

The Structure of Ions near Carbon Nanotubes: New Insights into Carbon Surface Chemistry and Implications for Water Purification

Carbon-based materials have long been used for a variety of water purification operations. Researchers have investigated carbon materials as adsorbents for decades, but only limited information on the precise details of aqueous ion interactions with carbon surfaces has been uncovered. It is empirically known that the affinity of activated carbon for various hydrated ions depends critically on how the material is processed. Processing influences the types of chemical groups and the structure of the carbon surface, which in turn influences the strength of interaction between hydrated ions and the carbon surface. It is also believed that many of the puzzling properties of impurity-free carbon, such as ferromagnetism, are governed by specific modifications of the carbon surface. However, very little is known about the local structure of the carbon surface that is responsible for its aqueous ion affinity.

In a recent paper published in *Advanced Materials*, former Lawrence Livermore National Laboratory scientist Jason Holt, along with SSRL scientists Apurva Mehta, Erik Nelson, and Samuel Webb have found that both activated carbon and carbon nanotubes share a common surface site that binds bromide ions present in solution, and by implication other aqueous halides as well. These sites have a significant impact on the chemical properties of these materials and provide a picture of carbon surface chemistry that is consistent with the proposal of a recent theoretical study.[1]

To probe the details of ion structure, a technique was needed that is sensitive to the local environment around ions that may be trace in abundance in samples. The technique of extended x-ray absorption fine structure (EXAFS) is ideally suited for this purpose, and beamlines 10-2 and 7-3 at the Stanford Synchrotron Radiation Laboratory (SSRL) were used to carry out these measurements. Carbon materials were prepared for these measurements by taking them in powdered form and treating them with a concentration solution of rubidium bromide, followed by a series of washing cycles to remove excess ions present in the bulk solution.

Figure 1 shows the bromine EXAFS oscillations, $k^3\chi(k)$, for both a bulk solution sample (0.5M rubidium bromide) and an activated carbon sample (AC6), their pseudoradial distribution functions (R-function), as well the best model fits for $k^3\chi(k)$ and the R-functions. The k-space EXAFS of the bulk solution dies out rapidly by $k \sim 10 \text{ \AA}^{-1}$, indicating significant disorder in the outer coordination shells. This suggests that the interaction of the Br with more distant water molecules is very weak (and probably strongly screened by the first coordination shell). In contrast, the EXAFS of the activated carbon sample shows a beating of several frequencies and extends out beyond $k = 13 \text{ \AA}^{-1}$, indicating that Br binds to a very ordered structure in a very specific manner. The resulting R function is also much more complex, with multiple peaks observed, suggesting that the local structure around a Br ion in the activated carbon sample is dramatically different from that in aqueous solution. Similar results were seen with single wall carbon nanotube samples that were analyzed.

Because several close and partially overlapping scattering shells were visible in the experimental EXAFS data, due to Br attachment to the graphitic material, fitting consisted of creating a rigid graphitic sheet and refining the position of Br over this sheet. There are two

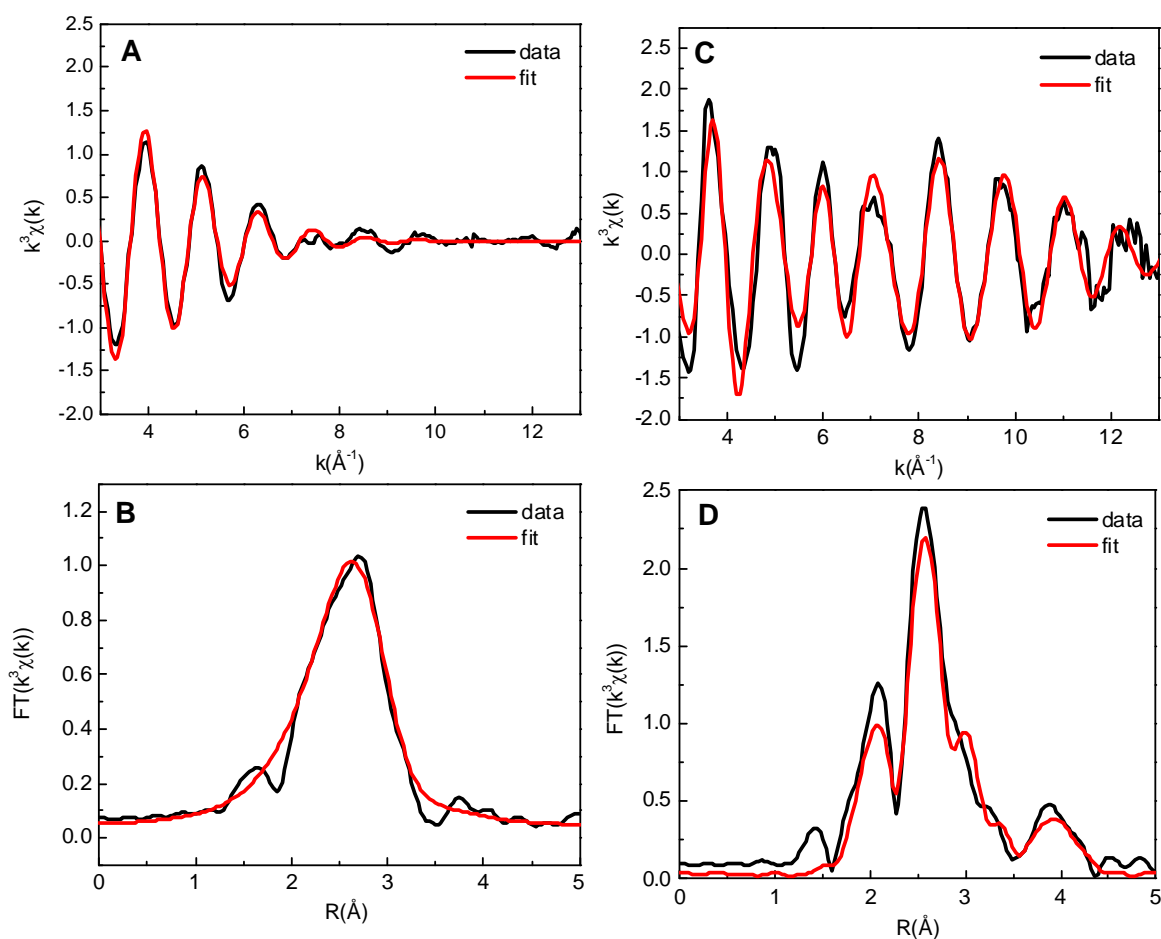


Figure 1. Bromine EXAFS signal (A) and the R-function (B) for the 0.5M rubidium bromide reference solution. Corresponding bromine EXAFS (C) and R-function (D) for the activated carbon sample, along with model fits (in red) derived from FEFF8.[3] The fit was performed over a k -space from 3 to 12.7 \AA^{-1} (R from 1 to 4.7 \AA) for the solution sample and the AC6 sample. The difference between the peak positions and the true Br coordination distances can be resolved by a phase correction term.

general types of locations available for an adsorbate on a graphitic sheet. The first places the Br ion in the middle of a complete graphitic sheet, either towards the broad end of the carbon ring or nearer to the triangular portion of the carbon ring. The second general location for an adsorbate is at the edge of the sheet. The first type of edge site corresponds either to the concave or the convex portion of the broad part of a “broken” carbon ring that has a 4 carbon periodicity (the “armchair” site). The second edge location corresponds to the concave or convex corner of the triangular part of the “broken” carbon ring. Such an edge has a 2 carbon periodicity and is referred to as a “zigzag site”. After considering all candidate locations and examining their fit statistics, it was concluded that the bromine ion does not attach to the middle of the graphitic sheet but to an edge site, with a strong preference for a convex, zigzag edge, as illustrated schematically in Figure 2. Note that in addition to actual edges of graphitic sheets, these edge sites can be in the middle of a graphitic sheet, or on the side of a carbon nanotube, provided the sheet or tube is punctured (i.e., vacancies are present). A recent theoretical study [1] proposes an oxygen-free basic site, the carbene site at graphene zigzag edges that appears consistent with the

experimental results reported here. These sites can be protonated in aqueous solution, producing a positively charged carbon with which anions may interact through ion pairing.

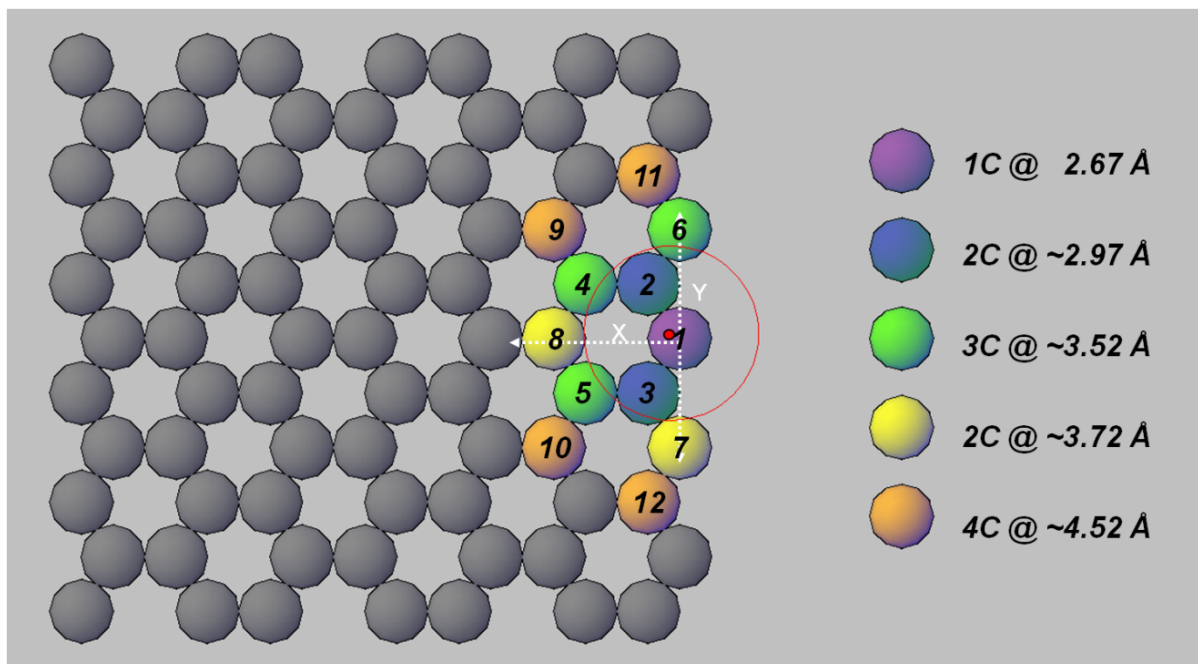


Figure 2. Illustration of the structural model for Br coordination to graphene materials, derived from a model fit of the activated carbon EXAFS data. Bromine sits atop a convex zigzag site on the edge of the graphene sheet (red dot above carbon atom #1). The Br position relative to the axes is $x = 0.199 \pm 0.040 \text{ \AA}$, $y = 0.076 \pm 0.029$, $z = 2.658 \pm 0.008$, where z is the direction above the graphitic sheet.

In conclusion, the present results provide the first structural picture of the location and binding geometry of aqueous halogen ions to a graphitic sheet. The results also suggest how the presence of zigzag graphitic edge sites can alter the ion affinity. These particular sites may prove important for proposed uses of carbon nanotube membranes [2] for desalination, as well as carbide-derived carbons for electrolytic supercapacitors.[3]

Primary Citation

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References

- [1] L.R. Radovic, B. Bockrath, *J. Amer. Chem. Soc.* 127, 5917 (2005).
- [2] J.K. Holt, H.-G. Park *et al.*, *Science* 312, 1034 (2006).
- [3] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P.L. Taberna, *Science* 313, 1760 (2006).

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