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# Synthesis of ultra-small platinum nanoparticles in a continuous flow microreactor

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ABSTRACT

In this work, we synthesized ultra-small platinum (Pt) nanoparticles, capped with poly(vinylpyrrolidone) (PVP), in a continuous flow microreactor. This method facilitated the synthesis Pt nanoparticles less than 5 nm at room temperature, as opposed to the conventional high-temperature synthesis. Further, we have demonstrated the effect of capping agent and flow rate on particle size and aggregation state of Pt nanoparticles. We found that the flow rate of reactants also has a significant effect on determining crystallinity of Pt nanoparticles. As-synthesized Pt NPs were analyzed by high-resolution transmission electron microscopy and X-ray diffraction, revealing a monodisperse distribution of Pt nanoparticles, marked by crystalline and stable Pt nanoparticles.



Platinum nanoparticles have attracted increasing attention in the field of nanoscience and other interdisciplinary areas due to their vital applications in catalysis, automobile exhaust purification, fuel cell technology, energy storage, and sensors [1–2]. The increasing interest in Pt nanoparticles is because of their well-established catalytic properties as well as extensive potential applications in biomedical, electronic devices and recently as a catalyst in electrochemical reactions of fuel cells [3]. However, particle size, its distribution, and morphologies Pt nanoparticles are decisive factors to claim their wide spread applications. Ultra-small particles of Pt nanoparticles exhibit a larger number of surface atoms which has a noticeable effect on its surface activity. Thus, it is of great importance to reproducibly synthesize ultra-small Pt nanoparticles.

Several researchers have synthesized small sized Pt nanoparticles using various methods such as sol-gel method, electrochemical deposition, solvothermal, hydrothermal, sonochemical, polyol method and various physical approaches [4,5]. Due to the nature of the Pt salt reduction system, the majority of the reports involve reduction of Pt precursor using a reducing agent, typically sodium borohydride, in the presence of a colloid stabilizer such as PVP, PEG, and CTAB [6]. Sodium borohydride reduction is a traditional method for synthesizing metal nanoparticles from their precursors by virtue of diversified capping agents. Recent advances revealed that $NaBH_4$ reduction was considered as most facile yet efficient method for the preparation of 1D, 2D and 3D nanostructures [7]. Krishna and co-workers reported a strikingly simple, kinetically controlled $NaBH_4$ reduction process without any capping agent to obtain different noble metal-based nanoparticles with high surface area [8]. Synthetic process using $NaBH_4$ reduction has some unique advantages: ability to prepare structures through the rapid fusion of initial bare metal nuclei and subsequent assembly of nanostructures can be completed at room temperature [9]. More importantly, the electrochemical performance can be improved through the formation of bimetallic/trimetallic nanostructures with tunable compositions [10,11]. A surfactant is also found to play a major role in controlling the size of Pt nanoparticles. Negro et al. have shown that the packing of a surfactant on nanoparticle surface was the only parameter in controlling the particle size of Pt [12]. Although few researchers have attempted alternate approaches of synthesis such as using Vitamin C as a reducing agent or ethylene glycol as a partial reducing agent but, the significantly high reaction temperature i.e. 105 °C was required [13]. The majority of the scientific reports on Pt nanoparticles have shown that the temperature more than 50 °C is required to synthesize ultra-small Pt nanoparticles in colloidal/wet chemical methods. There are very few reports of synthesis of Pt nanoparticles at a room temperature. Recently, Hossain et al. have shown the incomplete reduction of Pt ions at 80 °C due to the increased rate of degradation of a borohydride reducing agent [14]. Huang et al. synthesized of ultra-small Pt nanocrystals by borohydride reduction method at room temperature using peptide as a stabilizer [15]. However, to the best of our knowledge, there is no report of scalable synthesis of ultra-small Pt nanoparticles at ambient temperatures using a continuous flow microreactor.

In a broad context, a mechanism of nanoparticles synthesis involves the rapid reaction of precursors with the mixture of solvent and coordinating ligands, at temperatures more than 50 °C [16,17]. These reactions can suitably be carried out in the batch process but are limited to small-scale synthesis because of low yield, high temperature, and long

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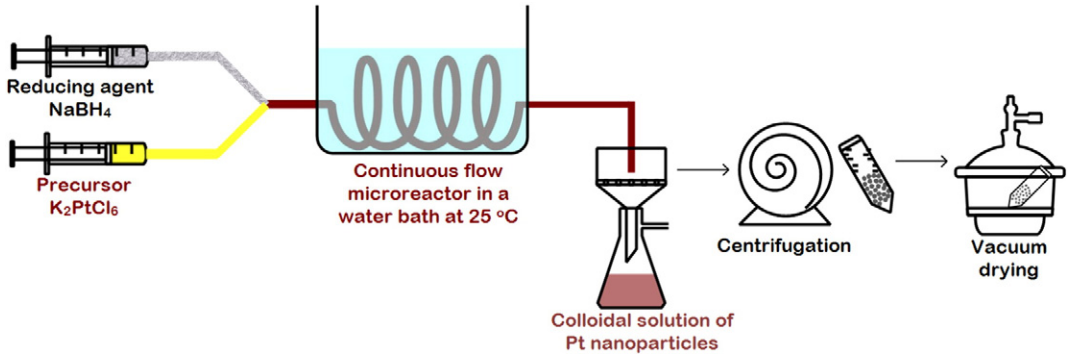


**Fig. 1.** Experimental set-up for synthesis of Pt nanoparticles in a continuous flow microreactor.

reaction times. In this regard, continuous flow microreactors are preferred over batch reactors, as flow microreactors can continuously generate nanoparticles once the reaction reaches steady state. The continuous flow synthesis of nanoparticles in microreactors is known to overcome the limitations of traditional batch preparative methods in terms of reproducibility, narrow size distribution, and easy scale up [18]. Although the homogeneous phase continuous flow synthesis methods are very good in getting a relatively narrow particle size distribution (as compared to conventional batch methods), the particle size distribution are still affected by the diffusive mixing and axial dispersion due to the parabolic velocity profile [19]. Gokmen et al. have successfully synthesized negatively charged platinum nanoparticles in microfluidic-based reactor [20]. Lin et al. synthesized silver nanoparticles in continuous flow reactor by thermally decomposing the silver precursor and obtained narrow size particle distribution [17]. Duraiswamy and Khan have examined the critical factors in translating the macroscale flask-based methods to a flow-based microfluidic method [21]. They demonstrated that the formation and tuning of droplets within the microreactor can help to fine-tune the size and shape of nanoparticles. Recently, microreactors have been used to synthesize, mostly, semiconducting nanomaterials such as CdSe and $TiO_2$ [22]. However, few reports show that in continuous flow microreactor, for a multi-reactant system, mixing largely occurs by molecular diffusion and micromixers may be needed [17,22,23]. Nevertheless, these studies reveal the potential of continuous flow microreactors for scalable synthesis of nanoparticles.

In this communication, owing to the aforementioned advantages, we demonstrate the synthesis of ultra-small, monodisperse Pt nanoparticles capped with PVP in a continuous flow microreactor. In this work, we studied the effect of flow rate of reactants and presence of a capping agent on particles size, morphology, and crystallinity. The synthesis was characterized by rapid nucleation and further, growth was controlled by steric repulsion due to adsorbed PVP layers. Complimentary techniques, such as high-resolution transmission electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy were used to characterize physicochemical properties of Pt nanoparticles.

Potassium (IV) Hexachloroplatinate ($K_2PtCl_6$) (Sainergy Fuel Cell Pvt. Ltd., India) and sodium borohydride (Molychem, India) were used as a precursor and reducing agent, respectively. Poly(vinylpyrrolidone) (PVP) ($M_w$ 40,000 Da, Hi-Media laboratories Pvt. Ltd., India) was used as a capping agent/stabilizer. The DI water (resistivity > 10 MU cm at 25 °C; total organic carbon < 20 ppb), obtained using a RiOs-DI Clinical system (Millipore Corporation), was used a solvent for both precursor and reducing agent.

A microreactor was fabricated using a copper tube of inner diameter 500 μm and the total length of 1250 mm, as shown in Fig. 1. The copper tube was looped in a spiral fashion where each loop had a diameter of 20 mm. Pt precursor and sodium borohydride solution were injected into the microreactor using two separate peristaltic pumps through Y-connector.

Precursor $K_2PtCl_6$ (0.25 mM) and reducing agent $NaBH_4$ (2.5 mM) were dissolved separately in DI water. The molar ratio of precursor to reducing agent was maintained at 0.10 in all experiments. The concentration of PVP was kept constant, near to its critical micelle concentration, at 0.025 mM. The PVP solution was prepared separately and its total volume was equally divided into two parts. Further, each part was added into solutions of precursor and reducing agent. The flow rate of both reactants was maintained at either 14 or 28 μL/s in different experiments. The microreactor was kept inserted in a temperature-

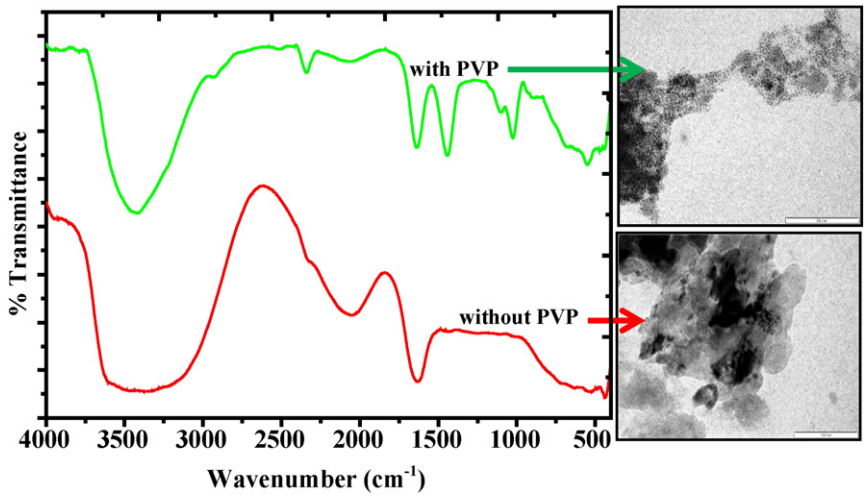


**Fig. 2.** FTIR spectra and corresponding TEM images of PVP-coated and uncoated Pt nanoparticles. Reaction conditions for both nanoparticles: precursor to reducing agent ratio = 0.10 and flow rate = 14 μL/s (Image scale: top TEM 50 nm and bottom TEM 100 nm).