Low Dimensional Materials and Catalysts

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Material characterization of N-doped graphene with Pt atoms and clusters for fuel cell application using a transmission electron microscope

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Fuel depletion and environmental degradation has led to the need for a new fuel source with the preference for a clean emission. The power supply of the proton exchange membrane (PEM) fuel cell makes it ideal for the replacement of the internal combustion engine. Current PEM fuel cells utilize electrodes composed of carbon black with Pt catalysts, as Pt most efficiently facilitates the oxygen reduction reaction (ORR) [1]. Unfortunately Pt adds a large cost of the fuel cell, thus impeding economic mass production. In effort to decrease the cost while maintaining the catalytic efficiency, the surface area to volume ratio of the Pt is decreased through the formation of nanoparticles or Pt clusters.

Recently, graphene has been examined as a possible substitution for the electrode support in the PEM fuel cell due to its enhanced electrical conductivity, mechanical robustness, and large surface area [2,3]. The intrinsic sp^2 bonding of the C lattice in graphene also provides a chemically inert surface, which is undesirable for Pt adsorption. Defects can be induced in the graphene lattice through functionalization, where the use of N atoms have the additional benefits of acting as active ORR sites, and increasing the Pt-C binding energy which can facilitate adsorption and decrease the Pt nanoparticle size [4,5]. However, the specific effect of each N-dopant is still controversial in the scientific literature. The size of the Pt clusters can be further decreased through the use of atomic layer deposition, as ultrasmall nanoparticles (<1 nm) are produced [6]. It is expected that the combination of ALD and increased binding energy from the N-doped graphene should produce Pt clusters.

To fully understand and design the most efficient fuel cell the material must be characterized at the atomic level to determine the size and size distribution of Pt, the predominant N-dopant type (amino, pyridinic, pyrrolic, graphitic) within the electrode, and the presence of the graphene lattice to maintain the electrical conductivity. Through the use of an aberration-corrected transmission electron microscope (TEM), sub-angström resolution imaging is possible. Various imaging and spectroscopy techniques can be utilized to fully determine the material structural and chemical characteristics. Specifically, high resolution TEM (HRTEM) under negative C_s imaging conditions can be utilized to observe the graphene lattice and observe defects, while high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) is ideal for imaging heavy atoms on light atomic substrates as it is sensitive to Z-contrast. Through the use of HRTEM and HAADF the graphene structure, and the size and size distribution of Pt can be determined, respectively. Further, electron energy loss spectroscopy (EELS) can be utilized to examine local chemical composition and binding within a material from a small spatially resolved area (~1 nm) [7]. This proves useful in the determination of the specific N-dopants in the graphene lattice.

The N-doped graphene is highly folded and multilayered, however upon the examination with high magnification (Figure 1. (a)) the graphene hexagonal lattice is visible, while the computed diffractogram illustrates the characteristic hexagonal pattern. Further, through the use of HAADF it is evident that the Pt forms atoms and clusters on the N-doped graphene surface (Figure 1. (b)), where an increase in ALD cycles increases the Pt density but does not increase the size. Image processing clearly demonstrates that the Pt sits predominately at edge locations with few atoms sitting on the N-doped graphene surface (green arrows). Lastly, the EEL spectra further indicate that the graphene lattice is maintained after N-doping as the strong π* and σ* peaks are present in the C-K edge. Each

possible N-dopant (P1-P4 in the N-K edge) is present in the graphene lattice, however the specific distributions across sheets are inhomogeneous (Figure 2.).

The preservation of the graphene lattice will permit the high electrical conductivity of the support material, while the incorporation of the N-dopants creates defect sites thus allowing Pt to strongly bind. It is illustrated that Pt clusters and atoms form due to the use of ALD in combination with N-doping. An increase in ORR and decrease in cost is expected for this electrode support, as many active sites are available through N-doping and the extremely large surface area to volume ratio of the Pt.

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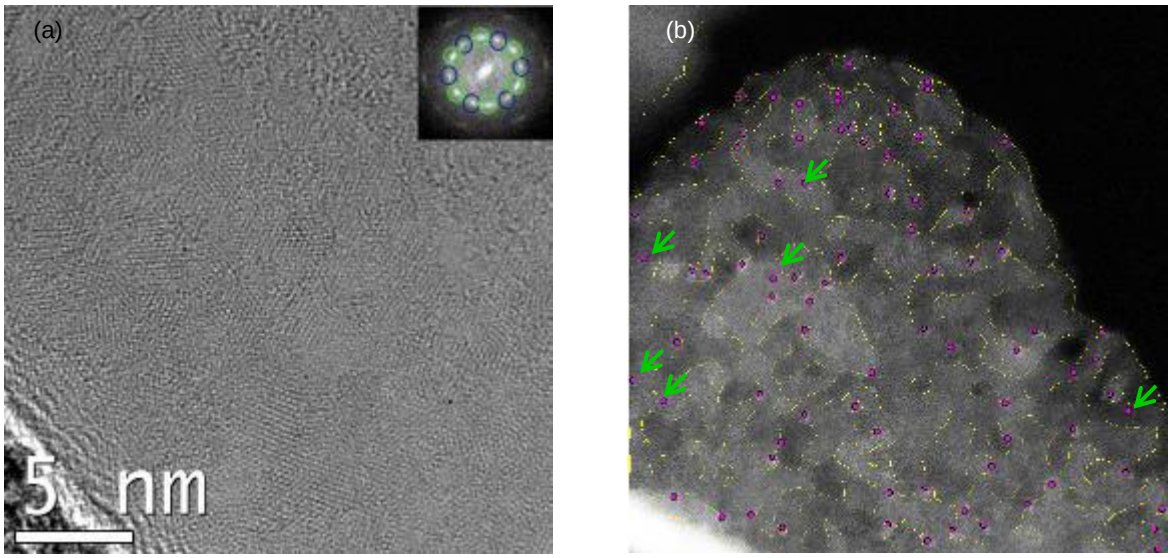

Figure 1. N-doped graphene with 50 ALD cycles of Pt using (a) HRTEM and (b) HAADF. Inset in (a) is the computed diffractogram illustrating the characteristic hexagonal pattern of graphene.

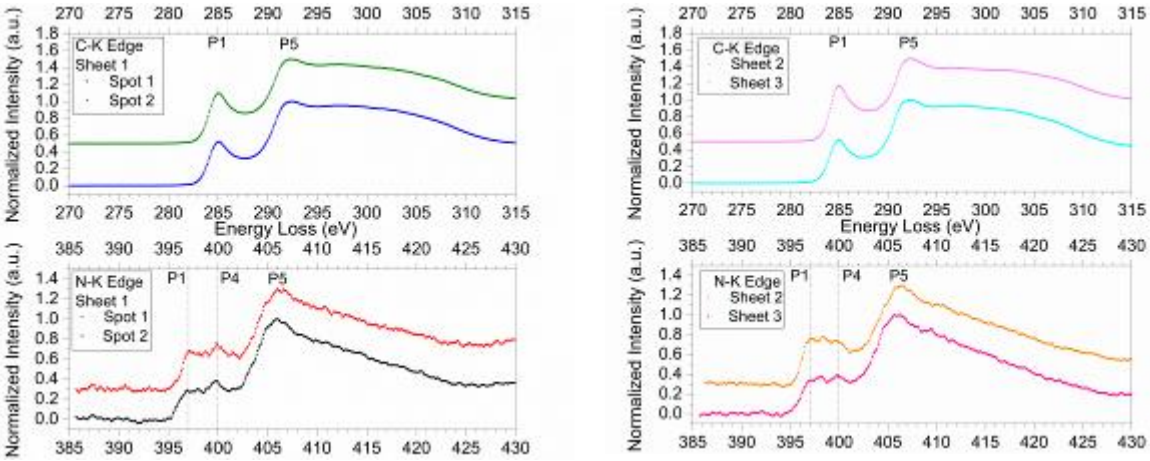

Figure 2. EEL spectra of N-doped graphene with 50 ALD Pt cycles of the C-K and N-K edge from various sheets within the graphene lattice.