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Seed-mediated synthesis of dendritic platinum nanostructures with high catalytic activity for aqueous-phase hydrogenation of acetophenone

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ABSTRACT

This work reports a facile and efficient seed-mediated method for the synthesis of dendritic platinum (Pt) nanoparticles (NPs) at low temperatures of 55–60 °C in water, using L-ascorbic acid as a reducing agent and sodium citrate as a capping agent. It is found that the dendritic Pt NPs (10–150 nm) are composed of tiny Pt nanocrystals, which nucleate and grow through the introduced smaller Pt seeds with diameters of 3–5 nm. Further investigation shows that the dendritic Pt nanostructures display excellent catalytic performance in an aqueous-phase aromatic ketone hydrogenation reaction, including: (i) acetophenone conversion rate of > 90%, with smaller dendritic Pt NPs (10–46 nm) offering a higher conversion efficiency; (ii) high chemoselectivity toward carbonyl group (90.6%–91.5%), e.g., the selectivity to 1-phenylethanol is ~90.1% with nearly 100% acetophenone conversion for 10 nm dendritic Pt NPs within 60 min, under mild reaction conditions (20 °C, 1.5 bar H_2 pressure, and 1.5 mol% catalyst). The high catalytic activity, selectivity and stability of the dendritic Pt nanostructures under the organic solvent-free conditions make them promising for many potential applications in green catalytic conversion of hydrophilic biomass derived compounds.

1. Introduction

Platinum (Pt) has been commonly utilized in many areas, such as fuel cells [1], organic synthesis [2], petrochemical industry [3], energy industry [4], catalysis [5–9] and environment protection [10], due to its excellent catalytic performance. However, the scarcity and preciousness of Pt have urged researchers to find an efficient way to lower the consumption of this noble metal without forgoing its use [11]. One strategy to achieve this goal is to disperse the metal NPs on various inorganic supports currently used by industries, such as zeolites, mesoporous materials, and metal oxides [12]. Another way is to control the structure (size, shape) and composition of the metallic catalyst to achieve larger surface area and higher catalytic activity [13,14].

Dendritic nanostructures have received considerable attention in recent years due to their distinct structural properties from their solid counterparts [1,15–17]. For example, Yan et al. demonstrated that dendritic single-crystalline palladium (Pd) NPs exhibit an enhanced catalytic performance for Suzuki coupling reaction, compared to carbon-supported Pd catalysts [16]. Wang et al. reported that porous dendritic Pt–Pd NPs exhibit a higher catalytic activity for methanol oxidation than commercial Pt black catalyst [18]. These studies suggest that dendritic materials exhibit advantages which may be beneficial for catalytic applications. For example, the interconnected structure can provide a higher surface area than the standard Pt black or supported Pt/C catalysts, due to the presence of a large number of edges, corners and surface stepped atoms, as well as a larger pore volume which provides more active sites for enhancing the catalytic reaction [15,19]. Furthermore, the dendritic structures do not easily aggregate, which make them attractive for catalytic applications [18].

Various methods have been reported for the preparation of dendritic Pt-based nanocrystals, such as a multi-step Pt seed-mediated method at 100 °C, Au and/or Pd seed-mediated method [20], Fe-assisted method [21], templated synthesis [17,22] and solvothermal method using organic solvents at 200 °C for 2.5 h [18] or 160 °C for 10 h [8]. Many of these methods however suffer from one or more drawbacks which may limit their applications, including complicated

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procedures, use of harmful organic solvent, lack of reproducibility, introduction of impurities, or harsh reaction conditions. To overcome such problems, the development of a simple yet green chemical approach for the synthesis of dendritic Pt nanostructures with controllable size and superior catalytic performance is highly demanded.

Regarding the catalytic applications, the hydrogenation of aromatic ketones, such as acetophenone into their corresponding alcohols was usually carried out over the supported palladium catalysts, using organic solvents [23]. The use of organic solvents in the hydrogenation reaction frequently leads to the formation of hazardous wastes, which may be detrimental to the environment. Due to the toxic nature of these wastes, they have to be removed at the end of these reactions by means of fractional distillation. In some cases, the hydrogenation of acetophenone, using copper-based catalysts usually requires a higher reaction temperature of over 350 °C, which may lower the selectivity toward 1-phenylethanol [24]. Thus, it is necessary to develop an environmentally friendly approach for the hydrogenation of acetophenone in water at low temperatures, in order to address these challenges.

This study reports the development of a green and effective method for the synthesis of dendritic Pt NPs with controllable size, through a one-step seed-mediated approach at low temperatures of 55–60 °C. In the proposed method, L-ascorbic acid and sodium citrate were used as the reducing agent and the capping agent, respectively. The pertinent parameters involved in the synthesis process of the dendritic Pt NPs (e.g. temperature, reaction time and concentration) along with their nucleation and growth mechanisms were investigated. Finally, the catalytic performance of the dendritic Pt NPs was evaluated in the hydrogenation of acetophenone, which has practical relevance to the production of 1-phenylethanol in the perfumery and flavor industries. Furthermore, in this study, the hydrogenation of acetophenone was carried out in water (H_2O) rather than in organic solvents, at a low reaction temperature of 20 °C, which will eliminate the formation of hazardous wastes and the need for further distillation of the solvent during the waste recycling process [25]. The results will be beneficial for future design and construction of metallic nanostructures with unique and novel structures for promising applications in industrial catalysis.

2. Experimental

2.1. Materials

Citric acid ($C_6H_8O_7$, 99.5%) was purchased from Alfa Aesar, dihydrogen hexachloroplatinate ($H_2PtCl_6{\bullet}6H_2O$, ≥ 99.9%, trace metal basis), sodium borohydrate ($NaBH_4$, 98%), sodium citrate ($Na_3C_6H_5O_7$, ≥ 99.9%), acetophenone (C_8H_8O, ≥ 98%), and L-ascorbic acid ($C_6H_8O_6$, reagent grade) were obtained from Sigma Aldrich. All the chemicals were used without further purification.

2.2. Synthesis of Pt seeds

The Pt seeds were synthesized by modifying a previously reported method [19]. In a typical protocol, a 6 mL of 0.2% solution of chloroplatinic acid solution was added into 78 mL of boiling H_2O, and stirred for a few minutes to achieve homogeneity. Second, 1.84 mL of aqueous solution containing 1 wt% sodium citrate and 0.05 wt% citric acid was added into the above solution after 1 min, followed by a quick injection of 0.92 mL freshly prepared sodium borohydrate solution (0.08 wt%) containing 1 wt% sodium citrate and 0.05 wt% citric acid, and stirred for several minutes to ensure a homogeneous reaction was achieved. Finally, the resultant solution was cooled down to room temperature, and used as seeds with diameter of 3–5 nm and an estimated concentration of 3.34×10^{-4} M (Fig. S1).

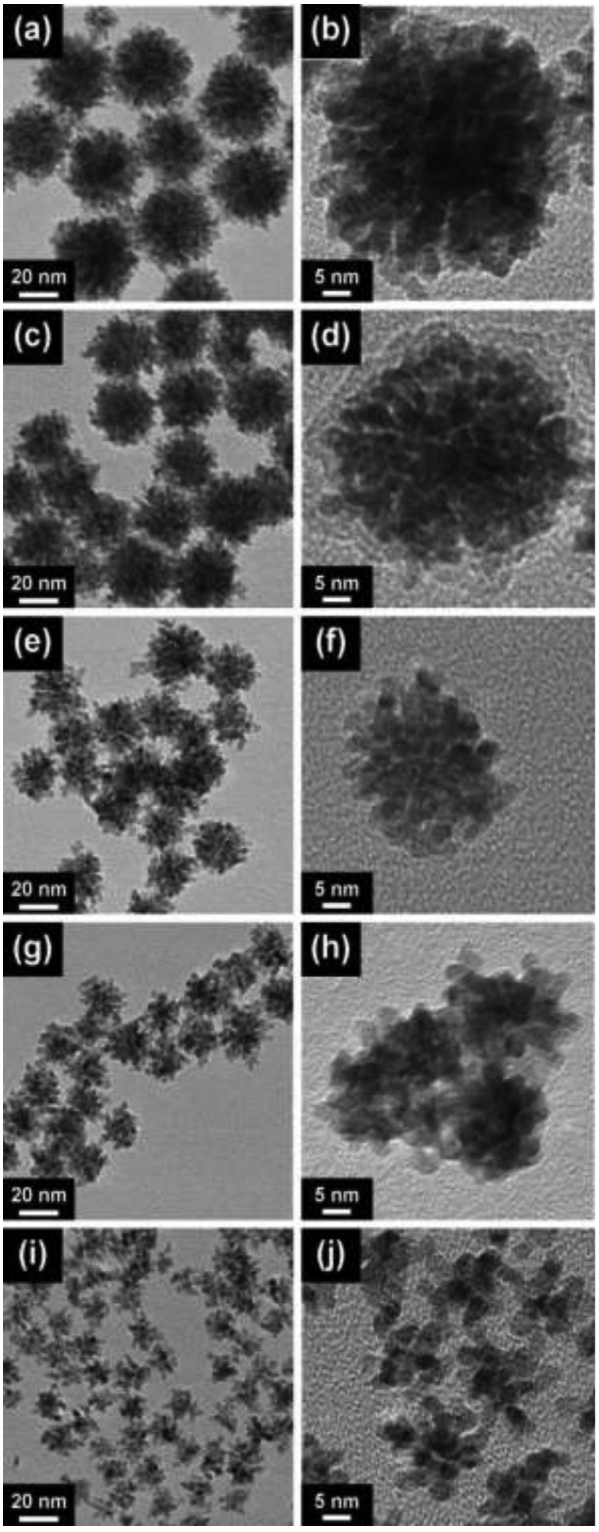

Fig. 1. TEM images of the porous dendritic Pt NPs with 5 different sizes: (a, b) 46 nm; (c, d) 36 nm; (e, f) 28 nm; (g, h) 18 nm; (i, j) 10 nm.

2.3. Synthesis of porous dendritic Pt nanoparticles

An oil bath and a hot plate equipped with a temperature controller were used for the synthesis of porous dendritic Pt NPs. A custom-made vial holder was placed on the top to fix the four vials (Fig. S2). Different volumes of the as-prepared seed solution (~3.34×10^{-4} M) from 1.5, 2.5, 5, and 10 mL were added into 18.5, 17.5, 15 and 10 mL