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# New strategy to prepare platinum salts by electrochemical methods and subsequent synthesis of platinum nanoparticles

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#### ABSTRACT

As shown in the literature, most of Pt nanoparticles (NPs) were synthesized from precursors of commercial Pt salts. However, the impurity of the commercial Pt salts is a concerned issue. In this work, we report a new pathway based on electrochemical methods to prepare Pt-containing complexes with high purity in aqueous solutions from bulk Pt substrates. Experimental results indicate that Pt complexes with higher concentration can be obtained in 0.1 N HCl by using square-wave oxidation-reduction cycles (ORCs) under a frequency of 8 Hz with a step potential of 6.3 mV. Moreover, concentrations of other heavy metals of Hg and Cr in 65 ppm Pt complexes-containing solution are just 0.65 and 0.78 ppb, respectively. These Pt complexes were further reduced to Pt NPs by using NaBH<sub>4</sub> and poly(vinylpyrrolidone) (PVP) as reducing agent and stabilizer, respectively. The concentration and the particle size of synthesized Pt (1 1 1) NPs are ca. 60 ppm and smaller than 5 nm, respectively.

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## 1. Introduction

Recently, applications of gold and platinum nanoparticles (NPs) in the fields of protein detection [1,2] and catalyst modification [3,4] are rapidly growing because of their unique electronic structure and extremely large surface areas. As shown in the literature, the developed methods for fabrications of NPs of noble metals include chemical [5], electrochemical [6], sonochemical [7] and sonoelectrochemical [8] reductions, laser ablation [9], annealing from high-temperature solutions [10], metal evaporation [11], Ar<sup>+</sup> ion sputtering [12], and UV light irradiation [13]. Meanwhile, some stabilizers, like sodium dodecyl sulfate [14], sugar ball [15] and poly(vinylpyrrolidone) (PVP) [16] were used, and some stabilization technologies of thiol-ligand coatings [17] and polymer capping agents [18] were developed to prevent the prepared NPs from aggregating. Also, it is necessary to develop effective methods for size- and shape-controlled synthesis of metal NPs due to these properties can significantly influence their corresponding characterization [19,20].

Recently, electrocatalysts of Pt NPs were popularly used in proton-exchange membrane fuel cells [21,22] and oxidation of small organic molecules [3,23]. Sanles-Sobrido et al. [24] proposed a one-step method for the preparation of single-crystal dendritic Pt NPs with no need of organic solvents, templates, or seeded growth. It is shown that Pt NPs with two different shapes (spherical or dendritic) can be efficiently supported onto the sidewalls of carbon nanotubes. Notably, the supported dendritic Pt NPs yield unprecedented catalytic activity, evidenced through the lowest activation energy within an electron-transfer reaction as compared with those reported in the literature for Pt NPs. Hsu et al. [25] developed a novel method to debundle carbon nanotubes (CNTs) and load Pt NPs on them without damaging their graphene structures. In this article, the aniline acts as a very efficient dispersing agent to debundle CNTs from 200 to 50 nm at a very low concentration of 0.5% in an isopropanol (IPA)/water solution. The result indicates that aniline is an efficient dispersant and stabilizer for the preparation of Pt NPs deposited on CNTs. Additionally, the whole process, which could be easily scaled up for industrial production, is simple, efficient, and inexpensive. Zhang et al. [26] reported a novel experimental protocol for the preparation of stable and exfoliated nano-Pt catalysts supported on layered silicate clay surfaces. Uniformly dispersed highly crystalline Pt NPs with diameters between 2 and 5 nm were chemically adsorbed on to the layered silicate surfaces using a chemical vapor deposition (CVD) method employing organoclay

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as the initial support. The as-prepared catalysts were found to be extremely stable against both intensive mechanical agitation and high temperature treatment.

As shown in the literature, most of Pt NPs were synthesized from precursors of commercial platinum salts. The impurity of the commercial platinum salts is a concerned issue. It would reduce the purity of the synthesized Pt NPs. Therefore, the synthesized Pt NPs from commercial platinum salts are unfavorable for their subsequent applications. In this work, we propose a new pathway based on electrochemical methods to prepare Pt-containing complexes with high purity in aqueous solutions from pure Pt substrates. These complexes can be further reduced to platinum NPs.

# 2. Experimental

### 2.1. Chemical reagents

Chemical reagents of HCl, NaBH<sub>4</sub> and PVP (p.a. grade) purchased from Acros Organics were used as received without further purification. All of the solutions were prepared using deionized 18.2 M $\Omega$  cm water provided from a MilliQ system.

#### 2.2. Preparation of platinum nanoparticles

All of the electrochemical experiments were performed in a three-compartment cell at room temperature (22 °C) and were controlled by a potentiostat (model PGSTAT30, Eco Chemie). First, a sheet of platinum with bare surface area of  $4 \text{ cm}^2$ , a sheet of  $2 \text{ cm} \times 4 \text{ cm}$  platinum, and a KCl-saturated silver-silver chloride (Ag/AgCl) rod were employed as the working, counter and reference electrodes, respectively. Before the square-wave oxidation-reduction cycles (ORCs), the Pt electrode was mechanically polished (model Minimet 1000, Buehler) successively with 1 and 0.05 µm of alumina slurries to a mirror finish. Then the electrode was cycled in a deoxygenated aqueous solution of 40 mL containing 0.1 N HCl from -0.1 to +2.4 V vs Ag/AgCl for 300 scans. A frequency of 8 Hz and a step potential of 6.3 mV was used. The solution was slightly stirred during the ORCs treatment. After this dissolving procedure, Pt-containing complexes were left in this aqueous solution at pH 0.95. Immediately, 1 mg stabilizer of PVP was added in this solution under slight stirring for 5 min. Then 1 mg reducing agent of NaBH<sub>4</sub> was subsequently added to prepare Pt NPs in solution. The prepared colloidal solutions were further centrifuged at 15,000 rpm for 3 min and then ultrasonically redispersed in aqueous solutions for three cycles to remove impurities.

#### 2.3. Characteristics of platinum nanoparticles

The concentrations of Pt NPs and impurities of Hg and Cr were measured from inductively coupled plasma-mass spectrometer (ICP-MS) analyses. A single drop of the sample-containing solution was placed on a 300 mesh Cu/carbon film transmission electron microscopy (TEM) sample grid and was allowed to be dried in a vacuum oven. Then the sample was examined by using a Philips Tecnai G2 F20 electron microscope with an acceleration voltage of 200 kV. Ultraviolet-visible absorption spectroscopic measurements were carried out on a Perkin-Elmer Lambda 35 spectrophotometer in 1 cm quartz cuvettes. Before recording the high resolution X-ray photoelectron spectroscopy (HRXPS) spectra sample powders were obtained via centrifugation collections at 15,000 rpm for 3 min and being rinsed with deionized water for three cycles. For HRXPS measurements, a ULVAC PHI Quantera SXM spectrometer with monochromatized Al Kα radiation, 15 kV and 25 W, and an energy resolution of 0.1 eV was used. To compensate for surface charging effects, all HRXPS spectra are referred to the C 1s neutral carbon peak at 284.8 eV.

#### 3. Results and discussion

#### 3.1. Preparation of platinum-containing complexes

As shown in the literature [27,23], most of noble metal NPs were conveniently synthesized from precursors of commercial metal salts. However, the impurity of the commercial platinum salts is a considerable issue for their practical applications. The aim of this work is to find a suitable electrochemical method to prepare Pt-containing complexes with high purity in aqueous solutions from pure bulk Pt substrates. Certainly, these prepared complexes should be successfully reduced to Pt NPs. In the triangular-wave ORCs treatment, the chloride electrolyte was selected since this facilitates the metal dissolution-deposition process that is known to produce surface-enhanced Raman scattering (SERS)-active surfaces [28]. Meanwhile, the Au-containing complexes were also left in the solution after roughening the Au substrate, as reported in our previous study [29]. These prepared precursors of Aucontaining complexes can be further reduced to Au NPs by sonoelectrochemical reactions [12]. For preparing Ag-containing complexes based on triangular-wave ORCs treatment electrolytes of HNO<sub>3</sub> were suggested because the concentration of the prepared Ag-containing complexes would be reduced due to the formation of settlement of AgCl in electrolytes containing chloride. These prepared precursors of Ag-containing complexes can be also reduced to Ag NPs by heating under aid of chitosan [30]. Tian et al. [31] reported a square-wave ORCs treatment to Pt substrates in electrolytes of H<sub>2</sub>SO<sub>4</sub> to prepare weakly SERS-active Pt substrates. However, there are no Pt-containing complexes available in the solution after roughening the Pt substrate. These experimental experiences encourage us to find some suitable electrochemical ORCs method to prepare Pt-containing complexes in aqueous solutions. First, we employed different triangular-wave ORCs treatments to Pt substrates in general electrolytes of chloride, or HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> to prepare Pt-containing complexes in aqueous solutions. However, these treatments did not succeed. Encouragingly, Pt-containing complexes with considerable concentrations in aqueous solutions can be obtained by using suitable squarewave ORCs treatment to Pt substrates in specific electrolytes, as discussed below.

Fig. 1 shows the typical *I*–*E* curve in roughening the Pt substrate in 0.1 N HCl by using the square-wave ORCs treatment under a frequency of 8 Hz. In experiment, the upper and lower potentials are 2.4 and -0.1 V vs Ag/AgCl, respectively. The step potential is 6.3 mV. This *I*–*E* curve is quite different from that shown in the SERS study based on a roughened Pt electrode reported by Tian et al. [31]. In our system, considerable amount of Pt-containing complexes can be obtained in solution after the square-wave ORCs treatment to a Pt substrate in an acidic solution of 0.1 N HCl.

Fig. 2 shows the UV–vis spectra of Pt-containing complexes after the square-wave ORCs treatments to Pt substrates in solutions containing different electrolytes. As shown in spectrum a of Fig. 2 (in a solution containing electrolytes of acidic HCl), the absorbance maximum appears at ca. 261 nm, which can be assigned to Pt-containing complexes due to the ligand-to-metal charge–transfer transition [32]. However, there are no absorbance maxima, as shown in spectra b and c of Fig. 2 (in solutions containing electrolytes of neutral KCl and acidic H<sub>2</sub>SO<sub>4</sub>, respectively). Therefore, electrolytes of acidic HCl are favorable for preparing Pt-containing complexes in solutions with higher concentration based on our proposed square-wave ORCs treatment.



**Fig. 1.** Square-wave oxidation-reduction cycles (ORCs) of the 300th scan under a frequency of 8 Hz with a step potential of 6.3 mV for electrochemically roughening platinum substrate in 0.1 N HCl.

As shown in our previous report [33], the SERS effects observed on the silver substrates are dependent on the scan rates used in the triangular-wave ORCs preparations. Thus the effects of the step potentials used in these square-wave ORCs treatments to Pt substrates on the corresponding Pt-containing complexes obtained in solutions were also examined in this work. Fig. 3 shows the UVvis spectra of Pt-containing complexes in 0.1 N HCl solutions by using the square-wave ORCs treatments with different step potentials. Basically, these three spectra are similar. The absorbance maxima appear at ca. 261 nm, which can be assigned to Ptcontaining complexes [32]. The only differences between them are the absorbance values, which are proportional to the concentrations of Pt-containing complexes. The highest absorbance can be



**Fig. 2.** UV-vis spectra of Pt-containing complexes in solutions after roughening the Pt substrates by square wave ORCs under a frequency of 8 Hz with a step potential of 6.3 mV for 300 scans in different solutions: (a) 0.1 N HCl; (b) 0.1 N KCl; (c) 0.1 N H<sub>2</sub>SO<sub>4</sub>.



**Fig. 3.** UV–vis spectra of Pt-containing complexes in solutions after roughening the Pt substrates by square wave ORCs under a frequency of 8 Hz for 300 scans with different step potentials: (a) 0.63 mV; (b) 6.3 mV; (c) 63 mV.

obtained with a low step potential of 0.63 mV. The absorbance values were reduced to 70% and 8% of magnitudes when the step potentials were increased from 0.63 to 6.3 and 63 mV, respectively. Although a higher concentration of Pt-containing complexes can be prepared with a lower step potential of 0.63 mV, it takes much time to perform the experiment. Therefore, a suitable step potential of 6.3 mV was adopted in this work to prepare considerable concentration of Pt-containing complexes in solutions. The concentrations of prepared Pt-containing complexes were also investigated by increasing the frequency from 8 to 80 Hz with a step potential of 6.3 mV. The obtained concentration of complexes was correspondingly reduced to 60% of its original value. Conclusively, Pt-containing complexes with high purity can



Fig. 4. UV-vis spectrum of chemically prepared Pt(0) nanoparticles.

50 m

Fig. 5. TEM micrograph of synthesized Pt(0) nanoparticles, showing size and dispersion; scale of nano-bar being 50 nm.

be efficiently prepared by using square-wave ORCs methods in 0.1 N HCl under a frequency of 8 Hz and a step potential of 6.3 mV.

#### 3.2. Preparation of platinum nanoparticles

Subsequently, as-prepared Pt-containing complexes were further reduced to Pt NPs by reducing agent of NaBH<sub>4</sub> and protected by stabilizer of PVP. Fig. 4 demonstrates the UV-vis spectrum of the synthesized elemental Pt NPs in solutions. Along with the adding of NaBH<sub>4</sub>, the color of the solution becomes yellow-brown and finally becomes black after 5 min. The absorbance band at 261 nm disappears. It indicates that all of the Ptcontaining complexes are reduced. Instead, the synthesized Pt NPs have absorption band in all range of the UV-vis spectrum. Moreover, the absorption increases gradually with the decrease of the wavelength. These phenomena are consistent with the reports shown in the literature [32,34]. Further ICP-MS analyses

2.2 A

**Fig. 6.** High-resolution TEM micrograph of synthesized Pt(0) nanoparticles, showing the (1 1 1) lattice fringes with an interplanar spacing of 2.22 Å; scale of nano-bar being 5 nm.

indicate that the concentrations of the prepared Pt-containing complexes and the elemental Pt NPs in solutions are ca. 65 and 60 ppm, respectively. Meanwhile, concentrations of other heavy metals of Hg and Cr are just 0.65 and 0.78 ppb, respectively. However, these concentrations are 13 and 29 ppb for Hg and Cr, respectively, in commercial Pt salts based on the same Pt complexes concentration prepared in this work. In the electrochemical ORCs method, the impurity mainly comes from the dissolution of the Pt substrate. Therefore, the content of impurity can be controllably reduced by using pure Pt substrate. The concentrations of impurities discussed above are average values based on three measurements.

The dispersion and the particle size of prepared Pt NPs in solutions are examined by using HRTEM images, as shown in Fig. 5. The particle sizes of the prepared Pt NPs are smaller than 5 nm. They demonstrate no aggregation and fairly even dispersion. Fig. 6 shows the moiré patterns of the Pt NPs. It exhibits a one-



Fig. 7. EDX spectrum of high-resolution TEM of synthesized Pt(0) nanoparticles, showing the nanoparticles being platinum.



Fig. 8. HRXPS Pt 4f7/2-5/2 core-level spectra of different platinum: (a) positively charged Pt-containing complexes after electrochemical treatment; (b) synthesized Pt(0) nanoparticles; (c) polished Pt substrate before electrochemical treatment.

dimensional fringe lattice due to moiré interference. It indicates that these NPs are crystalline [35]. Also (111) lattice fringes with an interplanar spacing of 2.2 Å were measured for all lattice planes. This is reasonable since the low index plane (111) has the lowest surface energy [36]. Further EDX spectrum of HRTEM of prepared Pt NPs, as shown in Fig. 7, also confirms the successful fabrication of Pt NPs from precursors of Pt-containing complexes prepared by square-wave ORCs methods proposed in this work.

Fig. 8 displays the HRXPS Pt  $4f_{7/2-5/2}$  core-level spectra of the prepared Pt-containing complexes, the synthesized Pt NPs and a polished Pt substrate for comparison. As shown in spectra b (representing Pt NPs) and c (representing a polished Pt substrate), the doublet peaks located at 70.9 and 74.3 eV can be assigned to Pt(0) according to a previous report [3] and a XPS handbook. Due to these two similar spectra, the Pt NPs prepared by chemical reduction can be confirmed to be metallic Pt. As comparing spectrum a with doublet peaks located at 71.5 and 74.9 eV (representing the positively charged Pt-containing complexes before reduction), with spectrum b (representing the metallic Pt NPs), it is found that there are extra oxidized components of Pt shown in the higher binding energy side. Thus, the Pt in the Pt-containing complexes can be confirmed to be positively charged Pt according to a previous report [3] and a XPS handbook. HRXPS experiment also reveals that negatively charged Cl is present in the Pt-containing complexes. Thus, the prepared Pt-containing complexes are composed of positively charged Pt and negatively charged Cl. Moreover, the Ptcontaining complex can be assigned to PtCl<sub>6</sub><sup>2+</sup>, which is similar to that of commercial Pt salt of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O.

#### 4. Conclusions

In this work, we have successfully developed a new electrochemical pathway to prepare Pt-containing complexes with high purity from pure bulk Pt substrates. Pt-containing complexes can be efficiently prepared by using square-wave ORCs methods in 0.1 N HCl under a frequency of 8 Hz and a step potential of 6.3 mV. This method can overcome the general issue of impurity in synthesizing Pt NPs from precursors of commercial Pt salts. The concentrations of the prepared Pt-containing complexes and the synthesized elemental Pt NPs in solutions are ca. 65 and 60 ppm, respectively. Meanwhile, concentrations of other heavy metals of Hg and Cr in 65 ppm Pt complexes-containing solution are just 0.65 and 0.78 ppb, respectively. Also, the particle sizes of the synthesized Pt(1 1 1) NPs are smaller than 5 nm.

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