Uncovering the structure of N-doped graphene with Pt atoms using high resolution electron microscopy and EELS

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Abstract

N-doped graphene has been investigated as a potential new electrode support material for the proton-exchange membrane fuel cell (PEMFC), as it facilitates increased Pt-C binding energy, and acts as an oxygen-reduction reaction (ORR) catalyst.[1,2] Further, through the atomic layer deposition (ALD) technique, ultra-small nanoparticles (NPs) (<1 nm) can be produced. It is expected that the combination of ALD and N-doped graphene will produce stable Pt clusters/atoms, resulting in the ultimate increase in Pt utilization and cost reduction.[3]

To fully understand and design the most efficient PEMFC the material must be characterized at the atomic level. Aberration-corrected transmission electron microscopes (TEM) make sub-angström resolution imaging possible. Various imaging and spectroscopy techniques can be utilized to fully determine a material's structural and chemical characteristics. Specifically, high resolution TEM (HRTEM) can be employed to observe the graphene lattice and identify defects, while high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) is ideal for imaging heavy atoms on light-atom substrates as the technique is sensitive to atomic (or Z)-contrast. Through the use of HRTEM and HAADF the graphene structure, the size, and size distribution of Pt clusters on the graphene support can be determined. Furthermore, electron energy loss spectroscopy (EELS) can be utilized to examine local chemical composition and bonding within a material from a small spatially resolved area (~1 nm), which can be used to determine the specific N-dopants present in the graphene lattice (i.e. amino, pyridinic, pyrrolic, graphitic).[3]

The full atomic structure of single-graphene sheets has be characterized using HRTEM (figure 1(a)) and STEM imaging, where point defects, grain boundaries, and preferred defect configurations (pentagon/heptagon organization) can be examined through the observation of single carbon atoms. Using the same techniques, thermally-exfoliated graphene (figure 1(b)) was also investigated. Through HRTEM, the atomic structure of the graphene lattice was observed to maintain its short-range order (figure 1 (a) and (b)), however long-range order was lost due to the presence of steps, folds, defects, and incomplete exfoliation.[3] HAADF imaging also confirmed the numerous steps and ledges in the N-doped graphene nanosheets through mass-contrast, and more importantly showed that the Pt appears as stable single atoms and clusters on the N-doped graphene (figure 1 (c)) without the formation of NPs.[3] Moreover, using image processing techniques it was determined that the Pt atoms are predominantly located at the edges of the graphene nanosheets with few atoms sitting on the N-doped graphene surface. Lastly, using EELS we found that various N-dopants were present in the graphene lattice (figure 1 (d)); however, the specific distributions across and within the graphene nanosheets were inhomogeneous, which was not previously shown in x-ray studies.[3]

References

[1] Wei, D. Liu, Y. Wang, Y. Zhang, H. Huang, L. Yu, G. Nano Lett. **9** (2009), 1752–1758.
[2] Holme, T. Zhou, Y. Pasquarelli, R. O'Hayre, R. Phys Chem Chem Phys, **12** (2010), 9461-9468.
[3] Stambula, S. *et al*. J. Phys. Chem. C, **118** (2014), 3890-3900.

Figures

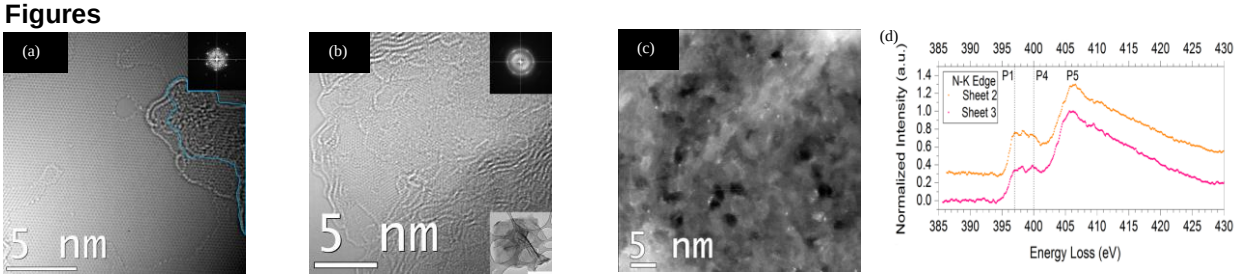

Figure 1: HRTEM image of (a) single layer graphene reference material and (b) thermally exfoliated N-doped graphene with inset showing low magnificaiton overview of the graphene nanosheet (inset field of view is 1 μm). High resolution HAADF (c) image of N-doped graphene shows Pt atoms and clusters located on edge sites. (d) EELS N-K edge spectra acquired from various N-doped graphene sheets.