-synthesized Pd-Pt alloy nanostructures showed an enhanced performance and stability for electro-oxidation of both ethanol and methanol in an alkaline solution [6]. She et al. also observed a significant higher EOR activity of Pd/Pt/glassy carbon (GC) catalyst over Pd/GC and Pt/GC catalyst which they attributed to synergistic effect [9].

The activity of a catalyst is highly dependent on its structure. It is well known that porous or flowerlike metal nanostructures with controlled morphology have large surface area to volume ratio resulting in more active centers [10,11]. Syntheses of these porous or flowerlike structures are very challenging to synthesize, which require artificial template or stabilizers, complex procedures and specialized machinery [2,9]. Qiu et al. synthesized Pt-Pd porous nanostructures using electrostatic-attraction-directed layer-by-layer assembly using $SiO_2$ as a template [12]. Zhang et al. synthesized porous Pd-Pt nanoflowers by first synthesizing Pd seeds using sodium borohydride as reducing agent and cetyltrimethylammoniumchloride (CTAC) as stabilizer, followed by the addition of Pt processor [13]. Lu et al. using galvanized replacement method, synthesized Pt-Pd NRs at 90 °C in a mixture of PVP (68.8 mg) and NaBr (518 mg) [14].

To circumvent this drawback, Fu et al. proposed a water-based route to synthesize porous Pt-Pd nanoflowers using hydrazine hydrate as the reducing agent in poly (allylamine hydrochloride) based aqueous solution [11]. However, highly toxic hydrazine according to the US Environmental Protection Agency and the adjustment of pH using NaOH and HCl make the process

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environmentally unfriendly. In addition, the as-synthesized Pt-Pt catalyst had to be cleaned with UV/Ozone to remove the capping agent.

Plant-mediated synthesis represents a simple, milder, less expensive and environmentally benign protocol for synthesis of nanomaterials over the traditional chemical and physical means [15–17]. In addition, plant biomolecules can act as reducing and capping agent and the products can be used without special treatment to remove capping agents [18]. Our group in a previous work synthesized flowerlike Au-Pd nanostructures which could directly be used in the catalytic oxidation of benzyl alcohol [19]. Inspired by this work, for the first time, we report the rapid synthesis of size and morphology controllable flowerlike Pd-Pt nanostructures using *Cinnamomum camphora (C. Camphora)* as bio-template and reducing agent assisted by ascorbic acid (AA). The obtained Pd-Pt NFs showed excellent electro-catalytic activity in the oxidation of ethanol in alkaline media.

## 2. Experimental Section

### 2.1. Materials and reagents

*Cinnamomum camphora (C. camphora)* leaves were purchased from Xiamen Peony Perfume and Chemical Industry Co. Ltd. Ascorbic acid (AA) and potassium tetrachloroplatinate ($K_2PtCl_4$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) while palladium nitrate (Pd $(NO_3)_2$) and Pt-black (50 nm) were purchased from Aladdin Reagent Co., Ltd. (China) and Pd-black (30 nm) were obtained from Hongwu International group Ltd (China). All chemicals were used as received without further purification.

### 2.2. Preparation of C. camphora extract

The leaf extract was obtained following our previous study [20]. In brief, 1 g of milled powder of *C. camphora* was immersed in 100 mL of distilled water (DI) in a conical flask. The flask was then shaken in a water bath shaker at 30 °C for 6 hr. The suspension was filtered to remove debris. The obtained liquid extract was stored in a refrigerator for further use.

### 2.3. Synthesis of Pd-Pt NFs

To synthesize Pd-Pt NFs, 1 mL of 10 mM Pd $(NO_3)_2$and $K_2PtCl_4$ solutions were added to 20 mL of DI water in a 100 mL round bottom flask. The flask was kept in an oil bath at 60 °C with a magnetic stirrer rotating at 600 rpm. Then 1 mL of 1 M AA and 20 mL *C. camphora* leaf extract mixture was added to the mixture under vigorous stirring in 10 min. The resulting solution was centrifuged at 9000 rpm for 10 min. After the powders were collected, they were further washed with DI water and ethanol for three times. The powders were finally dispersed in 200 μL DI water for further characterization. More samples with different Pd/Pt ratios were synthesized by changing the molar ratio of the precursors. For comparison, Pd and Pt NFs were also prepared in a similar way, PdPt NPs synthesized in the absence of *C.Camphora* leaf extract and commercial Pd and Pt-black were also tested.

### 2.4. Characterizations

Transmission electron microscopy (TEM) and selected area (electron) diffraction (SAED) characterizations were conducted on Tecnai F30 (FEI; Netherlands) with an accelerating voltage of 300 kV. Size distribution analysis of Pd- Pt NFs were conducted by using the SigmaScan Pro software (SPSS Inc, Version 4.01.003) [21]. XRD patterns were collected on a Rigaku Ultima IV (Rigaku, Japan Netherlands) using Cu Kα radiation (40 kV, 30 mA). X-ray photoelectron spectroscopy (XPS) studies were carried out on PHI-1600 (Perkin-Elmer) using the Al Kα line as the excitation source. Brunauer-Emmett-Teller (BET) surface area analysis of the as-synthesized Pd-Pt NFs was done on ASAP 2020 (Micromeritics).

### 2.5. Electrocatalytic test

The electrochemical tests were conducted on a CHI 660 D electrochemical analyzer (CH Instrument Shanghai, Chenghua Co., Ltd). A Pt wire and standard calomel electrode were served as the auxiliary and reference electrodes, respectively. To prepare the working electrode, 1 mg of the as-prepared catalyst powder was dispersed in 1 mL DI water; the suspension was sonicated for 30 min to make a uniform ink. The suspension (6 μL) was pipette and dropped on the glassy carbon electrode (3 mm diameter, 0.071 $cm^2$ geometric area). The cyclic voltammograms (CV) measurements were conducted in a standard three-electrode cell at room temperature with a scanning rate of 50 mV $s^{-1}$ in $N_2$ saturated 1 M KOH solutions with and without ethanol (1 M).

CO stripping experiment was carried out as in a previous work [22] by bubbling CO gas (99.9% purity) into 1 M KOH solution for 20 min at −0.2 V to ensure CO saturated absorption on the working electrode. It was then transferred into another KOH solution in a flow of $N_2$ gas atmosphere. In this case, no CO was present in the solution and only adsorbed state CO ($CO_{ad}$) was on the electrode surface. Subsequently, $CO_{ad}$ oxidation test was achieved using cyclic voltammetry.

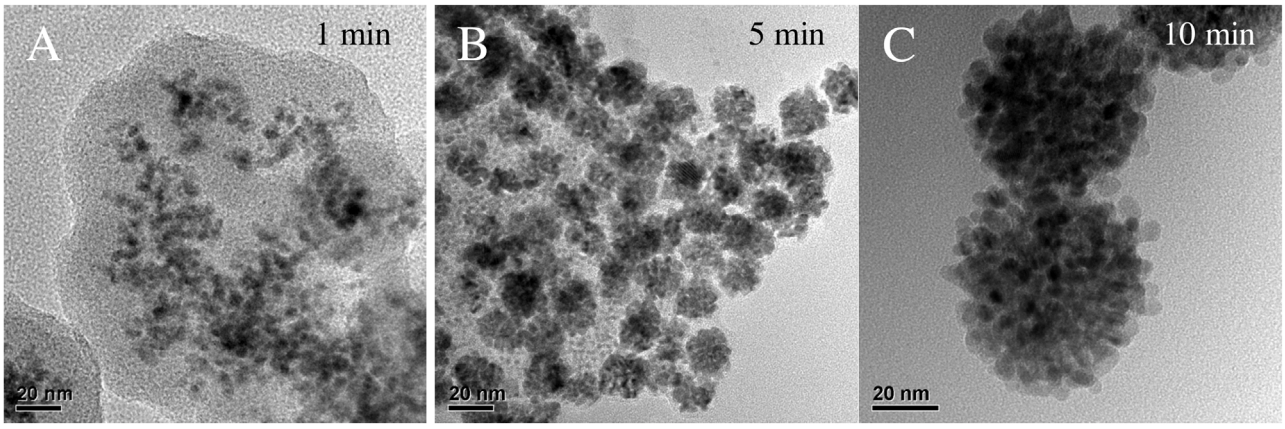


**Fig. 1.** TEM images of PdPt materials at different reaction stage. After (A) 1 min, (B) 5 min, and (C) 10 min of reaction.