Structural and chemical characterization of ALD Pt on N-doped graphene using atomic resolution transmission electron microscopy

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Fuel cell technology is still plagued by high cost and low efficiency at the electrode, due to the requirement for Pt to facilitate the electrochemical reactions and the degradation of the electrode support over time, respectively. Conventionally carbon black supports are utilized in proton exchange membrane fuel cells with a multitude of catalyst deposition techniques. The downsizing of Pt nanoparticles or designing a more efficient and readily available catalyst, in addition to increasing the chemical and mechanical stability of the support can address these issues.

Research points to the use of graphene as a new electrode support, due to its high electrical conductivity, mechanical robustness, and high surface area for catalysis loading [1]. The electrode can be enhanced by doping the graphene with various N components that have shown to facilitate the O reduction reaction (ORR), while also enhancing the electrical conductivity of the support and increasing the Pt-C binding energy [2, 3, 4]. Further, through the use of atomic layer deposition (ALD), ultrasmall Pt nanoparticles (<1 nm) are formed [5]. It is expected that the N-doped graphene with ALD Pt will produce atomic clusters and atomic Pt rather than nanoparticles, resulting in the ultimate increase in surface area to volume ratio for the catalysts.

The transmission electron microscope has proven invaluable to characterize the Pt size and the quality of the graphene lattice, due to its ability to image materials at a sub-angstrom resolution. Through the use of electron energy loss spectroscopy (EELS) it is possible to observe variations in N-doping on a small spatially resolved area (~1 nm) [6]. Also by utilizing the high angle annular dark field detector (HAADF) the Pt atoms and clusters can be directly viewed, as this technique is sensitive to atomic number.

It has been observed that the graphene quality is maintained after N-doping, however it is defective and multilayered as outlined by the black lines in Figure 1(a). The arrows indicate the location of the Pt atoms and clusters, which are predominately situated at edge sites. The presence of Pt atoms on the surface of graphene is made possible by the increased Pt-C binding energy from the N-dopants. It was also verified that the concentration of the specific N-dopants are not consistent across graphene sheets, as evident by the EEL spectra (Figure 1(c)). Lastly, in Figure 1(b) it is confirmed with HAADF that the combination of N-doping and ALD results in the formation of Pt atoms and clusters, rather than nanoparticles.

The fact that the graphene quality is maintained and N-doping is present suggests that a high electrically conductive electrode can be achieved. Further, the presence of atomic Pt, Pt clusters, and N-doping indicates that the fuel cell efficiency should increase, as more active sites will be available for the ORR.

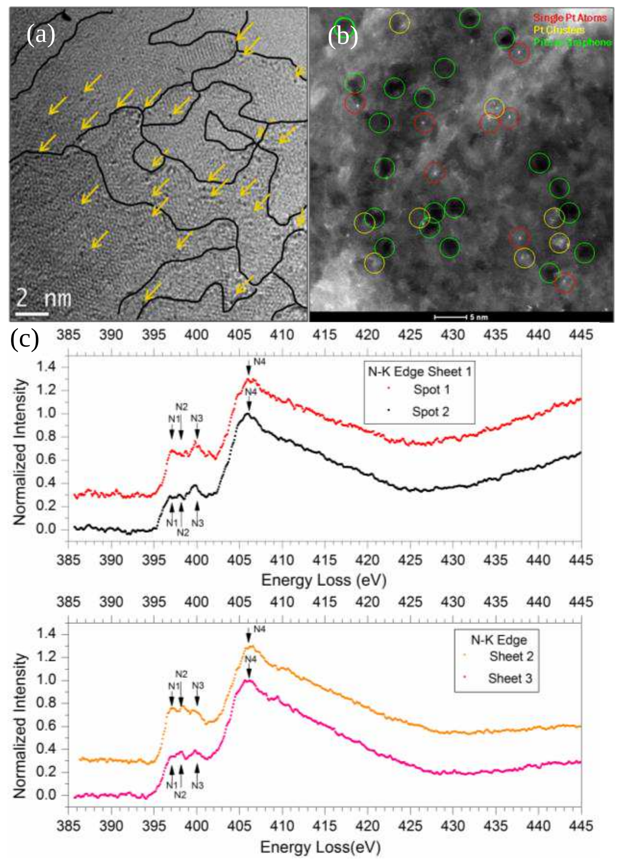

Figure 1 ALD Pt on N-doped graphene. (a) HRTEM image of 150 ALD Pt cycles with black lines on graphene sheet edges and yellow arrows on Pt atoms and clusters. (b) HAADF image of 150 ALD Pt cycles with single Pt atoms, clusters of Pt atoms, and pits in the graphene labeled, and (c) N-K edge EEL spectra acquired from three graphene sheets.

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