Electrophoretic preparation and characterization of porous electrodes from diamond nanoparticles

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Abstract. We carried out chemical purification of commercially available diamond nanoparticles by refluxing in aqueous HNO₃ and characterized the samples by spectroscopic and surface techniques before and after purification. As a first step in the preparation of electrodes for electrochemistry, we have electrophoretically deposited thin, highly uniform films of controlled thickness (1–8 µm) on silicon substrates using the purified diamond nanoparticles. These have been characterized by scanning electron microscopy (SEM). All films obtained were homogeneous in thickness and without macroscopic holes or cracks. Such structures could also be used in many other applications such as fuel cells or lithium batteries. We have performed cyclic voltammetry experiments with these electrodes. The voltammograms of diamond nanoparticles electrophoretically deposited on silicon indicate hydrogen evolution. This demonstrates that the material is useful as electrocatalitic support. This conclusion is supported by the cyclic voltammograms obtained using ferricyanide (III) chloride and hexaamineruthenium (III) chloride complexes as redox probes. However, these redox probes showed very small peak currents. This behavior could be improved by doping the diamond nanoparticles with an impurity such as boron.

1. Introduction:

Due to its chemical stability, diamond is a promising candidate for electrode materials. In initial studies, where undoped diamond films of very perfect crystallinity were used, the conductivity was ascribed to unidentified structure defects introduced by using a special temperature mode of film deposition.

When new electrode materials are evaluated and designed for electrolysis, electroanalysis, electrochemical sensors and others, attention is paid to their corrosion resistance, background current value and the potential window in which the current remains reasonably low and thus does not interfere with the measurements and performance of the process of study. Doped diamond meets these criteria perfectly with good films; the potential window extends from -1.35 to 2.3 V (vs. NHE). However, the widening of the potential window, which used to be restricted by the potentials of electrochemical decomposition of solvent, became feasible because an increased overvoltage of these reactions [1].

Several studies [2-3] have been carried out in order to understand the physical and chemical properties of nanosized materials. Nanocrystalline diamond would present different electrochemical characteristics due to the higher surface/volume ratio and nature of its surface sites (carbon – oxygen functions) on the hydrogen edges of diamond nanoparticle surface [4-5]. Synthetic nanodiamond powders have been used as catalysts for the oxidation of carbon monoxide to carbon dioxide. These powders were modified at the nanodiamond surface through thermal and electrochemical treatments and deposition of metallic palladium in microquantities onto this surface [6]. In the field of catalysis, the type of support material used is a critical factor.

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in the performance of the resulting supported catalyst or reagent in a reaction system. The main factors that should be considered when employing a material as a support are: thermal and chemical stability during the reaction processes and separation stages; accessibility and good dispersion of the active sites. There are a number of materials that, partially or wholly satisfy these requirements, like pillared clays, some carbons and mesoporous aluminosilicates [7, 8]. However, carbon blacks are somewhat unstable for electrochemical oxidation, which is a disadvantage of this type of support.

One suitable technique to obtain dispersed and homogeneous supports is Electrophoretic Deposition (EPD), in which, charged particles in a liquid suspension are moved to the electrode surface by the applied voltage, and then the particles are deposited and distributed homogeneously on the substrate. The low solid concentrations of suspensions that can be used in EPD become an advantage in handling the suspensions. The equipment is very specific depending on the application.

2. Experimental section:

The electrochemical measurements were carried out in a Teflon cell at room temperature, and air environment using an Autolab PGSTAT30 computer controlled potentiostat. Ag/AgCl saturated was used as reference electrode, a graphite rod as counter electrode and the electrophoretically deposited diamond nanoparticles on highly conducting p-Si (100) wafers as working electrode.

The working electrode was fabricated using the EPD technique as described in an earlier article [9]. In this method a constant voltage is applied between two pieces of highly conducting p-Si (100) wafers (~ 10⁻³ Ωcm, Virginia Semiconductor, Inc.) anode and cathode separated at a fixed distance, both submerged in a suspension of diamond nanoparticles prepared with a sample purified by acid reflux (aqueous HNO₃) [9]. The voltage, time of deposition and concentration of suspension can be tuned to obtain electrodes of varying thickness. See Figure 1. These electrodes were characterized by scanning electron microscopy (SEM) to determine subsequently the thickness of the diamond nanoparticles layer. Some examples of those images are shown in Figure 2.

The working electrode is pressed against the bottom of the Teflon cell. Carbon tape was used to fix the working electrode on a glass plate which is fixed to a Teflon plate to seal the electrochemical cell.

To determine the potential window of the fabricated working electrode a 0.1 M H₂SO₄ solution was used. The first potential range applied was from 0.0 V to 0.3 V (OCP = 0.37 V), which was increased until hydrogen evolution was observed.

After the determination of the potential window, the cell was cleaned several times with nanopure water (~18 MΩ-cm), and the electrochemical cell was refilled with a 1 mM ferricyanide/ferrocyanide (Fe(CN)₆³⁻ /Fe(CN)₆⁴⁻) redox couple solution. The potential range applied to this redox couple is -0.1 to 0.5 V. We studied the behavior of this redox couple at different scan rates: from 10 mV/s to 50 mV/s in increments of 5 mV/s. The same procedure was performed using a 1 mM hexamine ruthenium (III) redox couple solution. Its potential range is from 0.0 to 0.5 V. All electrochemical experiments were repeated several times to check the reproducibility of the process.

3. Results and discussion:

The EPD results shown in figures 1 and 2 demonstrate that the method used is convenient to obtain the desired layer thickness by varying parameters such as voltage, concentration and time of deposition. A more exhaustive analysis of the procedure was carried out to verify the reproducibility of the experimental conditions (i.e. temperature, sonication time of the
suspension). For all electrochemical experiments, we used the electrode with the thinnest thickness, just necessary to cover the silicon substrate and to assure that only the diamond particles are in contact with the studied solution or redox system.

Figure 1. Thicknesses of electrophoretically deposited layers of diamond nanoparticles at different deposition time, suspension concentrations and voltages.

![Figure 1](image1.png)

Figure 2. SEM images of electrophoretically deposited layers of diamond nanoparticles at 40 s, 260 V and different suspension concentrations.

![Figure 2](image2.png)

In figure 3 the cyclic voltammograms of silicon wafer (solid line) and of the fabricated diamond thin film (dotted line) working electrodes in 0.1 M H₂SO₄ solution are shown. The difference in background current between them is noteworthy. The fabricated working electrode background current is lower than the silicon wafer alone, and its potential window is slightly wider. This potential window is limited by hydrogen evolution at negative potentials and by oxygen evolution at positive potentials.

In figure 4 the electrochemical response of the ferrycyanide/ferrocyanide (Fe(CN)₆³⁻/Fe(CN)₆⁴⁺) redox couple is shown. Their ΔEp values ranged from 100 mV at scan rate (s/r) of 10 mV/s to 128 mV at 50 mV/s. In Fig. 5 the electrochemical response of the hexamine ruthenium (III) chloride redox couple is shown. Their ΔEp values were similar to those seen with ferrocyanide: 101 mV at 10 mV/s to 131 mV at 50 mV/s. These results mean that the electrochemical process is quasireversible. According to the Nernst Equation the ΔE in each voltammogram should be near to 59mV/n. However the electron transfer kinetics is not rapid because those ΔE values are not constant. Analyzing the relationship between iₑ and (s/r)¹/², we can determine the reversibility of the redox process and as we can see in the insets in Figures 3 and 4 this reversibility is confirmed. Those graphs show a linear behavior because by increasing the scan rate, a higher current peak is obtained. Thus, at slow scan rates the diffusion layer will grow much more from the electrode in comparison to a fast scan rate.
Figure 3. Cyclic voltammogram of silicon wafer (solid line) and electrophoretically deposited diamond nanoparticles on silicon wafer as working electrodes (dotted line). H₂SO₄ 0.1 M as supporting electrolyte. Voltage range -0.6 to 0.9 V vs. Ag/AgCl scan rate (s/r) 20 mV/s.

Figure 4. Cyclic voltammogram of (Fe (CN)₆)³⁻/Fe (CN)₆⁴⁻ 1 mM in KCl 0.1 M, at different scan rates, using an electrophoretically deposited diamond nanoparticles on silicon wafer as working electrode.

Figure 5. Cyclic voltammogram of hexaaminerruthenium (III) chloride 1 mM in KCl 0.1 M at different scan rates, using an electrophoretically deposited diamond nanoparticles on silicon wafer as working electrode.
4. Conclusions

The EPD technique is an extremely convenient way to obtain diamond thin films of different thicknesses from diamond nanoparticle suspensions. The thickness can be controlled by the applied voltage, deposition time, and diamond nanoparticle concentration.

Using the electrodes fabricated by EPD, we have obtained good results which demonstrated that diamond powder can be used as electrode material because it allows the oxidation and reduction reactions to occur on the surface of diamond layer. These results indicate that diamond will be an excellent support for catalysts. We are currently performing experiments on methanol oxidation reaction in our research laboratory. The behavior of diamond nanoparticles can be improved by doping. The result of doping will allow better conductivity in the working electrode system.

5. References

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Acknowledgments

We would like to acknowledge the assistance of members of the Material Characterization Center, and the NASA Center of Nanoscale Materials both at the University of Puerto Rico, Rio Piedras Campus. The authors acknowledge the financial support from the ARL Collaborative Technology Alliance in Powder and Energy Cooperative Agreement No. DAAD19-01-2-0010 and NASA-URC Grant NCC3-1034.