How can we describe the adsorption of quinones on activated carbon surfaces?

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Hyung-Jin Kim, Young-Kyu Han[*]

Department of Energy and Materials Engineering and Advanced Energy and Electronic Materials Research Center, Dongguk University-Seoul, Seoul, 100-715, Republic of Korea

ABSTRACT

Quinone molecules have been widely studied as effective redox-active species for supercapacitors, but an understanding of the adsorption of quinones on activated carbon electrodes is very scarce. A hydroquinone molecule does not form a strong bond on pristine graphene, Stone−Wales defect, and double-vacancy surfaces, but it forms strong adsorption on single-vacancy surface. We demonstrate from first-principles calculations for various quinones that selecting an appropriate surface model is crucial in conducting a proper comparative study of the adsorption of quinone molecules. We suggest the single-vacancy graphene surface as a useful model for studying the adsorption of quinone molecules on an activated carbon electrode.

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1. Introduction

Activated carbons have been widely studied as electrode materials for supercapacitors due to the large surface area originating from their highly developed porous structures [1–9]. A great surface area implicates the large double-layer capacitance of a supercapacitor, but there are technical limitations to increasing the surface area of electrode material. Therefore, as an alternative solution to improving the energy density of supercapacitors, many researchers are investigating methods by which to obtain pseudocapacitance by applying redox-active materials to the electrode surface [8–16]. In the case of pseudocapacitance, electric charge is stored through the redox reactions of redox-active molecules that are grafted on the electrode surface, unlike double-layer capacitance which involves electrostatic charge storage on the electrode surface without charge transfer. Therefore, effective pseudocapacitive behavior requires the stable adsorption of redox molecules on the surface of an activated carbon electrode.

Quinone molecules are representative redox-active species that can be applied to the electrodes of supercapacitors to obtain pseudocapacitance. Many studies have been reported to increase the capacitance of supercapacitors using various quinone molecules such as hydroquinone (HQ), benzoquinone (BQ), 1,4-naphthoquinone (NQ), anthraquinone (AQ), and 9,10-phenanthrenequinone (PQ) [14–25].

In our previous research, we used HQ as an additive to the activated carbon electrode, and the total capacitance increased as pseudocapacitance was generated [15]. The redox reactions of HQ molecules grafted onto the activated carbon were confirmed through electrochemical experiments, and a pore size distribution experiment showed that the grafting of HQ molecules occurred inside the pores of activated carbon, reducing the pore size. The reduction of pore size with the HQ molecules was explained by the calculations of a surface adsorption model of HQ. According to a study by Isikli et al. [14], similarly to the case of HQ, an activated carbon electrode modified by BQ showed a significant increase in gravimetric capacitance values that was maintained even after 2000 cycles. The reduced pore size of the activated carbon after the addition of BQ indicates the uniform grafting of BQ onto the activated carbon pore. AQ grafting onto the activated carbon also increased the total capacitance by generating pseudocapacitance, and the surface area of the activated carbon also decreased by the grafting of AQ molecules [19]. Thus, the attachment of the quinone molecules on the carbon surface greatly increases the energy storage capacity of a supercapacitor and also affects the pore texture of the activated carbon. It is crucial to understand the adsorption of redox molecules on activated carbon when utilizing this molecule as an additive to supercapacitor electrode application. However, theoretical studies on the electrode surface

adsorption of quinone molecules is still rare.

The graphene model, which is easy to use due to its simple structure, has often been used for theoretical studies of the surface of active carbon materials [10,26,27]. However, as the pristine graphene surface has high stability and weak reactivity, it is inadequate for the explanation of a carbon surface with high reactivity, such as activated carbon. Tikmo et al. [28] reported that the activated carbon must have defects within the carbon basal planes and that these sites are readily accessible through near-edge X-ray absorption spectroscopy and Raman spectroscopy on the activated carbon.

For the stable adsorption of adsorbed quinone molecules, one can think of a surface model that has introduced curvatures or defective sites onto the graphene surface. The carbon surface model that describes activated carbon as curved carbon fragments, containing pentagonal and heptagonal rings as well as hexagonal rings [29,30], has been applied to the research into phenol on activated carbon [31] and aurocyanide on activated carbon [32]. However, the adsorption energies of these molecules on the surfaces of curved carbon fragments with no defect showed no significant differences compared to that on the planar surface of graphene (energy difference ≤ 0.06 eV). Therefore, the curvature of the surface is probably not a cause of strong adsorption of quinone molecules.

In this work, we used the graphene model with defective sites to investigate the adsorption of quinone molecules on the activated carbon surface. Various shapes of defect structures can be formed on the pristine graphene surface, and the structures we considered are a Stone−Wales (S−W) defect and single- and double-vacancy surfaces (Fig. 1). These structures contain various shapes of carbon ring structures, such as pentagons, heptagons, and octagons that are transformations of the hexagon rings in graphene. To the best of our knowledge, there has been no previous such attempt in the research into quinone molecule adsorption for activated carbon. The adsorption of HQ, BQ, NQ, AQ, and PQ quinone molecules (Fig. 2) on various carbon surfaces was calculated, and the adsorption characteristics were compared in terms of the surface structure and molecule type.

HQ molecules that have been experimentally known to be strongly bonded are found to have strong chemical bonding only on the single-vacancy surface and weak bondings via π−π interaction on the other three surface models including pristine graphene. For BQ, NQ, AQ, and PQ adsorption, the pristine graphene model and the single-vacancy model showed strikingly different results, which are theoretically interpreted. We present the graphene surface with a single-vacancy site as a useful model by which to describe the stable adsorption of quinone molecules on an activated carbon surface.
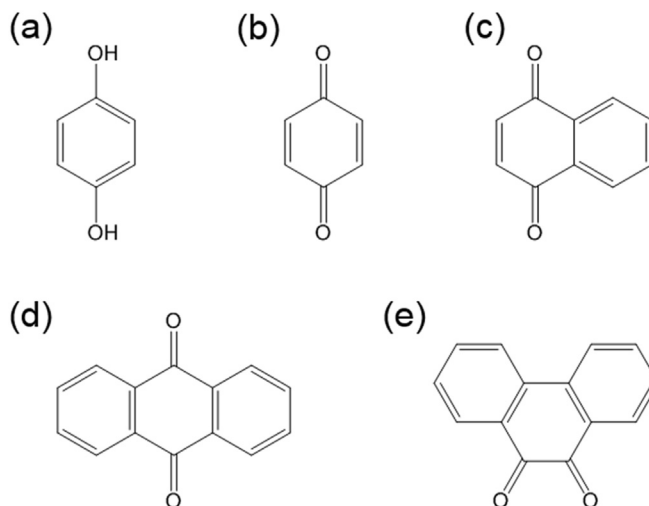

Fig. 2. Various quinone molecules: (a) HQ, (b) BQ, (c) NQ, (d) AQ, and (e) PQ.

2. Computational details

First-principles calculations were performed using density functional theory (DFT) with projector-augmented wave pseudopotentials, as implemented in the Vienna ab initio simulation package (VASP) [33,34]. We employed the revised Perdew−Burke−Ernzerhof type exchange and correlation functional [35,36] combined with the introduction of vdW-DF [37,38] for the non-local correlation part to accurately account for the dispersion interactions [39]. The projector augmented wave (PAW) method was used for the ion interaction. The Brillouin zone was sampled using a Γ-centered $3 \times 3 \times 3$ k-point mesh, while the electronic states were smeared using the Methfessel−Paxton scheme with a broadening width of 0.1 eV. A cutoff energy of 400 eV was chosen for the plane-wave basis expansion, and the atomic relaxation was continued until the Hellmann−Feynman forces acting on the atoms were less than 0.02 eV Å^{-1}. Periodic supercell geometries were employed to model the graphene surfaces with 6×4 unit cells, and a vacuum layer of 18 Å was added onto the graphene sheets.

3. Results and discussion

The pristine graphene and defective graphene models used for calculations are shown in Fig. 1. The pristine graphene surface (Fig. 1a) is inactive, with a very stable structure. To simulate the
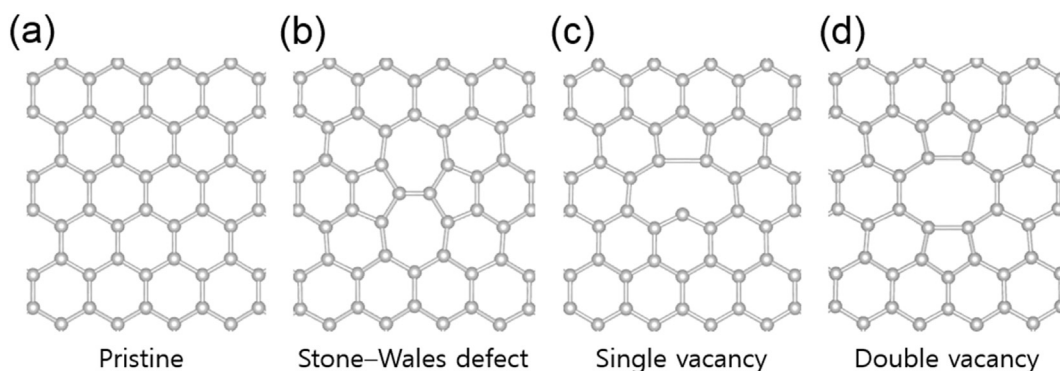

Fig. 1. Various graphene surface structures: (a) pristine, (b) Stone−Wales defect, (c) single vacancy, (d) double vacancy.