

Fe-doped carbon nanotubes: towards the molecular design of new catalysts for the oxygen reduction reaction

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Abstract

Using DFT computational methods, single-walled carbon nanotubes (CNT) are explored in different geometric configurations (armchair, chiral and zigzag) doped with Fe. Geometry, electronic structure and magnetic properties are investigated for all systems, in order to evaluate a potential application of these structures as electrocatalysts in efficient and low-cost fuel cells.

In search for a better electrode material, we turn our attention on nature for help. Oxygen molecules are well-known to reveal a remarkable affinity to the heme group. Therefore, we model the adsorption/dissociative behavior of oxygen molecules on carbon nanotubes doped with Fe atoms. We analyze in detail the effect of the chiral nature of carbon nanotubes that governs their electric, magnetic and chemical behavior. Our results indicate that the dissociation phenomenon involving the armchair (5,5) Fe@CNT is more favored than other chiralities and other doped CNT systems, leading to the lowest activation barrier.

Keywords: Oxygen reduction reaction, DFT, Fe-doped CNT, Electrocatalysts.

1 Supporting information

1.1 AIMD simulations

The geometrical stability of the three doped CNTs has been evaluated by Ab Initio Molecular Dynamics (AIMD) simulations in a canonical (NVT) ensemble. The temperature were controlled using a Nosé-Hoover thermostat at 300 K. The simulations were carried out for 5 ps with a time step of 1 fs. See Figure S1

1.2 Considerations of ORR reaction

As the second step in the suggested mechanism ($O_{\text{ads}} + H_2O + e^- \rightleftharpoons OH_{\text{ads}} + OH^-$) is a bond breaking electron transfer, its energy barrier (ΔE_a) at zero electrode overpotential can be estimated as follows [1],

$$\Delta E_a = (\lambda + D)/4, \text{ (S1)}$$

where λ is the solvent reorganization energy and D is the bond energy in initial state.

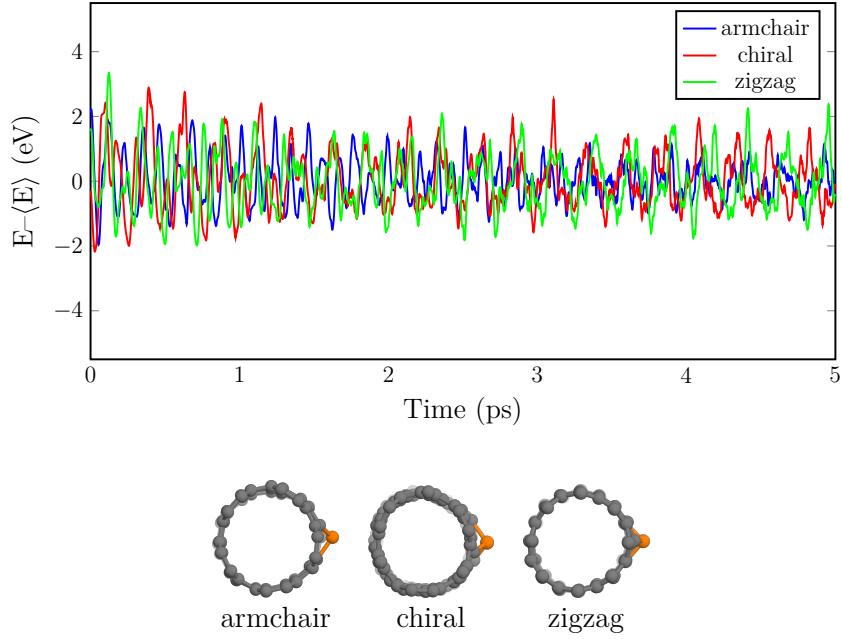


Figure S1. AIMD simulations for the three Fe@CNTs at 300 K with a time step of 1 fs. Snapshots of each material geometry during the simulations are shown.

Similarly, for the third step ($\text{OH}_{\text{ads}} + \text{e}^- \rightleftharpoons \text{OH}^-$), it can be written,

$$\Delta E_a = \lambda/4, \text{ (S2)}$$

D can be estimated as the heat of the model process $\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{OH}$ and λ value can be taken as a half of the hydration energy for H_2O^- (the second step) and OH^- (the third step).

We have performed DFT calculations using the b3lyp hybrid functional and the standard basis set 6-311++g(p, d) as implemented into the Gaussian 16 software package [2]. Open-shell systems were addressed in terms of the spin-polarized formalism. Solvent effect was addressed implicitly with the help of PCM [2]. The following values were obtained: $D = 0.64$ eV, $\lambda = 0.7$ eV (H_2O^-) and 1.8 eV (OH^-). Then, ΔE_a values were found to be 0.33 eV (the second step) and 0.45 eV (the third step).

2 References

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