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Plant-mediated synthesis of platinum nanoparticles and its bioreductive mechanism

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ABSTRACT

Pt nanoparticles (PtNPs) were biologically synthesized by reducing Na_2PtCl_4 with *Cacumen Platycladi* Extract (CPE). The effects of reaction temperature, initial Pt(II) concentration, and CPE percentage on Pt(II) conversion and the size distribution of the PtNPs were studied. The results showed that the Pt(II) conversion rate reached 95.9% and that PtNPs measuring 2.4 ± 0.8 nm were obtained under the following conditions: reaction temperature, 90 °C; CPE percentage, 70%; initial Pt(II) concentration, 0.5 mM; reaction time, 25 h. In addition, the bioreduction of Pt(II) was attributed to reducing sugars and flavonoids rather than proteins. The elucidation of bioreductive mechanism of Pt(II) ions was achieved by investigating the changes that occurred in the reducing sugar, flavonoid and protein concentrations in the plant extract, leading to a good insight into the formation mechanism of such biosynthesized PtNPs.

1. Introduction

Pt and its alloys are mainly used as excellent catalysts for oxidation and hydrogenation processes in the petrochemical industry [1]. With the development of nanotechnology, Pt nanoparticles (PtNPs) have been demonstrated to exhibit high catalytic activity owing to their high surface area, making synthesis of PtNPs for catalytic applications one of the highlights in related fields [1]. Consequently, well-defined PtNPs of particular shapes and sizes have been synthesized through various methods. However, conventional physical and chemical methods are not only energy intensive, because of stringent conditions, but also environmentally unfriendly, due to the use of toxic solvents or additives [2,3]. Compared with conventional methods, biosynthetic methods based on microorganisms or plants have been regarded as cost-effective and environmentally benign approaches for producing highly stable metal NPs in recent years. Some efforts have been directed toward the intracellular or extracellular biosynthesis of PtNPs using microorganisms under mild conditions without auxiliary capping agents [4–7]. However, subsequent processing of NPs via intracellular biosynthesis is generally difficult, and microorganisms used for the extracellular biosynthesis of NPs must be extensively screened [8]. Living plants, plant extracts, and plant biomass are attracting more attention due to the fact that, they are simple but an effective alternative candidate for the extracellular biosynthesis of metal NPs. In the plant-based biosynthesis, green and rapid synthesis of metal NPs could be achieved. Moreover, shape and size of metal NPs could be more controllable, compared with the microorganism-based biosynthesis. For instance, the biomass of alfalfa [9] and *Cinnamomum camphora* leaves [10,11] as well as extracts of geranium leaves [12], neem leaves [13], *Emblica officinalis* fruit [14], *Aloe vera* leaves [15], *Chlorella vulgaris* [16], *Capsicum annuum* L. [17], coffee [18], tea [18], and *Camellia sinensis* [19] have all been employed to synthesize Au or Ag NPs. However, plant-mediated synthesis of PtNPs has received little reported hitherto. *Diospyros kaki* leaf extract [20], *Cochlospermum gossypium* extract [21], and honey [22] have recently been used to prepare PtNPs. Interestingly, biogenic PtNPs with honey can be used to catalyze the reaction of aniline with 4-aminoantipyrine in acidic aqueous medium [22]. Nevertheless, the bioreductive mechanism involved in the biogenic of PtNPs is not well understood. In this work, PtNPs were biosynthesized by reducing aqueous Na_2PtCl_4 with *Cacumen Platycladi* Extract (CPE) as reducing agent. The factors affecting the biosynthesis of PtNPs, including reaction temperature, initial Pt(II) concentration, and initial CPE percentage, were optimized by analyzing Pt(II) conversion and the size distribution of the PtNPs. In our previous studies, we proposed that the contents of the reducing sugars, flavonoids, saccharides, proteins in plant extracts, and antioxidant activity of plant extracts were closely associated with the bioreduction of silver or gold ions [23,24]. The contents of the reducing sugars, flavonoids, saccharides, proteins, and antioxidant activity during the bioreduction process, were measured by 3.5-dinitrosalicylic acid colorimetric assay, rutin-based spectrophotometry, phenol–sulfuric assay, and Coomassie brilliant blue assay, as well as

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2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging assay. In addition, transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to characterize the PtNPs, and inductively coupled plasma atomic emission spectroscopy (ICP-AES) for determining the concentration of residual Pt(II) ions after reaction. The bioreductive mechanism of Pt(II) ions with biomolecular components in plant extract was discussed. Furthermore, CPE was analyzed before and after reaction by Fourier transform infrared spectroscopy (FTIR) to elucidate the biosynthetic mechanism.

2. Experimental section

2.1. Preparation

2.1.1. Materials and reagents

Sundried *Cacumen Platycladi* and sodium tetrachloroplatinate (Na_2PtCl_4) were purchased from Xiamen Jiuding Drugstore Co. Ltd. (China) and Aladdin Chemistry Co. Ltd. (China), respectively.

2.1.2. CPE

The biomass of *Cacumen Platycladi* for reduction was milled, and the powder was screened with a 20-mesh sieve. Three grams of the powder was then dispersed in 90 mL of deionized water in a 200 mL beaker and boiled for 5 min. Thereafter, the resulting broth was cooled down to room temperature and filtered to obtain the filtrate, which was then subsequently adjusted to 100 mL by adding deionized water. The resulting CPE was refrigerated at 6 °C for the biosynthesis of PtNPs within 7 days after preparation.

2.1.3. PtNPs

In a typical synthesis for the PtNPs, 10 mL of CPE was first heated at constant temperatures of (30, 60, and 90 °C) in an oil bath, with stirring for 10 min. Afterward, some amount of aqueous Na_2PtCl_4 (52.24 mM) was added suddenly to the flask in order that the reaction solution possessed the initial Na_2PtCl_4 concentrations of 0.5, 1, 1.5, or 2 mM.

2.2. Characterization

2.2.1. ICP-AES analysis

Conversion of Pt(II) ions during biosynthesis was monitored by sampling the reaction solution at intervals to measure the Pt(II) concentration. The PtNPs in the hydrosol were completely precipitated thrice, via centrifugation at 13,000 rpm for 20 min, after which the concentration of the residual Pt(II) in the final supernatant was measured using an ICP-AES analyzer (Thermo Spectronic, USA) at a wavelength of 214.423 nm, with the Pt(II) conversion Q calculated as follows:

$$Q = \left(1 - \frac{N \cdot C_f}{C_0 \cdot M_{Pt}}\right) \times 100\% \quad (1)$$

where N, C_f, C_0, and M_{Pt} represents the dilution time, final concentration of Pt(II) (mg L^{-1}), initial concentration of Pt(II) (mM), and molecular weight of Pt (g mol^{-1}), respectively.

2.2.2. Biomolecular components

The methods for determining biomolecular components in the CPE before and after reaction are the same as those used previously [24,25]. The contents of the reducing sugars, flavonoids, saccharides, and proteins were measured using 3.5-dinitrosalicylic acid colorimetric assay, spectrophotometry (with rutin as the standard sample), phenol–sulfuric acid assay, and Coomassie brilliant blue assay, respectively. Antioxidant activity was investigated by DPPH free radical scavenging assay in a process regulated by its discoloration [23–25] (each parameter was assayed in duplicate).

2.2.3. FTIR analysis

The CPE before reaction and the resulting solution after reaction were completely dried at 60 °C, with subsequent characterization using an Avatar 660 FTIR spectrophotometer (Nicolet, USA).

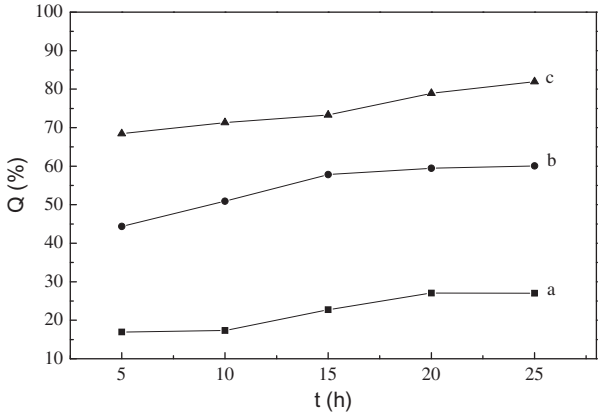

Fig. 1. Pt(II) conversion versus reaction time at (a) 30 °C, (b) 60 °C, and (c) 90 °C when the CPE percentage and initial Pt(II) concentration were 50% and 1 mM, respectively.

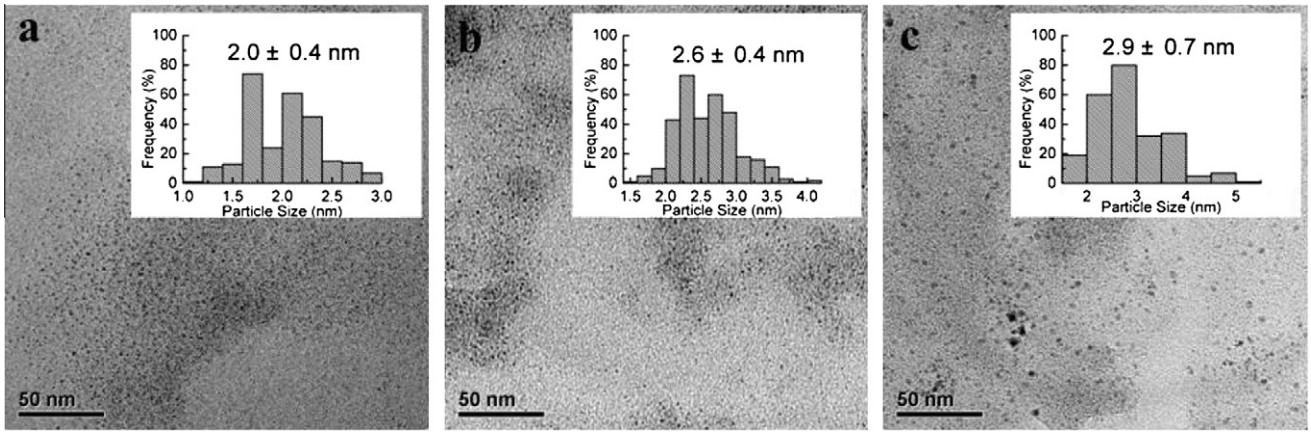

Fig. 2. TEM images of the PtNPs synthesized at (a) 30 °C, (b) 60 °C, and (c) 90 °C when the CPE percentage and initial Pt(II) concentration were 50% and 1 mM, respectively.