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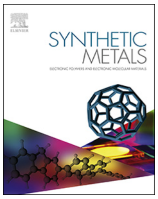

Fe/N_x clusters embedded in graphene with tunable properties for gas separation

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ABSTRACT

Increasing concerns about capture and separation of CO_2 and its impact on the global warming are motivating researchers to discover new materials and strategies for efficient CO_2 capture. Here, we explored the possibility of conductive Fe/N_x clusters embedded in graphene (Fe/N_x/G) as an adsorbent for electrocatalytically switchable CO_2 capture. Using density functional theory including long-range dispersion corrections, we investigated the adsorption process of CO_2 on Fe/N_x/G ($x = 0$, 2, and 4) systems with various charge states. We found that CO_2 molecule - forms weak interaction with the neutral Fe/N_x/G systems. On the contrary, the adsorption behavior of CO_2 molecule on the Fe/N_x/G systems can be significantly enhanced by adding extra charges into the Fe/N_x/G. Our results show that by removing the charges, CO_2 molecule automatically desorbs from Fe/N_4/G. Thus, by switching on/off the charges carried by Fe/N_x/G systems the CO_2 capture/release procedures can be easily controlled without any energy barrier. Moreover, these Fe/N_x/G systems are highly selective for separating CO_2 from its mixtures with methane, hydrogen, and nitrogen. These predictions open the route for the further studies of charge-modulated systems with switchable capture/release capabilities that present high selectivity for CO_2.

1. Introduction

The world is seeking new energy resources, because of the gradual reduction of fossil fuels, industrial evolution, and the fast increase of energy consumption in the recent years. In this respect, shale gas, which is mainly included of methane (CH_4), has demonstrated as a promising natural gas resource, because it is expected to remarkably provide the energy resource worldwide [1–3]. In shale gas, however, CH_4 is normally mixed with other gases, such as carbon dioxide (CO_2)- and steams. Therefore, it is essential to separate CO_2, which is the main impurity, from CH_4 before further usage of shale gas. Furthermore, CO_2 is considered a major part to the greenhouse effect, which is believed to have a large effect on worldwide warming [4–7]. - Hence, extensive researches have been conducted to pursue the effective methods for separation of CO_2 and CH_4. Among the present techniques, activated carbons [8], zeolites [9], clays [10], biosorbents [11], polymeric adsorbents [12], polymeric/inorganic hybrids [13], and silica-based mesoporous materials [14] have been suggested but represented low separation efficiencies [15]. On the other side, because of their large interior surface areas, good selectivity and excellent tunability, metal-organic frameworks (MOFs) have been proposed as favorable materials for CO_2 adsorption [16–22]. However, the difficult regeneration reaction due to the large adsorption energy, which generally demands high temperatures to release adsorbed molecule, considerably hinders their practical applications [23]. In this respect, there is a strong requirement for a major breakthrough in searching an efficient adsorbent for separating CO_2 from CH_4 mixture, which must provide the following aims: high capacity, good selectivity, long-term durability, fast uptake, reasonable low cost, and easy regeneration consistent with insignificant capacity loss on many capture/release cycles [15,24]. Recently, charge-modulated, selective and reversible CO_2 capture strategies have been suggested based on bare boron nitride sheet (BN-S) [25], carbon nanotubes (CNTs) with pyridinic-nitrogen [26], and hybrid BN-S and graphene (BN/G) [27] nanomaterials. However, BN-S is large-band gap semiconductor (~6.0 eV) [23,28,29] and it is not clear how to charge up pristine BN-S due to its insulating nature. Also, the synthesis of CNTs with pyridinic-nitrogen doping and hybrid BN/G nanomaterials are difficult to control in experiment [23]. Given this scenario, to overcome the problems of mentioned CO_2 capture strategies, in the present study, a new electrocatalytically switchable CO_2 capture method has been investigated. Graphene layer-embedded transition metals (TMs) and/or N atom (TM/N/G) have been represented to have technical

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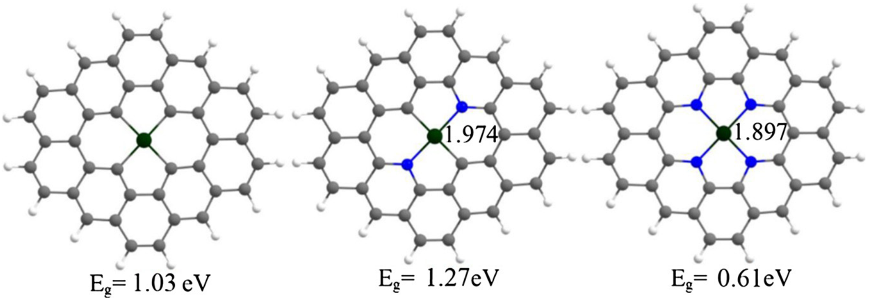

Fig. 1. Optimized structures of the considered $Fe/N_x/G$ (x = 0, 2, 4) systems. C, H, N and Fe atoms are shown in gray, white, blue, and green, respectively. The numbers are Fe-N bond lengths in angstrom. The HOMO-LUMO energy gap (E_g) values of the $Fe/N_x/G$ systems are also given. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

performance as electrocatalysts for oxygen reduction reaction (ORR) [30–38]. These materials are most often synthesized through heat-treating carbon supports in the presence of TM and N precursors [37,39–44]. X-ray photoelectron spectroscopy (XPS) analysis revealed that there are diverse TM-N clusters on the heat-treated TM/N/G materials [35,41–43,45]. Furthermore, density functional theory (DFT) calculations have been performed to explore the thermodynamic stability of the TM/N_x clusters embedded in carbon based nanomaterials [34,46–50]. These studies revealed that the formation of diverse N moieties alone in perfect graphitic layer is not energetically favorable [38,46,47]. In contrast, the formation of TM/N_x (TM = Fe and Co, x = 2 and 4) clusters embedded in graphene was found to be energetically favorable [47]. Moreover, previous works showed that the binding energy of the ORR species on the TM/N_x clusters could vary significantly with changes of the TM type (TM = Fe, Co, or Ni) and N coordination number [49,51–53]. However, although these materials have been widely studied in the ORR, the performance of $TM/N_x/G$ for application in other research area remains largely unknown. It is well-known that the modifications of nanomaterials by introduction of heteroatoms or transition metals in the nanomaterial framework can alter their properties in a large range [54–58]. Accordingly, the extensive exploration of novel nanostructures as practical gas-adsorbent materials for electrocatalytically switchable CO_2 capture inspired us to ask an interesting question: can the conductive $TM/N_x/G$ systems be utilized as good sorbent materials for electrocatalytically switchable CO_2 capture? In this respect, in the present work, by studying CO_2, CH_4, N_2, and H_2 adsorptions on the Fe/N_x clusters (x = 0, 2 and 4) embedded in graphene, we have explored the feasibility of using these materials for gas separation applications. In fact, this study is in continuation of our previous works where we have investigated the applications of TM/N_x clusters embedded in various nanomaterials as ORR catalysts and gas sensors [59–61]. We propose that the $Fe/N_x/G$ might perform well, as an experimentally possible material [62–64], for electrocatalytically switchable CO_2 capture because they have good electrical conductivity and large surface area.

2. Computational details

All quantum chemical calculations were carried out using the general theoretical and computational method based on all-electrons DFT with the generalized gradient approximation (GGA) in Perdew- Burke-Ernzerhof (PBE) [65] functional form and the 6-31 + G(d) basis set, as implemented in GAUSSIAN 09 [66]. Considering the standard PBE functional is incapable of giving an accurate description of weak interactions, we adopted a DFT + D (D stands for dispersion) method with the Grimme's van der Waals (vdW) correction in our calculations [67]. Accordingly, in the present work, this level of theory has been applied to calculate the electronic structures as well as simulating gas adsorption on the $Fe/N_x/G$ systems. For exploring the binding stability of the gas molecules quantitatively, we calculated the adsorption energy (E_{ad}) using the following equation:

$$E_{ad} = [E(Gas\text{-}Fe/N_x/G)\text{-}E(Gas)\text{-}E(Fe/N_x/G)] \quad (1)$$

where the E(Gas-$Fe/N_x/G$), E(Gas), and E($Fe/N_x/G$) are the total energies of Gas-$Fe/N_x/G$ complexes, the gas molecules, and $Fe/N_x/G$ clusters, respectively. Thus, negative E_{ad} herein represents that the adsorption system is energetically more favorable than the isolated systems. The adsorption energies have also been corrected for basis set superposition error (BSSE), $E_{ad}^{Corr} = E_{ad} + BSSE$, using the standard counterpoise correction method of Boys and Bernardi [68]. Further, the natural bond orbital (NBO) analysis was used to obtain the given charge transfer in this study [69].

3. Results and discussion

3.1. Geometry and electronic properties of pristine $Fe/N_x/G$

We have performed full geometry optimizations for the $Fe/N_x/G$ systems with the chemical formula $C_{36}H_{16}$-Fe-N_x. The Fe/N/C atomic ratio of 1/4/36 is based on recent experimental study [70] and also a recent low-temperature scanning tunneling microscopy (STM) [71]. Moreover, the sufficiency of this size of $TM/N_x/G$ systems has been demonstrated recently for ORR applications [62]. However, the model size of $Fe/N_x/G$ system has broken σ- bonds of carbon atoms at the edge which were saturated with hydrogen atoms to avoid boundary effects [72]. The optimized structures of the $Fe/N_x/G$, shown in Fig. 1, represent that the clusters are completely planar. This is in agreement with experimental results where the STM and scanning tunneling spectroscopy (STS) analyses all suggest that the Fe/N_x center is in the plane of graphitic layer [70]. Harmonic vibrational frequencies were performed at the PBE/6-31 + g(d) level of theory to confirm that the structures obtained corresponded to energetic minima. The calculated harmonic frequencies show that the structures are a true stationary point on the potential energy surface (PES), with the values being in the range of 31.8–3194.7 cm^{-1} for $Fe/N_0/G$, 27.5–3199.1 cm^{-1} for $Fe/N_2/G$, and 35.5–3203.5 cm^{-1} for $Fe/N_4/G$. Our results reveal that the Fe—N bond lengths of the $Fe/N_2/G$ and $Fe/N_4/G$ systems -are 1.974 and 1.897 Å, respectively. The energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), (HOMO-LUMO energy gap, E_g) for the $Fe/N_x/G$ systems are also reported in Fig. 1. It is obvious that the values of E_g could vary significantly with changes of nitrogen coordination number. Among the considered systems, the $Fe/N_4/G$ with the lowest E_g shows the highest conductivity. To verify the role of TM as well as number of N atom on the electronic properties of $Fe/N_x/G$ systems, the corresponding total and partial density of states (TDOS-PDOS) are plotted and represented in Fig. 2. This is consistent with the result of band structure analysis of Fe/N_4 center embedded in graphene layer [73], which revealed that the $Fe/N_4/G$ structure exhibits half-metallic character with accessible states near the Fermi level in both majority and minority spin channels. PDOS analysis across the Fe center show sharp resonance states both sides near the Fermi level representing hybridization of Fe center with the states of graphitic lattice. This is in agreement - with the result of STM simulation of Fe/N_4 center embedded in graphene layer, which revealed that the metal center remarkably modifies the DOSs of near atoms [71]. Fig. 2 also shows that