

Green Synthesis and Characterization of Platinum Nanoparticles

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Abstract: The noble metal of platinum nanoparticles (PtNPs) with attractive physicochemical properties would hold great promise in various fields of catalysis, electroanalytica, biomedical applications, chemical industry and biosensor. However, it still existed a great challenges in controlling its particle size, morphology and structure. Here, we developed an environmentally friendly, facile, cost-effective, and nontoxic approach for green synthesis of platinum nanochains and platinum nanopetals under ambient conditions in a shorter reaction time. Platinum nanoparticles was prepared by hydrothermal method, and the platinum nanopetals was synthesized by self-assembly on the basis of platinum nanochains sol. The synthesis process of platinum nanoparticles was monitored and analyzed by a UV-visible spectrophotometer and the stability of the synthesized products was scientifically evaluated. In addition, the micromorphology, crystal structure, valence state and characteristic absorption peaks of the products were characterized by transmission electron microscope (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-vis absorption spectras (UV-vis) and zeta potential, respectively. These characterization results inferred that platinum nanochains were well distributed with small spherical shape in single particle with average particle sizes of around 3 nm, platinum nanopetals with diameter of 20 nm. And their UV characteristic absorption peaks remained constant for 90 days at 4°C. This work output can acts as a valuable experience for other relevant researchers towards the synthesis, characterization and application formation.

Keywords: Synthesis, Platinum Nanochains, Platinum Nanopetals, Characterization

1. Introduction

With tremendous growth in materials science and engineering, platinum nanoparticles (PtNPs) plays a positive role in catalysis, electroanalytica, biomedical applications, chemical industry and biosensor due to its unique optical, crystalline and catalytic properties [1-6]. For instance, Berghian-Grosan et al. explored an efficient catalyst based on PtNPs with good electrocatalytic performance [7]. In recent years, large numbers of platinum organometallic had been constructed and applied for sensing, biomedical, tuning emissions and catalysis [8]. Furthermore, the novel mechanisms underlying sensitivity or resistance of Pt compounds had been discovered, which could be used not

only to identify biomarkers to stratify patients but also to optimize and personalize the treatment of multiple malignancies [9]. These superior properties of PtNPs are closely dependent on the method of preparation, which determines its size, morphology, structure and dispersion of the PtNPs [10]. Although various synthesis methods have been successfully used to prepare the noble metal of PtNPs such as laser ablation, UV irradiation, ultrasonic fields, aerosol technologies, lithography and photochemical reduction techniques, they involve the use of toxic chemicals posing potential environment and remain expensive [11, 12]. Therefore, there is a significant interest in design simple operation, environment friendly and high stability methods for production of PtNPs with novel applications, which can

be achieved by controlling shape and size at nanometre scale.

Here, we prepared different desired shapes and sizes PtNPs by a simple, cost-effective, and environmentally friendly method under ambient conditions in a shorter reaction time. The synthesized PtNPs were thoroughly evaluated for preparation condition, stability and characterizations by transmission electron microscope (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-vis absorption spectras (UV-vis) and zeta potential, respectively. The result of this work promises an interesting strategy to prepare PtNPs with novel morphology and application.

2. Experimental

2.1. Chemicals

Citric acid monohydrate, chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and trisodium citrate used in this work were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ascorbic acid was provided by Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Sodium borohydride was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China).

All glassware were soaked in aqua regia for 3 hours, rinsed with tap water, deionized water, and ultrapure water in turn, and then dried in drying oven prior to use.

2.2. Instruments

The morphologies and microstructures of the samples were carried out on a TEM (Tecnai G2 F20 S-TWIN). Phase structures were recorded using a XRD (EMPYREAN). UV-vis absorption spectras were characterized by means of a 2450 UV-vis spectrophotometer. XPS measurements were performed on an AXIS Supra spectrometer. The potential values of the samples were measured by a Zetasizer Nano ZS Zeta potential analyzer.

3. Results

3.1. Preparation of PtNPs

The platinum nanochains with 3 nm diameter for a single particle were prepared by a hydrothermal route [13]. Briefly, 25 mL H_2PtCl_6 aqueous solution (0.01%) was treated to a boil at 280°C under vigorous stirring. Then 0.5 mL sodium citrate (1%), 0.5 mL citric acid solution (0.05%) and 0.25 mL sodium borohydride (1%) were added, respectively. The color immediately turns yellowish brown and the mixture was rapidly heated to boiling at 280°C under vigorous stirring. In order to avoid rapid volatilization of the solution and agglomeration, resulting in preparation failure, the temperature was adjusted to 100°C and continuously heated for 15 min. Next, the resulting light brown products was stirred at room temperature, diluted to 25 mL with ultrapure water.

The platinum nanopetals sol with a diameter of 20 nm were made from the previously prepared platinum nanochains [13]. To shorten the time of preparation of platinum nanoparticles, the 25 mL mixture solution containing 1 mL of platinum nanochains sol, 0.325 mL H_2PtCl_6 aqueous solution (1%), 0.5 mL of sodium citrate solution (1%) and 0.5 mL ascorbic acid solution (1.25%) was rapidly heated to a boil at 280°C under vigorous stirring and keep reaction for 15 minutes at 100°C . After stirring 15 minutes at room temperature, the prepared sol was diluted to 25 mL with ultrapure water.

3.2. TEM Analysis

As shown in Figure 1, the microstructure of the PtNPs were measured by TEM. It can be observed from Figure 1A that platinum nanochains are well distributed with small spherical shape in single particle with particle sizes of around 3 nm [13]. Platinum nanopetals with diameter of 20 nm can be seen in Figure 1B, and we speculated that they were formed by self-assembly of platinum nanochains.

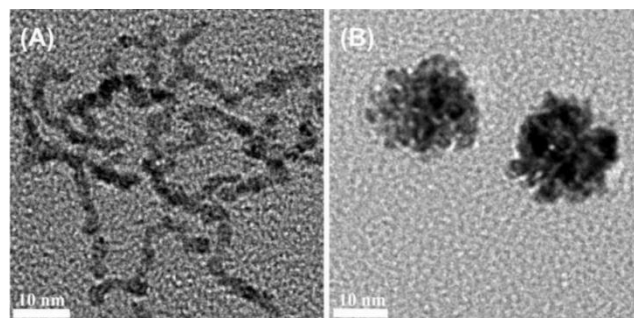


Figure 1. TEM images of PtNPs (a) platinum nanochains and (b) platinum nanopetals.

3.3. XPS and XRD Results

The XRD pattern of the prepared platinum nanochains and platinum nanopetals were shown in Figure 2. Four diffraction peaks at about 39.80° , 46.3° , 67.50° , and 81.40° correspond to the (111), (200), (220) and (311) Pt facets, respectively. All these peaks were indexed to the centred cubic Pt (PDF#88-2343), indicating that the products were single-phase sample of Pt. Figure 3 showed the magnified view of the spectrum for metal Pt 4f. The two peaks with a binding energy of 70.8 eV and 74.2 eV correspond to $4f_{7/2}$ and $4f_{5/2}$ of Pt, respectively, which further suggested the synthesis of PtNPs.

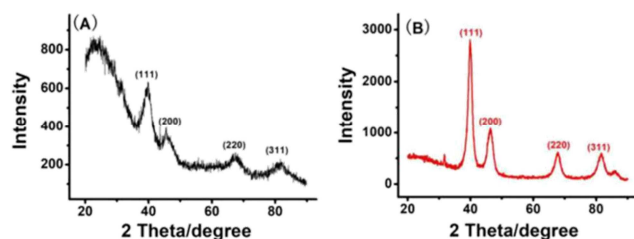


Figure 2. XRD patterns of PtNPs: (A) platinum nanochains and (B) platinum nanopetals.

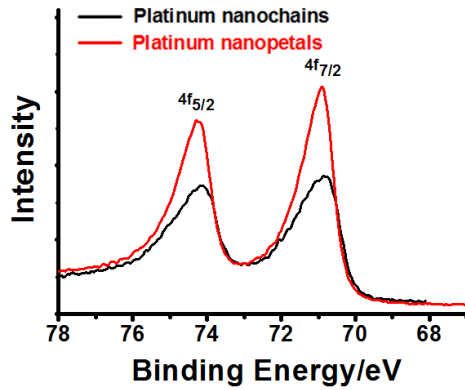


Figure 3. XPS spectrogram of PtNPs.

3.4. UV-Vis Characterization Analysis

PtNPs possess a distinctive absorption band in the UV-vis

region, due to having a localized surface plasmon resonance [14-15]. Figure 4A depicted the UV visible absorption spectrum of platinum nanochains (curve a) and chlorplatin acid (curve b). It can be seen that chlorplatin acid solution had obvious UV characteristic absorption peak at 259 nm, and no UV characteristic absorption peak at 259 nm of the platinum nanochains sol obtained after the synthesis reaction, indicating that PtCl_6^{2-} had been completely reduced. The prepared platinum nanochains sol was placed for 0, 10, 30, 50, 70 and 90 days to verify its stability. After characterizing the platinum nanochains placed for different days using UV visible absorption spectra (Figure 4B), no significant changes was found, indicating that the prepared platinum nanochains was stable. The prepared platinum nanochains had a band gap E_g of 9.8×10^{-19} eV (Figure 4C). In addition, the potential was -21.5 mV measured by the zeta potential analyzer.

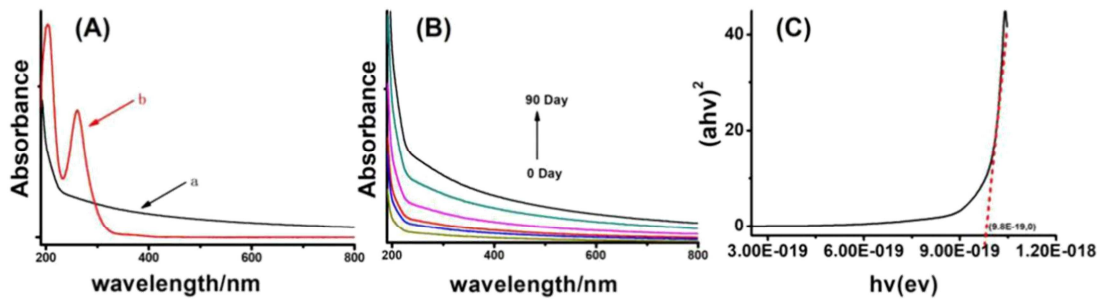


Figure 4. UV-vis spectra of platinum nanochains (A) and (B); Band gap of platinum nanochains (C).

The synthesis of platinum nanoflowers was recorded using a UV visible absorption spectrometer (Figure 5A). When the synthesis reaction proceeds to 20 min, the UV characteristic absorption peak disappears at 259 nm and appears at 293 nm. After 3 days of placement, the UV characteristic absorption peak disappeared at 293 nm, but it appeared at 245 nm and remained unchanged for 90 days thereafter (Figure 5B and Figure 5C). According to the

preparation method of this experiment, the experimental glassware and preparation reagent were re-processed, and the preparation was repeated for 5 times. After placement for 3 days after preparation, there was no difference in the UV characteristic absorption peak position (Figure 5D), indicating that the method had good reproducibility. By calculation, the band gap of platinum nanopetals was 9.8×10^{-19} eV (Figure 5E).

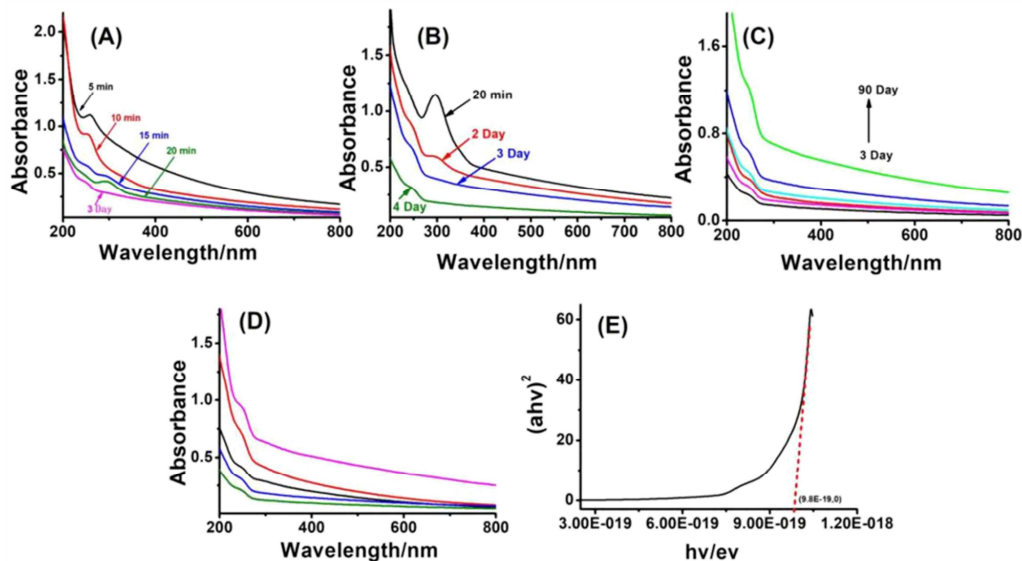


Figure 5. UV-vis spectra of platinum nanopetals (A), (B), (C), and (D); Band gap of platinum nanopetals (E).

4. Conclusion

In this work, PtNPs were successfully fabricated by hydrothermal and self-assembly method under ambient conditions in a shorter reaction time. The preparation process of PtNPs and its stability were successfully recorded by UV, and the results showed that their UV characteristic absorption peaks remained constant for 90 days at 4°C. TEM characterizations showed platinum nanochains were well distributed with small spherical shape in single particle with average particle sizes of around 3 nm, platinum nanopetals with diameter of 20 nm. In addition, crystal structure, valence state and potential of the products were characterized by XRD, XPS and zeta potential, respectively. In the future, researches in the PtNPs will likely be further studied towards the synthesis, characterization and application formation of more complicated suprastructures.

Conflicts of Interest

An invention patent has been applied for in this work (No.: ZL 2020 1 0196764.8).

The authors declare no competing financial interest.

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