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Inducing Regioselective Chemical Reactivity in Graphene with Alkali Metal Intercalation

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Supporting Information

Carbon Atom Curvature

Previous studies on carbon nanotubes have shown a linear relationship between the inverse of the radius of the carbon nanotube and the adsorption energy of reactions onto that nanotube.[1, 2] We employ the same definition of carbon atom curvature in this work. Any carbon atom on the graphene sheet is surrounded by 3 other carbon atoms. This gives 4 points through which a sphere can be mapped to, the inverse radius of which is analogous to the inverse radius of a carbon nanotube. The radius of each mapped sphere was determined using the determinant method

$$\begin{vmatrix} x^2+y^2+z^2 & x & y & z & 1 \\ x_1^2+y_1^2+z_1^2 & x_1 & y_1 & z_1 & 1 \\ x_2^2+y_2^2+z_2^2 & x_2 & y_2 & z_2 & 1 \\ x_3^2+y_3^2+z_3^2 & x_3 & y_3 & z_3 & 1 \\ x_4^2+y_4^2+z_4^2 & x_4 & y_4 & z_4 & 1 \end{vmatrix} = 0$$

Where x_n, y_n and z_n are the x, y and z co-ordinates of the central carbon atom and the 3 carbon atoms surrounding it. Solving this determinant gives the equation of the sphere from which the radius r_0 is derived. This radius is then inverted to give the curvature C. This curvature is then be graphed as a function of the distance from the central carbon atom to the alkali metal via

$$d_n = \sqrt{(x_n - x_{am})^2 + (y_n - y_{am})^2 + (z_n - z_{am})^2}$$

Where x_n, y_n and z_n are the z, y and z co-ordinates of the central carbon atom (i.e. Figure 3)

Bader Charge Transfer Calculations

The extent of charge transfer (ΔQ) from the intercalated alkali metal atom to each carbon atom in the adsorbed graphene monolayer was gauged via two successive Bader charge analyses. Firstly, the charge on each carbon atom in the graphene sheet adsorbed on the doped substrate was calculated at the fully relaxed geometry (denoted $Q_{complete}$). The alkali metal atom was then removed manually, and a 2nd Bader charge analysis was performed at the same geometry. These carbon charges are denoted $Q_{graphene-metal}$. The extent of charge transfer at each carbon atom is then defined as,

$$\Delta Q = Q_{complete} - Q_{graphene-metal}$$

Charge Density Difference Analysis

Charge transfer from the alkali metal to the adsorbed graphene monolayer is elucidated via the charge density difference method. Figure 6 presents $\Delta\rho$, where

$$\Delta\rho = \rho_{complete} - \rho_X - \rho_{graphene\text{-}metal}$$

where ρ_{tot}, ρ_X and $\rho_{graphene\text{-}metal}$ are, respectively, the electron densities of the complete graphene – alkali metal – substrate interface, the alkali metal (X), and the graphene-metal interface (at the fully relaxed structure of the complete graphene – alkali metal – substrate interface).

References

1. J. Li, G. Jia, Y. Zhang and Y. Chen, *Chem. Mater.*, 2006, **18**, 3579-3584.
2. G. Zheng, Z. Wang, S. Irle and K. Morokuma, *J. Am. Chem. Soc.*, 2006, **128**, 15117-15126.