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Synthesis of palladium nanoparticles using continuous flow microreactor

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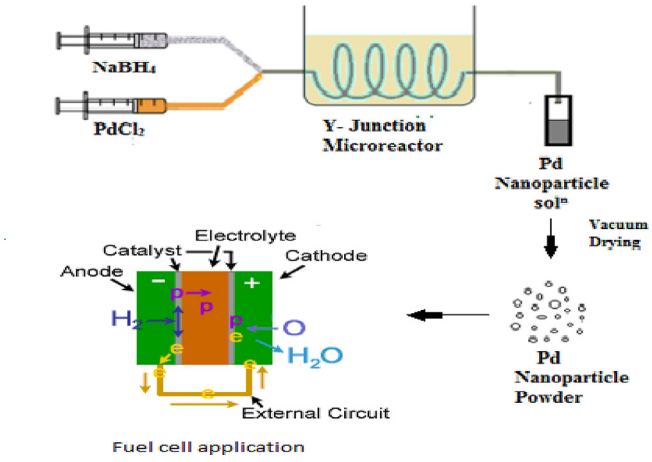
HIGHLIGHTS

- Continuous flow microreactor based synthesis of Pd nanoparticles.
- At optimum reaction conditions 5 nm Pd particles were obtained.
- The electrochemical surface area (ECSA) of Pd nanoparticles was 2.6 cm^2/mg.
- Pd nanoparticles size decreases with an increase in concentration of precursor and reducing agent.
- The average size of Pd nanoparticles increases with increase in flow rate.

GRAPHICAL ABSTRACT



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ABSTRACT

This study reports on the use of a continuous flow microreactor for the synthesis of palladium (Pd) nanoparticles. The size of Pd nanoparticles could be controlled in the range 5–200 nm by varying the flow rate of the solution containing the precursor and reducing agent. TEM analysis showed cubic morphology of the particles. The electrochemical activity and electro-reduction reaction on Pd/carbon electrode were monitored using cyclic voltammetry (CV) and linear sweep voltammetry (LSV), respectively. The surface area of Pd nanocatalyst was determined to be about 2.6 cm^2/mg using CV data. The open circuit potential (OCP) was found to be 0.77 V using LSV measurement.

1. Introduction

Palladium nanoparticles are widely used in various technological applications, e.g., microelectronics, bio-sensing, catalysis and

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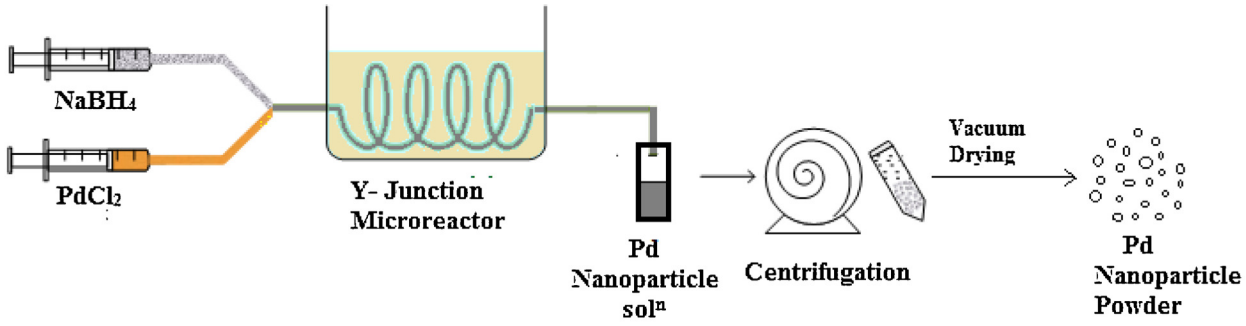

Experiment No.	$PdCl_2$ (M)	$NaBH_4$ (M)	Ratio (precursor to reductant)	Flow rate (mL/h)	Particle size (nm) (using DLS)
1	0.001	0.004	1: 4 (0.25)	30	287
2	0.0005	0.002	1: 4 (0.25)	30	278
3	0.00025	0.002	1: 8 (0.125)	30	105
4	0.001	0.004	1: 4 (0.25)	50	309
5	0.00025	0.002	1: 8 (0.125)	50	216

Fig. 1. Experimental setup for stable palladium (Pd) nanoparticle (NP) synthesis using continuous flow microreactor.

fuel cells [1,2]. Over last few decades, some of the methods have been documented for synthesis of palladium nanoparticles [2,3]. Precise control over the size of palladium nanoparticles and reproducibility are important issues [3–7]. It is important to note that the catalytic activity and electron transport properties of nanoparticles depend on their size. Investigators have explored a wide variety of synthetic techniques for the preparation of palladium nanoparticles with a narrow particle size distribution. However, robust synthetic techniques are required for specific applications [8,9]. A number of methods were reported for the synthesis of Pd nanoparticles such as microwave assisted synthesis, chemical reduction method and sol-gel technique [10–13]. These conventional methods exhibit lack of precise control over mixing, nucleation and growth, which subsequently affect the particle size, particle size distribution and reproducibility [12,13]. Rapid mass transfer associated with intense mixing can significantly improve the physical and chemical properties of palladium nanoparticles.

Microreactor technologies offer several advantages over conventional 'beaker-based' method and it is a part of process intensification used in chemical synthesis [14]. Microreactors exhibit large surface area compared to their volume, which enhances the mass transfer, which in turn improves the physical and chemical properties of the nanoparticles [15]. Microreactors offer a small volume for the reaction, which allows precise control over the synthesis of nanoparticles such as palladium (Pd), platinum (Pt) and gold (Au) etc. [16–18]. Rebrove et al. [19] have shown that a microreactor system increases the heat transfer within the reaction mixture and hence improves the reaction kinetics. The key advantage of microreactor is the ability to realize the 'lab-on-chip' design. Scale up is relatively easier by multiplying the number of reactors [20,21]. Recently, Woitalka et al. [22] reported that the flow pattern in a continuous flow microreactor affects the mixing, which inturn controls the mass transfer in a reactor, the particle size and its distribution. Synthesis of Pd nanoparticles in a continuous flow microreactor is a paradigm-shift opportunity to explore the versatility of this technique for the preparation of nanoparticles [23,24]. Pd nanoparticle is efficient metal catalyst for hydrogenation and electrochemical reactions in fuel cells [25–29]. The cost of Pd nanocatalyst is lower than the Pt catalyst and it is abundantly available on earth than Pt catalyst. It has more oxidation potential than Pt [2,30]. Pd is suitable for hydrogen storage and sensing applications [31]. There are several methods available for synthesizing Pd nanoparticles using precursors such as palladium chloride ($PdCl_2$), potassium tetrachloropalladates (K_2PdCl_4), palladium nitrate, palladium acetate with reducing agents such as hydrogen, ethylene glycol, $NaBH_4$, xanthan gum, hydrazine, alcohol, sodium ascorbate and sodium citrate and along with capping agents such as cetyl trimethylammonium bromide (CTAB), polyvinylpyrrolidone (PVP) and sodium dodecyl sulfate (SDS) [32–45].

Therefore $PdCl_2$ was chosen as a precursor and $NaBH_4$ as a reducing agent for the preparation of palladium nanoparticles (Pd NP). We have successfully synthesized Pd nanoparticles in a continuous flow microreactor. Further, we have demonstrated the feasibility to use the synthesized Pd nanoparticles as an electrochemical catalyst.

2. Experiment

2.1. Materials

Palladium(II) chloride ($PdCl_2$, 99%, analytical grade) was purchased from Merck specialties Pvt. Ltd., Mumbai, India and used as a precursor for the synthesis of Pd nanoparticles. Sodium borohydride ($NaBH_4$, 99%, analytical grade) was used as a reducing agent and *N*-cetyl-*N*,*N*,*N* tri-methyl ammonium bromide (CTAB) was procured from Thomas Baker Ltd., Mumbai, India and used as a surfactant. Millipore deionized water was used in all experiments for the preparation of all solutions.

2.2. Synthesis of nanofluids

The experimental setup of continuous flow microreactor and reaction conditions for various experiments are shown in Fig. 1.