

Characterisation of Platinum Nanoparticles Electrodeposited on Carbon Felt

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Abstract

Monodispersed and uniform sized platinum nanoparticles were electrodeposited on carbon felt from aqueous hydrogen hexachloroplatinate solution by a potential cycling method. The deposited nanoparticles were characterized by electrochemical technique and by scanning electron microscopy. It was found that the size and distribution of the nanoparticles could be controlled by changing the deposition parameters such as the scan rate and the number of cycle. The electrocatalytic property of the nanoparticles was tested by the oxidation of hydroquinone and phenol. It was found that the felt supported nanoparticles were effective towards electrodegradation of phenolic compounds.

Keywords: Electrocatalyst; Electrodeposition; Hydroquinone; Phenol oxidation; Platinum nanoparticles; Carbon felt.

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1. Introduction

There is much research interest in carbon supported platinum nanoparticles for their use as electrode materials in electrochemical catalysis and sensing [1–19]. A very important step in designing a structurally and dimensionally stable nanoparticle based electrode is the incorporation of electrocatalytically active nanoparticles onto a suitable support. This can be accomplished by pasting chemically synthesized nanoparticles on the catalyst support or by electrodepositing the nanoparticles on the support. Direct electrochemical reduction of platinum ions on a support is a relatively convenient way to fabricate nanoparticle based electrodes. There are some reports in the literature on the preparation of supported

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platinum nanoparticles by electrochemical route [20–31]. The catalytic activity of the nanoparticles has also been tested. The catalytic performance of nanoparticles is crucially dependent on their size and shapes. The dispersion of the nanoparticles on the support has significant influence on the catalytic property. Monodispersed smaller particles with uniform size and distribution are normally desired for enhanced activity. Carbon materials such as powder, ink, cloth, paper, glassy carbon etc. are generally used as catalyst support. In the present work, platinum nanoparticles were grown on carbon felt by an electrochemical deposition method. Carbon felt was chosen because of its high surface area and it is commercially available. The characterization of the supported nanoparticles has been carried out by electrochemical technique and by scanning electron microscopy (SEM). The electrocatalytic property of the nanoparticles was tested by the oxidation of hydroquinone and phenol. These compounds are known as major organic pollutants in industrial waste and they are very difficult to treat in other conventional ways [32–40].

2. Experimental

Platinum nanoparticles were electrodeposited on carbon felt from 1 mM aqueous solution of hydrogen hexachloroplatinate. Tri-sodium citrate was used as a complexing agent and its concentration was 1 mM. Tri-sodium citrate was chosen because it was non-toxic and had brightening, levelling and buffering actions [41]. Moreover, citrate electrolyte was recently used for precision electrodeposition [42–46]. The solution was prepared by dissolving appropriate amount of the chemicals in de-ionised water. The chemicals used in this work were of analytical grade. Approximately 10 ml solution was taken in a cell for electrodeposition of platinum nanoparticles. Commercially available carbon felt was used as substrate without any pre-treatment. The felt was cut to make rectangular electrode which had a length of approximately 4.0 cm and width of 0.7 cm. The electrical contact was made with crocodile clip. Approximately 1 cm of the felt was immersed in the electrolyte for the deposition of nanoparticles and for subsequent electrochemical experiments.

An EG&G (Model 273) potentiostat was used for the deposition of the nanoparticles and their electrochemical characterization. Platinum nanoparticles were deposited by potential cycling between 100 and –500 mV versus saturated Ag/AgCl electrode. The scan rate was varied between 50 and 1500 mV/s and the cycle number was varied between 30 and 900. In all cases, the scanning was started and ended at 0 mV versus a saturated Ag/AgCl electrode. After the completion of the deposition of the nanoparticles, the felt electrode was washed with de-ionised water followed by ethanol and dried in oven at 100 °C. The electrochemical characterization of the deposited platinum nanoparticles was performed by cyclic voltammetry in 1 M H₂SO₄. In this case, the potential was swept between –200 and 1500 mV at the rate of 50 mV/s.

For scanning electron microscopic examination of the deposited nanoparticles, several trends of the fibres were pulled out from the rectangular electrode with a tweezers and placed on a carbon tape pasted on the sample holder. To test the electrocatalytic activity of

the platinum nanoparticles, various concentrations of hydroquinone (HQ) were used. The HQ concentration was varied between 1 and 10 mM. The HQ solution was prepared by dissolving appropriate amount of the reagent in aqueous solution of 1 M H₂SO₄. The electrooxidation of phenol at the nanoparticle based electrode was also tested. In this case, 5 mM phenol in phosphate buffer (pH 7) solution was used. For HQ degradation experiments, 10 ml of 10 mM HQ solution (in 1 M H₂SO₄) was taken and performed cyclic voltammetry on a glassy carbon electrode. Then a platinum nanoparticle deposited felt electrode was immersed in the solution and a constant potential of 900 mV was applied on the nanoparticle/felt electrode for a certain amount of time. Subsequently, cyclic voltammetry was performed using a glassy carbon electrode to see any change in the magnitude of the oxidation peak of HQ. This procedure was repeated several times on the same electrolyte.

3. Results and Discussion

3.1. Electrodeposition of platinum nanoparticles

The platinum nanoparticles were electrodeposited on carbon felt by potential cycling between 100 and -500 mV from an aqueous electrolyte containing 1 mM hydrogen hexachloroplatinate and 1 mM tri-sodium citrate. The cyclic voltammograms are shown in Fig. 1. In this case, the scan rate was 50 mV/s and the number of cycle was 30. It can be seen from the figure that the deposition current was increase with increasing number of cycle. This is possibly due to the creation of some new nucleation sites in the subsequent cycles or hydrogen evolution on the already deposited platinum nanoparticles.

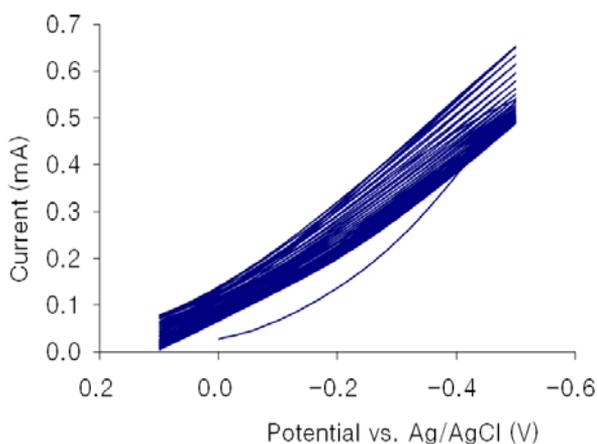


Fig. 1. Typical cyclic voltammograms for the deposition of platinum nanoparticles on carbon felt. The electrolyte contained 1 mM sodium hexachloroplatinate and 1 mM tri-sodium citrate. The scan rate was 50 mV/s and the number of cycle was 30.

3.2. Characterisation of the deposited nanoparticles

As shown in Fig. 2, the electrochemical characterization of the deposited platinum nanoparticle/felt electrode was carried out by potential cycling in 1 M H₂SO₄. Curve 'a' in Fig. 2 shows a typical polarization curve of an aqueous solution containing 1 M H₂SO₄ at a platinum coil electrode. Curve 'b' and 'c' show voltammograms at a bare felt electrode and platinum nanoparticle deposited felt electrode, respectively, in 1 M H₂SO₄. As seen in the figure, curve 'c' exhibits the characteristic peaks of those of pure platinum. This suggests the existence of platinum on the carbon felt.

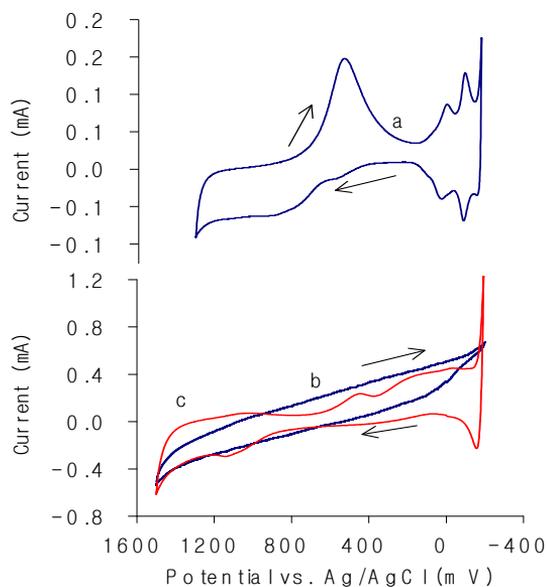


Fig. 2. Cyclic voltammograms of (a) platinum wire, (b) carbon felt and (c) platinum nanoparticle deposited carbon felt in 1 M H₂SO₄; scan rate was 50 mV/s. Platinum nanoparticles were deposited on carbon felt by potential cycling between 100 and -500 mV at the rate of 50 mV/s and the number of cycle was 30.

The electrochemical characterization provides no information about the shape and size of the deposited platinum. Therefore, SEM image of the platinum deposited felt was taken. Fig. 3 shows SEM micrographs of three samples prepared under three different electrochemical parameters. The corresponding deposition parameters of images 'a', 'b' and 'c' were given in the figure captions. It can be seen in Fig. 3 that the particle size decreases with increasing scan rate. Average diameter of the particles obtained at a scan rate of 50 mV/s is approximately 200 nm (Fig. 3a). On the other hand, average diameter of the particles prepared at 1500 mV/s is approximately 50 nm (Fig. 3c). A better particle distribution with an average diameter of 60 nm was observed when they were deposited at a scan rate of 800 mV/s (Fig. 3b).

3.3. Catalytic property of supported platinum nanoparticles

The catalytic activity of the carbon felt supported platinum nanoparticles was tested by the electrooxidation of hydroquinone and phenol. These compounds are chosen because they are considered as major organic pollutants in industrial wastewater, which have been found very difficult for treatment in other conventional ways. Fig. 4 shows cyclic voltammograms of a solution containing various concentrations of HQ in 1 M H₂SO₄ at the felt supported platinum nanoparticle electrode. It can be seen in the figure that the redox reaction occurs at the electrode and the currents (both oxidation and reduction) increase with increasing concentration of hydroquinone.

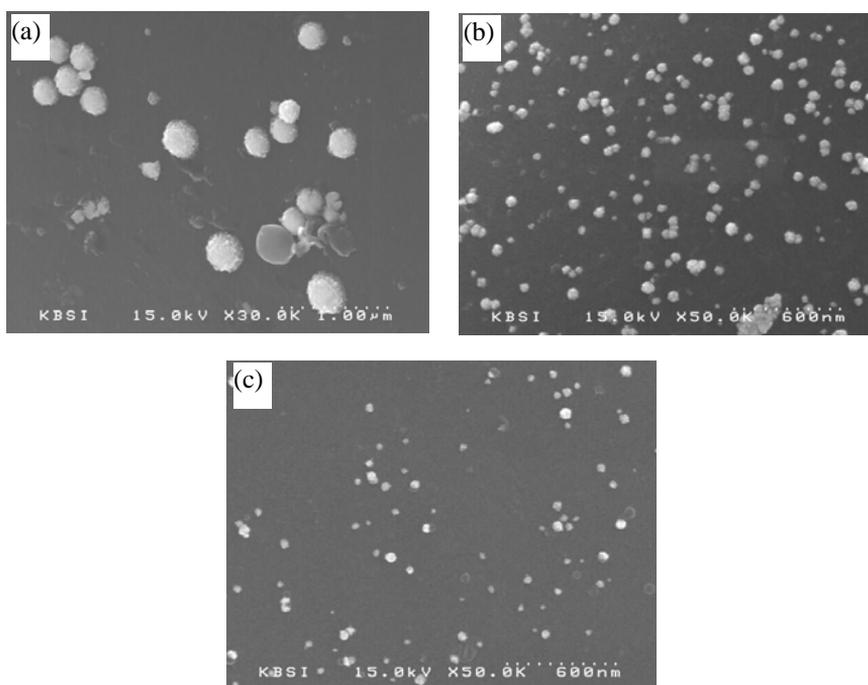


Fig. 3. SEM micrographs of platinum nanoparticles deposited on carbon felt at various scan rates and cycles. (a) scan rate was 50 mV/s, number of cycle was 30 and average diameter of the nanoparticles was 280 nm, (b) scan rate was 800 mV/s, number of cycle was 430 and average diameter of the nanoparticles was 60 nm, and (c) scan rate was 1500 mV/s, number of cycle was 900 and average diameter of the nanoparticles was 55 nm.

The degradation of HQ on the nanoparticle/felt electrode was carried out by applying a constant potential of 900 mV on the electrode immersed in HQ solution and performing cyclic voltammetry using a glassy carbon electrode after a regular interval of time. It was visually observed that the colour of the HQ solution started to change into reddish-yellow 10 minute after the application of the potential on the nanoparticle/felt electrode. The

voltammograms of the degrading HQ solution at glassy carbon electrode in several intervals of time are shown in Fig. 5. The figure shows that the oxidation peak of the HQ solution decreased with increasing time of applied potential on the nanoparticle/felt electrode. Although the extent of decrease of the oxidation peak of HQ with time is very slow, it provides information about the effectiveness of such electrodes for the degradation of HQ.

Fig. 6 shows polarization curve of an aqueous phosphate buffer (pH 7) solution containing 5 mM phenol. The curve shows a clear oxidation wave of phenol electrooxidation. It has been found that the peak current for phenol oxidation decreased drastically in the subsequent cycle. In the case of phenol electrooxidation, the electrode fouling by sort of polymeric products is a well know phenomenon.

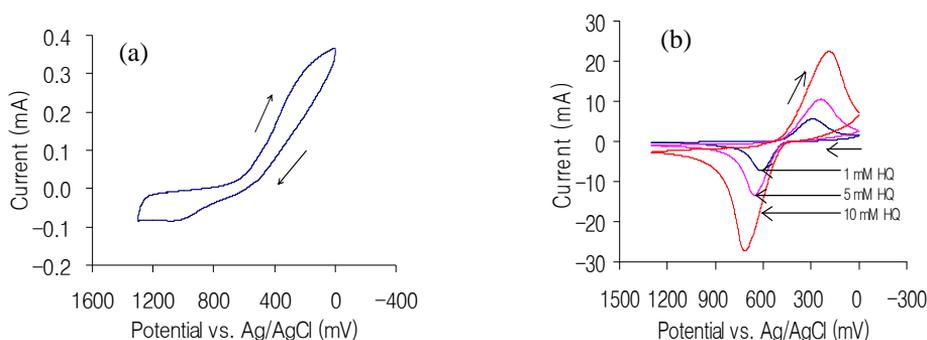


Fig. 4. (a) Cyclic voltammogram of 5 mM hydroquinone (HQ) in 1 M H_2SO_4 at bare felt electrode (no deposited platinum nanoparticle on the felt). (b) Cyclic voltammograms of solutions containing various concentrations of HQ in 1 M H_2SO_4 at platinum nanoparticle containing carbon felt working electrode. The nanoparticles were deposited from 1 mM Pt solution by potential cycling between 100 and -500 mV at a rate of 50 mV/s and number of cycle was 30.

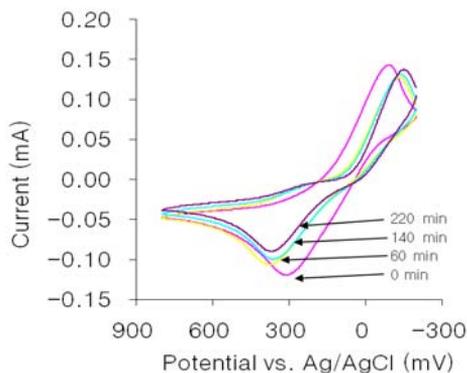


Fig. 5. Cyclic voltammograms of a solution containing 10 mM HQ in 1 M H_2SO_4 at a glassy carbon electrode after a regular interval of time. The solution was being oxidized simultaneously on the felt supported platinum nanoparticle electrode at a constant potential of 900 mV.

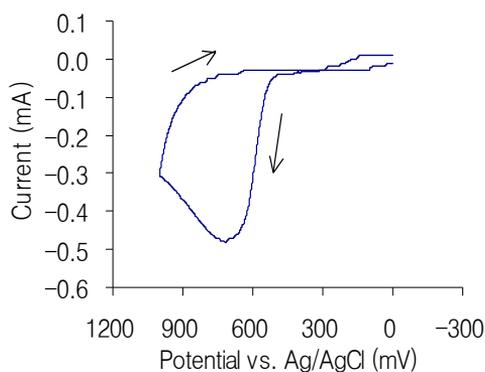


Fig. 6. A cyclic voltammogram of 5 mM phenol in phosphate buffer (pH 7) solution. The potential was swept at the rate of 50 mV/s. The working electrode was platinum nanoparticles deposited on felt by potential cycling between 100 and -500 mV at the rate of 50 mV/s and the total number of cycle was 30.

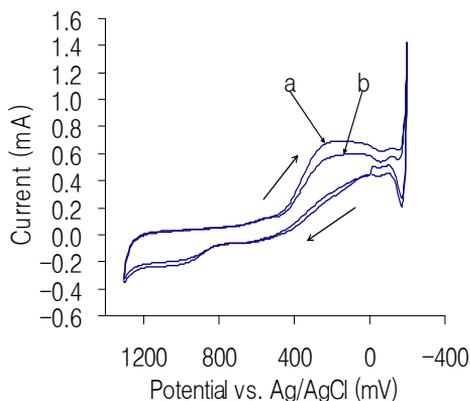


Fig. 7. Cyclic voltammograms at a platinum nanoparticle deposited felt in a 1 M H_2SO_4 for 1 hour; scan rate was 50 mV/s and number of cycle was 60, (a) the first cycle and (b) the last cycle.

3.4. Stability of the deposited nanoparticles

The stability of the plated nanoparticles on the surface of carbon felts was also tested. This experiment was carried out by consecutive cycling at the nanoparticle/felt electrode in H_2SO_4 and in hydroquinone. Fig. 7 shows voltammograms in 1 M H_2SO_4 at the platinum nanoparticle/felt electrode. There were 60 cycles at the rate 50 mV/s in the range between -200 and 1300 mV. Hence the potential cycling time was 1 hour. Curve 'a' in Fig. 7 is of the first cycle and curve 'b' is of the last cycle. The figure shows the characteristic polarization curves at platinum electrode (Fig. 2) even after one hour's of cycling in sulphuric acid. This suggests the existence of the nanoparticles on the carbon felt, i.e., the stability of nanoparticles on the felt. The figure also shows that the redox currents for the

oxide layer on the platinum surface decrease slightly with increasing number of cycles. However, these currents were found to attain at the level of the first cycle when a second potential sweeping experiment was started.

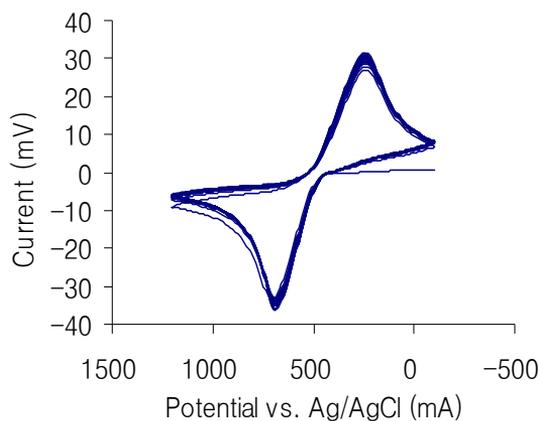


Fig. 8. Consecutive cyclic voltammograms (20 cycles) of 10 mM hydroquinone in 1 M H_2SO_4 using a platinum deposited felt working electrode. Platinum nanoparticles were deposited from 1 mM Pt solution by potential cycling between 100 and -500 mV at the rate of 800 mV/s, 430 cycles.

Fig. 8 shows consecutive cyclic voltammograms of 10 mM hydroquinone in 1 M H_2SO_4 solution at a platinum nanoparticle deposited felt electrode. There is a little decrease in the redox current with increasing number of cycle. This may be due to the change of the surface of the electrode but certainly not due to the loosing of the nanoparticles from the carbon felt. This experiment suggests that the platinum nanoparticles are very stable on the carbon felt when used them as electrodes for oxidation of phenolic compounds like hydroquinone.

4. Conclusions

Platinum nanoparticles were electrodeposited on carbon felt from an aqueous electrolyte containing hydrogen hexachloroplatinate by a potential cycling method. The felt supported nanoparticles were characterized by electrochemical means and by scanning electron microscopy. It was found that the particle size and distribution on the support were strongly dependant on scan rate. Monodispersed and evenly distributed nanoparticles were deposited at relatively higher scan rates. The size of the nanoparticles decreased with increase in scan rate. It was also found experimentally that the nanoparticles were very stable and strongly adherent to the felt support. Catalytic activity of the nanoparticles was tested by the oxidation of hydroquinone and phenol. Much higher oxidation current was found when carbon felt was reinforced with platinum nanoparticles. Therefore, there was

a bright prospect for the use of carbon felt supported platinum nanoparticles for industrial waste treatment.

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