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Electrochemistry of Undoped Diamond Nanoparticles: Accessing Surface Redox States

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We report the electrochemical response of undoped, insulating diamond nanoparticles, which we attribute to the oxidation and reduction of surface states. The potentials of the surface states are pH-dependent, and they are able to interact with solution redox species, such as $Fe(CN)_6^{3-/4-}$.

5 nm detonation nanodiamond (ND) particles are undoped; the resistance of the dry powder is very high, and when pelleted to form an electrode no electrochemical response is obtained other than that of a resistor. However, there are reports of its incorporation into electrodes for the detection of nitrite[1] and into glucose biosensors,[2] where ND was found to enhance the oxygen reduction current. Recently the use of ND for the direct electrochemical detection of hemoglobin was reported.[3] We have shown that electrode-immobilized ND enhanced the current response for different redox species.[4] Here we show the conditions required for electron transfer (ET) between a solution redox couple and ND and provide evidence for the existence of surface states at specific pH-dependent potentials.

ND particles of average diameter 5 nm have a core of crystalline sp^3 carbon, with the outer 3−4 atomic layers exhibiting increasing amorphous character.[5] Raman spectra show no extended graphitic content; any sp^2 carbon present is localized and associated with specific surface defects.[4,6] FTIR spectroscopy shows the ND surface to be terminated with oxygen containing moieties, mainly in higher oxidation states (e.g., C=O).[4,7]

The electrochemistry of the ND, drop-coated onto a boron-doped diamond (BDD) electrode, was investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). ND powder, obtained commercially, was further purified by treatment at 425 °C in air.[7] 0.5 ± 0.05 mg of ND powder was suspended in 1.5 ± 0.2 mL of ethanol, and a 1−50 μL aliquot of the suspension was drop-coated onto the BDD electrode to form a porous layer of ND of approximately 4−200 monolayers (see Supporting Information (SI)). Experiments were carried out in 0.2 M phosphate buffer solutions (PBS) at pH 5−9 and with $Fe(CN)_6^{3-/4-}$ or $IrCl_6^{2-/3-}$ present as a redox probe.

The CV response for the reduction of 100 μM $Fe(CN)_6^{3-}$ (pH 7) at an ND-modified electrode is similar to that at bare BDD, with only a small enhancement observed in the reduction current (Figure 1a). However, when the concentration of $Fe(CN)_6^{3-}$ is lowered to ≤10 μM, a significant enhancement in current is observed for the ND-modified electrode, as shown in Figure 1b (for 1 μM $Fe(CN)_6^{3-}$). Such enhancements can only be observed at scan rates <100 mV s^{-1}; at higher scan rates a *decrease* in reduction current is observed (Figure 1c), suggesting that the ND is acting as an inert, blocking layer under these conditions. At slow scan rates, increasing the coverage of ND from 4 monolayers (Figure 1b) to 40 monolayers (Figure 1d) results in a 3-fold increase in reduction current. The S-shaped current response is asymmetric with reduction currents being considerably more enhanced than the oxidation currents.

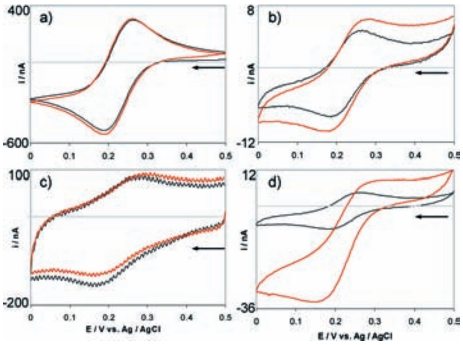

Figure 1. CVs of $Fe(CN)_6^{3-}$ reduction at a ND-modified BDD electrode (red) in 0.2 M pH 7 PBS (a) 4 monolayer (ML) ND, 100 μM $Fe(CN)_6^{3-}$, 10 mV s^{-1}; (b) 4 ML ND, 1 μM $Fe(CN)_6^{3-}$, 10 mV s^{-1}; (c) 4 ML ND, 1 μM $Fe(CN)_6^{3-}$, 500 mV s^{-1}; (d) 40 ML ND, 1 μM $Fe(CN)_6^{3-}$, 10 mV s^{-1}. Black lines: CVs under same conditions at a bare BDD electrode.

The oxidation of 1 μM $Fe(CN)_6^{4-}$ at ND-modified electrodes was investigated in different pH solutions (Figure 2a−e). The shape of the CV varies significantly with pH, but enhanced currents are always observed in the presence of ND. For solutions of pH ≤ 7 a reduction current of 7−10 nA flows at the start of the CV scan at 0 V, although no reducible species were intentionally present in the solution. During the CV, enhanced reduction currents are observed at pH 7 and below, but a more symmetrical response is obtained at pH 8, and at pH 9 a 2× increase in oxidation current is observed above 0.3 V, with little enhancement in reduction.

The CV response of an ND-modified electrode (4 monolayer) in background PBS (without $Fe(CN)_6^{4-}$) was identical to the bare BDD electrode in this potential range. However, the electrochemical response of a thicker layer of ND (∼200 monolayer) could be observed (Figure 2f−j) using DPV. The featureless response of the underlying BDD electrode has been subtracted for clarity (see SI) so the observed peaks can be unambiguously assigned to redox processes of the ND layer. The electrochemistry of the ND is pH-dependent, and in all cases the oxidation response is more complex than the reduction. Some processes are electrochemically reversible, as they exhibit reduction and oxidation peaks centered at a similar potential, for example, the reversible couple marked (*) which shifts ∼60 mV per pH unit. The oxidation of ND at pH 9 is dominated by large, featureless responses above 0.35 V with no corresponding reduction currents. This oxidation event is also pH-dependent and shifts to higher potentials as pH is decreased. The DPV responses increase in complexity as pH is decreased. At pH 5 four distinct oxidation peaks below 0.5 V are present, with corresponding reduction peaks obtained on the reverse scan. Redox activity associated with bulk properties should be surface insensitive and therefore independent of pH, indicating that the observed response of the ND must take place via surface states. The broad peaks obtained are likely due to surface functional groups undergoing oxidation or reduction at specific pH-dependent potentials. Possible

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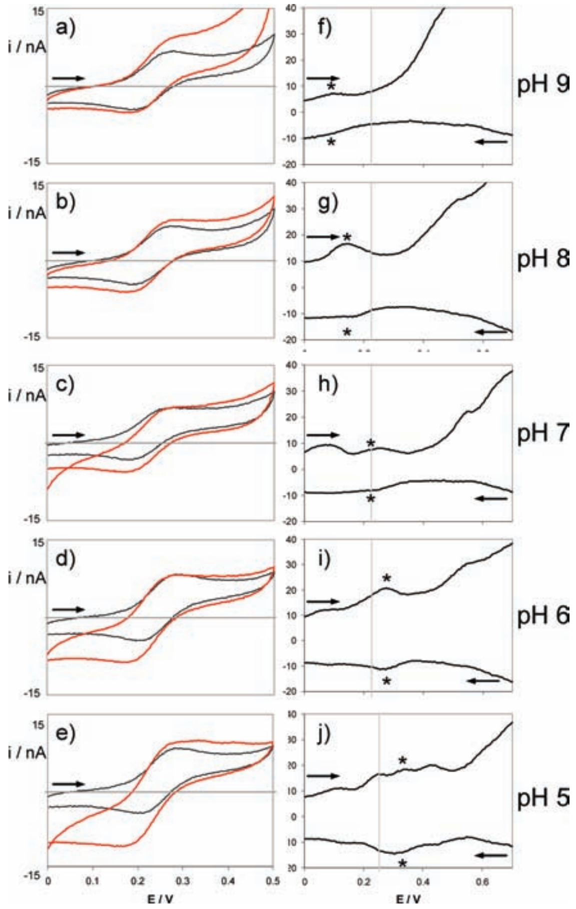

Figure 2. (a−e) CVs of 1 μM $Fe(CN)_6^{4-}$ in 0.2 M PBS at 10 mV s^{-1} at bare BDD electrode (black) and electrode modified with 4 ML of ND (red) (a) pH 9; (b) pH 8; (c) pH 7; (d) pH 6; (e) pH 5. (f−j) DPVs in 0.2 M PBS (Modulation potential = 45 mV; modulation time = 0.05 s; step potential = 5 mV; interval time = 0.5 s; scan rate = 10 mV s^{-1}) of ∼200 ML ND immobilized onto BDD electrode (background response of BDD electrode has been subtracted) (f) pH 9; (g) pH 8; (h) pH 7; (i) pH 6; (j) pH 5. Grey vertical line indicates E^0 for the $Fe(CN)_6^{3-/4-}$ couple.

candidates are quinone-type moieties on the ND surface. A shift of +60 mV with a decrease of 1 pH unit is indicative of electron transfer coupled with proton transfer.

Interaction of these surface states with $Fe(CN)_6^{3-/4-}$ is observed in Figure 2a−e. The greatest enhancements in oxidation current in the CVs are coincident with the oxidation potentials of the ND surface states, for example, in the region 0.3−0.5 V at pH 5 and above 0.3 V at pH 9. Similarly, on the reverse scan, current enhancements occur only when ND can also undergo reduction. Additionally, at pH ≤ 7 it seems the spontaneous oxidation of $Fe(CN)_6^{4-}$ occurs on contact with the ND surface, producing $Fe(CN)_6^{3-}$ in the interfacial region. This gives rise to initial reduction currents of up to 10 nA, consistent with an interfacial concentration of ∼1 μM $Fe(CN)_6^{3-}$, suggesting the majority of $Fe(CN)_6^{4-}$ molecules within the diffusion layer region have been oxidized. For this process to be feasible, it requires that ND can be reduced at potentials positive of E^0 for the $Fe(CN)_6^{3-/4-}$ couple. Inspection of the ND DPV in Figure 2 shows this is possible only at pH 7, 6, and 5 (considering state *). At pH 8 and 9 the ND reduction peak has shifted to potentials more negative than E^0 for $Fe(CN)_6^{3-/4-}$; hence the spontaneous oxidation of $Fe(CN)_6^{4-}$ at the ND surface is not thermodynamically possible, and no significant initial reduction currents are observed in Figure 2a and b.

A postulated mechanism to explain the current enhancement for reduction of $Fe(CN)_6^{3-}$ in the presence of ND is shown in Figure 3A.

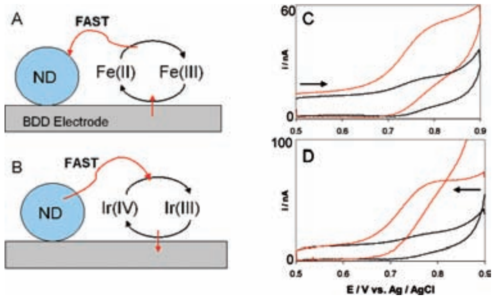

Figure 3. Postulated mechanisms for current enhancement (red arrows indicate direction of electron transfer) for (A) $Fe(CN)_6^{3-}$ reduction and (B) $IrCl_6^{3-}$ oxidation. (C) CV of 1 μM $IrCl_6^{3-}$oxidation at a bare BDD (black) and a 4 ML ND-modified BDD electrode (red) at 10 mV s^{-1}, 0.2 M pH 7 PBS. (D) CV of 1 μM $IrCl_6^{4-}$ reduction under same conditions.

$Fe(CN)_6^{3-}$ is predominantly reduced at the underlying BDD electrode, generating $Fe(CN)_6^{4-}$ which is then *spontaneously oxidized* by ND surface states resulting in regeneration of $Fe(CN)_6^{3-}$; enhanced currents are thus observed due to a redox cycling (feedback) mechanism. Under conditions where this process is most efficient (at pH ≤ 7 with high ND coverage), most $Fe(CN)_6^{4-}$ generated during reduction of $Fe(CN)_6^{3-}$ is immediately consumed, meaning there will be little or no enhancement in oxidation currents, as in Figure 1d. Sustaining this mechanism requires the reduced ND surface states become depopulated (oxidized) by some means, with possible routes being direct oxidation at the underlying electrode or oxidation by solution species such as oxygen or Fe(III) (see SI). Under conditions where reduction of surface states occurs too rapidly for such a depopulation to take place, enhanced currents are *not* observed, e.g., at high reagent concentrations (Figure 1a) and faster scan rates (Figure 1d). A reverse mechanism to Figure 3A explains enhancements in $Fe(CN)_6^{4-}$ oxidation when oxidizable ND surface states are available.

The influence of ND on the CVs of $IrCl_6^{3-}$ and $IrCl_6^{2-}$ (E^0 0.73 V) at pH 7 is shown in Figure 3C and D. In both cases oxidation currents *only* are enhanced in the presence of ND. The mechanism in Figure 3B would explain these observations. Inspection of Figure 2h confirms that the facile oxidation (but not reduction) of the ND occurs at potentials >0.5 V at pH 7. Spontaneous reduction of Ir(IV) to Ir(III) at the ND surface can thus be predicted to occur under these conditions and indeed is observed, as shown by the large initial oxidation currents in Figure 3D. Clearly different solution redox species will interact with specific ND surface states, depending on their relative standard potentials.

Supporting Information Available: Experimental procedures, calculations of ND coverage, ND surface chemistry, DPVs for BDD electrode and ND consecutive scans. CVs with $Fe(CN)_6^{3-}$, $IrCl_6^{3-/2-}$, and $Ru(NH_3)_6^{3+}$ at different pH and $Fe(CN)_6^{4-}$ at higher coverage. This material is available free of charge via the Internet at http://pubs.acs.org.

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