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N-doped peanut-shaped carbon nanotubes for efficient CO₂ electrocatalytic reduction



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ABSTRACT

Using first principles calculations and the computational hydrogen electrode (CHE) model, we present the first systematic study of CO₂ electrocatalytic reduction (CO₂ER) on recently synthesized peanutshaped carbon nanotube (FP5N) as well as N-doped FP5N structures. We find FP5N to be metallic with the symmetry of D5h point group. In addition, nitrogen doping in FP5N significantly reduces the overpotential of CO₂ER. In contrast to graphitic N that reduces CO₂ into CO with an overpotential of 0.65 V, the pyrrolic N, octatomic N and pyridinic N in FP5N convert CO₂ into CH₃OH with even lower overpotentials of 0.52, 0.52 and 0.60 V, respectively. These values are comparable to those of industrial transition metal catalysts and show that N-doped peanut-shaped carbon nanotubes can outperform conventional N-doped carbon nanomaterials in CO₂ reduction.

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1. Introduction

The excess emission of CO₂, due to growing utilization of fossil fuels, has adversely affected the natural carbon cycle, causing global warming [1]. To mitigate this greenhouse effect, considerable efforts are being made to convert CO₂ into valuable industrial chemicals [2] by using electrochemical, biochemical, thermochemical, and photochemical methods [3–6]. Among these various approaches, CO₂ electrocatalytic reduction (CO₂ER) has received much attention because of its moderate efficiency, controllable selectivity, and ambient operating environment [1,7]. It has been experimentally shown that heterogeneous catalysts can enhance CO₂ER with high selectivity and energy efficiency as well as low deactivation after long term use [8–10]. First principles simulations have also been successfully carried out to illuminate the mechanisms of CO₂ catalytic reductions at the atomic level and identify the reaction intermediates and final products [9,11]. This has

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resulted in a better understanding of the catalytic performance and hence in the design of new catalysts.

The widely used catalysts for CO₂ reduction are metals, metal oxides, metal chalcogenides and metal–organic complexes [1,11]. However, these metal-containing catalysts are costly and their energy efficiency is limited. Therefore, it is highly desirable to find new low-cost metal-free alternatives for efficient CO₂ reduction [11]. Carbon nanomaterials as metal-free catalysts for CO₂ER have attracted increasing attention because of their low cost, availability, large surface area, and flexibility in heteroatom doping (nitrogen, boron etc.) [9]. Although carbon nanotubes (CNTs) have been used as catalyst carriers in many cases [10,12–14], only a few of these have been directly used as the catalysts for CO₂ER. Incorporation of nitrogen dopants into CNTs has led to high electrocatalytic activity for oxygen reduction [15] and efficient CO₂ reduction [10,16].

Among the large family of CNTs, peanut-shaped carbon nanotubes (PSNTs) are of particular interest because of their exotic geometry with large specific surface area, negative and varying Gaussian curvature, and the existence of polarized charges [16]. Thus, PSNTs could have superior catalytic performance when used as the catalysts for CO₂ER because they can introduce *curvature*-



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induced catalytic selectivity. Polarized charges can further provide a special environment for CO₂ reduction. In addition, PSNTs can be synthesized though photopolymerization [17–19], mechanical pressure [20,21], high temperature treatment [20], and electronbeam (EB) irradiation [22,23]. Among the experimentally studied PSNTs, FP5N is found to be energetically stable with high symmetry [24], sharing structural features of C₆₀ cages and 1D uneven peanutshaped structures [25,26]. In FP5N, there exist 5-, 6- and 8membered rings where the carbon atoms have much more complicated bonding environment than that in CNTs. This offers more flexibility to tune the reactivity compared to conventional CNTs, and may improve its catalytic performance. Therefore, in this work, we focus on N-doped FP5N as a catalyst for the electrocatalytic reduction of CO₂. Based on density functional theory (DFT) and the computational hydrogen electrode (CHE) model [27], we systematically studied the electronic structures, thermodynamic potentials, and reaction pathways of N-doped FP5N, and its selectivity of different products including CO, HCOOH, CH₃OH, HCHO and CH₄ [28–30]. In order to better understand the effect of the Gaussian curvature on CO₂ER, we further explored a new 2D carbon allotrope consisting of 5-(penta), 6-(hexa) and 8-(octa) membered carbon rings (named as "phographene" hereafter), which is similar to the case with FP5N. We find that the differing charge density distributions are responsible for the corresponding catalytic performances of FP5N and phographene.

2. Computational methods

All calculations are carried out using density functional theory (DFT) and Projector Augmented Wave (PAW) potential [31] as implemented in the Vienna Ab initio Simulation Package (VASP) [32]. Perdew-Burke-Ernzerhof (PBE) [33] exchange-correction functional within the generalized gradient approximation (GGA) is used to describe interactions between electrons. The plane-wave cutoff energy of 520 eV is adopted in all calculations. The convergence criteria of total energy and force components are set at 0.0001 eV and 0.01 eV/Å, respectively. A vacuum space of 15 Å in the radial directions (y and z) is used to avoid mirror interactions. The reciprocal space is sampled using a $8 \times 1 \times 1$ Monkhorst-Pack [34] mesh. Bader analysis [35,36] is applied to calculate the partial atomic charges. Density of states (DOS) is calculated using Gaussian smearing with a broadening factor of 0.01 eV. The binding energy E_b of adsorbed species, A on a substrate is calculated as follows, where E_{*A} is the total energy of the system after intermediate A is adsorbed on the active site, E_* is the energy of the catalyst, and E_A represents the energy of the single A species. The binding energy is defined to be positive, which means the more positive it is, the stronger the binding is.

Computational hydrogen electrode (CHE) model [27] is used to calculate the free energy changes of the proton-coupled electron transfer (PCET) steps and to elucidate the electrochemical reaction pathways. More details can be found in the Supplementary Material (SM), Text S1.

3. Results and discussion

3.1. Geometric structure of FP5N

The geometry of FP5N can be derived by using generalized Stone-Wales (GSW) transformation based on the T3 structure [37,38]. The optimized geometry of FP5N is given in Fig. 1a and b. It has the point group of D5h with an axial lattice constant of 8.1 Å, which is larger than the diameter (7.1 Å) of C₆₀ cage, resulting from the elongation along the tube axis during coalescence. The C–C bond length in FP5N ranges from 1.36 to 1.50 Å, which is different

from the values of 1.45 and 1.41 Å in C_{60} fullerene [39,40]. Moreover, the C–C bond length is also different from that of single wall carbon nanotubes (SWNTs), although PSNTs share some geometrical features with C_{60} and SWNTs.

From a topological viewpoint, the linking region in FP5N, as indicated by a rectangular dashed line in Fig. 1d, has five octagons, besides pentagons and hexagons. Different from SWNTs, where Gaussian curvature is zero [41], FP5N contains both positive and negative Gaussian curvatures that can influence the electronic states of the PSNT, resulting in the Tomonaga-Luttinger liquid (TLL) behavior [16]. In addition, the average binding energy of FP5N is 8.91 eV per atom, which is 0.06 eV lower than that of the C_{60} molecule.

Based on the calculated band structure and DOS, as given in Fig. 1c, we see that FP5N is metallic as the partially occupied bands cross the Fermi level. The Young's modulus of FP5N is calculated to be 333 GPa by computing the variation of total energy with strain, which is about a quarter of the CNT [42]. The details are given in SM, Text S2 and Fig. S1.

3.2. Screening nitrogen doping sites

When one N atom is substitutional-doped into FP5N, there are four chemically nonequivalent doping sites, namely α , β , γ , and δ , as shown in Fig. 1b. To determine the most preferred doping site, we calculated the total energies for the four N-doped FP5N configurations mentioned above. The configuration with N on γ site is found to be energetically the most stable configuration which is lower in energy by 0.04, 0.07 and 0.17 eV than the α , β and δ sites, respectively (see Fig. S2 for details). The calculated band structure of this most stable structure of N-doped FP5N is given in Fig. 2a, which shows that the metallic feature of FP5N still remains after N doping.

When more N atoms are substitutional-doped into FP5N, the possible configurations can be obtained following the Czerw model for CNTs [43], where three C atoms are replaced by three N atoms with a shared carbon vacancy. There are four kinds of C vacancy sites in FP5N, which leads to 10 different possible N sites near the vacancies. These N doping sites can be categorized into three different types: pyridinic N (in the hexagonal ring), pyrrolic N (in the pentagonal ring) and octatomic N (in the octatomic ring), as shown in Fig. 2d. Each of these sites is unique in the N-doped FP5N. In order to screen the preferred electrocatalyst candidates, we have studied all these catalytic sites by calculating the free energy changes for both *COOH and *OCHO radicals in the first protoncoupled electron transfer (PCET) step. We find that the free energy change of *COOH adsorption is much smaller than that of *OCHO, suggesting that the first intermediate PCET step for CO₂ER is *COOH. The geometric structure of *COOH adsorbed on N-FP5N with COOH on top of the C atom near the graphitic N is shown in Fig. 2b and c. Meanwhile, by comparing the free energy changes of the first PCET step in all the catalytic sites, we have determined the site with the best catalytic performance among the four kinds of sites considered (see Fig. 2d).

3.3. CO₂ electrocatalytic reduction

Next, we studied all the pathways of CO₂ER on these active sites to determine the potential-determining steps as well as the distribution of products based on CNT and graphene system [11,44]. Taking into account the zero-point energy, vibrational entropy and solvent correction, we calculated the corresponding free energy diagram for the lowest energy pathways of CO₂ER to CO or CH₃OH. The results are plotted in Fig. 3a.

The pristine FP5N has the highest free energy barrier for the first



Fig. 1. (a) Front and (b) side views of FP5N. (c) Electronic band structure and DOS of FP5N. (d) Side view of a 1 × 1 × 3 supercell of FP5N. (A colour version of this figure can be viewed online.)



Fig. 2. (a) Electronic band structure and DOS of the N-doped FP5N structure. (b) Front and (c) side views of the *COOH adsorbed on N-doped FP5N. (d) Schematic diagram of different N doping catalytic sites on FP5N. (A colour version of this figure can be viewed online.)

step of CO₂ adsorption, which hinders CO₂ER. This is consistent with the experimental results in graphene [9] and CNT [10]. As for N doped graphene, the catalytic site is not on the N site but on the neighboring highly positively charged C atom, determined by using Bader charge analysis (Fig. S3). This agrees well with the previous study which found that the electrocatalytically active sites were highly positive carbon atoms, adjacent to the electronegative N

dopants [45], similar to the situation in graphene [9] and CNT [44]. The potential-limiting step (*COOH \rightarrow *CO) for graphitic N is 0.65 eV *CO prefers to decompose to carbon monoxide rather than getting further hydrogenated because of the much more negative free energy change of *CO \rightarrow CO (g). Even though the energy change (0.65 eV) for the graphitic N is larger than that of the pyrrolic N (0.52 eV), pyridinic N (0.52 eV) and octatomic N (0.60 eV), it



Fig. 3. (a) Free energy diagrams of different catalytic sites for the pristine and N-doped FP5Ns. (b) Configurations of the intermediates *COOH, *CO, *CHO,*HCOH, and *H₂COH for CO₂ER on the octatomic N. (A colour version of this figure can be viewed online.)

still lowers the overpotential by 0.92 V as compared to that in the pristine FP5N, which produces CO at a higher overpotential of 1.57 V. This demonstrates significant improvement of CO₂ER performance by N doping. Furthermore, the binding energy of *COOH to the graphitic N (2.67 eV) is higher than that of the pristine FP5N (1.58 eV). This suggests that *COOH binds more strongly on graphitic N.

As for the CO₂ER, the first electron transferred to the chemically stable CO₂ usually possesses a high overpotential in the first PCET step [46]. On the contrary, in our case, the free energy changes of $CO_2 \rightarrow ^*COOH$ for pyrrolic N, octatomic N and pyridinic N are only 0.04, -0.01 and 0.06 eV, respectively. These free energy changes are rather small in contrast to the pristine FP5N (1.57 eV), the graphitic N (0.48 eV) and many more promising electrocatalysts, including transition metal Cu (0.41 eV) [47]. The binding energies of *COOH in the pyrrolic N, octatomic N and pyridinic N are 3.12, 3.17 and 3.10 eV, respectively, which are all higher than that of graphitic N. The reason is that the pyrrolic N, pyridinic N and octatomic N are rich in electrons, which bind CO₂ while electrons in graphitic N are located in the π^* antibonding orbital, making them less accessible for CO₂ binding [10]. The strong binding of CO₂ to the pyrrolic N, pyridinic N and octatomic N sites accounts for the small free energy change for the first step: $CO_2 \rightarrow *COOH$. The free energy changes of *CO \rightarrow CO (g) in the pyrrolic N, octatomic N and pyridinic N are all larger than that of $*CO \rightarrow *CHO$, indicating *CO is likely to produce *CHO, rather than CO gas, and gets further hydrogenated.

In the next step, we have determined that *CHO tends to form *HCOH rather than *H₂CO. The potential-limiting steps for pyrrolic

N, octatomic N, and pyridinic N are *H₂COH \rightarrow CH₃OH (g), *CHO \rightarrow *HCOH, and *CO \rightarrow *CHO, respectively. The corresponding overpotentials of CO₂ER are at least be 0.52, 0.52 and 0.60 V, respectively, which can make the whole reaction pathway spontaneous and exergonic. For the octatomic N, all intermediates of CO₂ER pathways are CO₂ (g) \rightarrow *COOH \rightarrow *CO \rightarrow *CHO \rightarrow *HCOH \rightarrow *H2OH \rightarrow CH₃OH (l), as shown in Fig. 3b.

The final products for the pyrrolic N, octatomic N and pyridinic N are all CH₃OH, which is rare for all kinds of N-doped carbon nanomaterials [9,10] as catalysts in CO₂ER. The appearance of the final product CH₃OH in N-doped FP5N for CO₂ER is due to high free energy change of $*CO \rightarrow CO$ (g) that makes *CO get further hydrogenated. In N-doped graphene [9] and CNT [10,44], the free energy barrier is rather low or even nonexistent, leading to direct decomposition to CO (g). Sun et al. used Mo-Bi bimetallic chalcogenide as an electrocatalyst for CO₂ reduction into CH₃OH with an overpotential of 0.7 V [48]. Among the metal electrocatalysts studied, copper is the only metal that is capable of reducing CO_2 to significant amounts of hydrocarbons and oxygenates within a range of overpotentials (0.9–1.1 V) [29,30]. It is worth noting that the overpotential for metal-free pyrrolic N and octatomic N catalysts to convert CO₂ into CH₃OH is comparable to that of metals, namely 0.52 V [48,49]. The side reaction analysis is demonstrated in SM, Text S3.

3.4. CO₂ER comparison and electronic structure analysis

To better understand the underlying effect of the Gaussian



Fig. 4. (a) Geometric structure and (b) free energy diagram for different catalytic sites for the 2D phographene. (c) Partial charge density of the N-doped FP5N for the octatomic N (site 1) and pyridinic N (site 2). (A colour version of this figure can be viewed online.)

curvature on CO₂ER, we construct a 2D planar carbon allotrope named as phographene (containing pentagonal, hexagonal and octagonal carbon rings same as those in FP5N), as a model (see Fig. 4a). Following the same procedure as for the N-doped FP5N, calculations are carried out for N-doped phographene. Taking into account the zero-point energy, vibrational entropy and solvent correction, we calculated the corresponding free energy diagram for the lowest energy pathways of CO₂ER to CO or to CH₃OH. The results, given in Fig. 4b, demonstrate that the final products of the pyrrolic N, octatomic N and pyridinic N in phographene are all CH₃OH, which is same as that found in N-doped FP5N. This indicates that rolling the planar phographene to FP5N with positive and negative Gaussian curvature will not affect the final products in CO_2ER . The overpotential of the pyrrolic N (0.52 V) in phographene is same as that in FP5N, while it is larger than that for octatomic N and pyridinic N sites. To explain these results, we used partial charge density to study the three kinds of N-doped catalysts. This reveals that the electron density of the interior and exterior region of the pyrrolic N site in FP5N illustrated in Figs. S4a-b is same as that in pyrrolic N site for planar phographene, illustrated in Figs. S4c-d. Thus, rolling the planar phographene into FP5N would not change the electron density distribution of pyrrolic N site. This finding from partial charge density contributes to the same overpotential and same final products for pyrrolic N sites in phographene as that in FP5N. However, as for the octatomic N and pyridinic N sites, the result of partial charge density shows that the electron density in the exterior region is larger than that in the interior region of FP5N, as shown in Fig. 4c. This favors the activation of CO₂ to form adsorbed *COOH, suggesting a better catalytic performance for CO₂ER. Hence, the performance of CO₂ER for the octatomic N and pyridinic N in FP5N is better than that in the planar phographene, because the varying Gaussian curvature in FP5N contributes to the difference of electron density between the exterior and interior region of the tube. The effect of doping other atoms including B, S, P in FP5N on CO₂ER is also studied and the details can be found in Text S4 and Fig. S6 of SM.

4. Conclusions

In this work, we have systemically studied the geometric

structures, electronic and mechanical property of FP5N as well as the electrocatalytic reduction of CO₂ on the N-doped FP5N by using first principles calculations combined with the CHE model. FP5N is found to be metallic with a geometry having the D5h point group. Nitrogen doping makes FP5Ns catalytically active and selective for CO₂ electrocatalytic reduction. Compared to the widely used metal Cu for CO₂ conversion, the pyrrolic N, octatomic N and pyridinic N sites in N-doped FP5N exhibit lower overpotential of 0.52, 0.52 and 0.60 V for CH₃OH production. This result is outstanding for carbon nanomaterials. Note that graphitic N site is prone to reduce CO₂ directly into CO at an overpotential of 0.65 V. Comparing CO₂ER in both the N-doped FP5N and N-doped phographene, we conclude that FP5N with octatomic N and pyridinic N, respectively, outperforms the planar N-doped phographene because the varying Gaussian curvature of FP5N results in more charge density on the exterior wall of the peanut-shaped nanotube, which not only shares the features of fullerene cage, but also those of CNT. Our study shows that the N-doped peanut shaped carbon nanotube is a promising candidate to replace metal catalysts for effective CO₂ reduction.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbon.2019.05.078.

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