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# Silicon-coordinated nitrogen-doped graphene as a promising metal-free catalyst for N<sub>2</sub>O reduction by CO: a theoretical study†

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Metal-free catalysts for the transformation of N<sub>2</sub>O and CO into green products under mild conditions have long been expected. The present work proposes using silicon-coordinated nitrogen-doped graphene (SiN<sub>4</sub>G) as a catalyst for N<sub>2</sub>O reduction and CO oxidation based on periodic DFT calculations. The reaction proceeds *via* two steps, which are N<sub>2</sub>O reduction at the Si reaction center, producing Si–O\*, which subsequently oxidizes CO to CO<sub>2</sub>. The N<sub>2</sub>O reduction occurs with an activation energy barrier of 0.34 eV, while the CO oxidation step requires an energy of 0.66 eV. The overall reaction is highly exothermic, with a reaction energy of –3.41 eV, mostly due to the N<sub>2</sub> generation step. Compared to other metal-free catalysts, SiN<sub>4</sub>G shows the higher selectivity because it not only strongly prefers to adsorb N<sub>2</sub>O over CO, but the produced N<sub>2</sub> and CO<sub>2</sub> are easily desorbed, which prevents the poisoning of the active catalytic sites. These results demonstrate that SiN<sub>4</sub>G is a promising metal-free catalyst for N<sub>2</sub>O reduction and CO oxidation under mild conditions, as the reaction is both thermodynamically and kinetically favorable.

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## 1. Introduction

Nitrous oxide (N<sub>2</sub>O) and carbon monoxide (CO) are pollutant gases which are exhausted from various combustion sources, such as vehicles and electric power plants. Because removing them requires high temperatures and large amounts of energy, catalytic materials have been extensively explored for eliminating them more efficiently. The catalytic reaction of N<sub>2</sub>O and CO, namely, the oxidation of CO by N<sub>2</sub>O or the reduction of N<sub>2</sub>O by CO, is one of the useful techniques for converting N<sub>2</sub>O and CO into less harmful products *i.e.*, N<sub>2</sub> and CO<sub>2</sub>. In a direct N<sub>2</sub>O (g) + CO (g) → N<sub>2</sub> (g) + CO<sub>2</sub> (g) reaction, the activation barrier of 2 eV and the reaction energy of –3.6 eV were determined by a density functional theory (DFT) calculation.<sup>1</sup> Although the reduction of N<sub>2</sub>O by CO is an exothermic reaction, it is difficult to promote in the gas phase due to the large activation energy (*E*<sub>a</sub>) required.<sup>2,3</sup>

In the literature, various metals and metal ions such as Pt<sup>+</sup>, Ir<sup>+</sup>, Os<sup>+</sup>, Fe<sup>+</sup>, Ca<sup>+</sup>, Ge<sup>+</sup>, Sr<sup>+</sup>, Ba<sup>+</sup>, Eu<sup>+</sup>, and Yb<sup>+</sup> have been explored

for use as catalysts in the elimination of CO and N<sub>2</sub>O at low temperatures.<sup>4,5</sup> Also, the reduction of N<sub>2</sub>O by CO have been investigated on metal cluster catalysts such as Pt<sub>*n*</sub><sup>–</sup> (*n* = 3–4),<sup>6</sup> neutral Rh<sub>*n*</sub> (*n* = 10–28),<sup>7</sup> neutral Pt<sub>*n*</sub> (*n* = 4–12),<sup>8</sup> Pt<sub>*n*</sub><sup>+</sup> (*n* = 6–8),<sup>9</sup> Cu anions,<sup>10</sup> Cu<sub>*n*</sub> (*n* = 4–15),<sup>1</sup> Ag<sub>7</sub>Au<sub>6</sub> clusters,<sup>11</sup> *etc.* Although metal-based catalysts perform well when eliminating CO and N<sub>2</sub>O at low temperatures, their mass-scale uses are economically limited due to their cost. Various catalytic materials, such as metals on supports, metal complexes, metal oxides and metal-free catalysts have been sought in order to reduce costs while retaining good catalytic performance.<sup>12–17</sup>

Recently, nitrogen-doped graphene (NG) became a promising metal-free catalyst; it had been proposed for various catalytic applications, such as electrochemical, oxidation and other reactions.<sup>18–21</sup> A four pyridinic-N defect with a di-vacancy in graphene (*i.e.* 4N + DV) is one of the pyridinic forms that can be drawn from past experiments.<sup>22</sup> The pyridinic-N defect provides a greater chemical reactivity than the graphitic-N and it can trap a single metal atom, such as Mg, Al, Ca, Ti, Cr, Mn, and Fe.<sup>22</sup> This 4N + DV defective graphene (N<sub>4</sub>G) has a porphyrin-like core. Varying doping species at the porphyrin-like core can fine-tune its properties for desired applications. For instance, FeN<sub>4</sub>G, CoN<sub>4</sub>G, NiN<sub>4</sub>G, and MnN<sub>4</sub>G have been applied for the oxygen reduction reaction (ORR) applications.<sup>23–26</sup> Later, the possible use of FeN<sub>4</sub>G as a catalyst for NO reduction *via* the (NO)<sub>2</sub> adsorption mechanism was suggested by the periodic DFT method.<sup>27</sup> Very recently, water dissociation on MN<sub>4</sub>G (M = Mg, Ba, Ti) was theoretically studied by Liu

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*et al.*<sup>28</sup> They showed that Mg, Ba, Ti are energetically stable on the surface and  $\text{TiN}_4\text{G}$  displayed promising catalytic properties for  $\text{H}_2\text{O}$  dissociation.

For applications involving  $\text{N}_2\text{O}$  and CO removal, p-block element doped into carbon and other support materials have been used as catalysts.<sup>13,15–17,29</sup> Since Si is the second most abundant element on Earth,<sup>30</sup> it is attractive to incorporate with other elements for applying in various applications. From previous experimental work, Si coordinated with four nitrogen atoms has been proposed as the active site in Si-porphyrin and Si-corroles.<sup>31,32</sup> Si-porphyrin was successfully synthesized<sup>32</sup> and it has been further applied in a photochemical oxygenation of alkenes,<sup>30</sup> water oxidation to hydrogen peroxide,<sup>33</sup> and dye-sensitized solar cell applications.<sup>34</sup> For Si-corroles, Si-porphyrine derivatives, provides good luminescence properties and they have been applied as a sensor for  $\text{F}^-$  detection.<sup>31</sup> Interesting work has been reported recently by Tang *et al.*; they found that Si-coordinated nitrogen-doped graphene ( $\text{SiN}_4\text{G}$ ), which is a metal-free catalyst, had catalytic properties that promoted CO oxidation by  $\text{O}_2$ .<sup>35</sup> These reports noted that Si atoms doped into 2D materials are a reactive dopant for CO and  $\text{N}_2\text{O}$  gases. However, it is unclear why a Si dopant, which is a non-metal atom, was specifically reactive to those gases.

Moreover, to the best of our knowledge, Si doped into  $\text{N}_4\text{G}$  for the reduction of  $\text{N}_2\text{O}$  by CO has not been studied so far. Thus, we are motivated to ask: How feasible is this metal-free catalyst  $\text{SiN}_4\text{G}$  for the reduction of  $\text{N}_2\text{O}$  by CO? Is it possible to use this catalyst in a low temperature range? In this work, these questions are answered systemically using a plane-wave-based DFT investigation. The gas adsorption and detailed reaction mechanisms were examined. Moreover, the performance of  $\text{SiN}_4\text{G}$  is compared with other catalysts from the literature in order to determine the feasibility of using this catalyst for the reduction of  $\text{N}_2\text{O}$  by CO. The results will be valuable for developing low cost catalysts for pollutant gas abatement applications.

## 2. Method

The gas adsorption and the reaction mechanism of reduction of  $\text{N}_2\text{O}$  by CO over  $\text{SiN}_4\text{G}$  were examined by using plane-wave-based DFT calculations implemented in the Vienna *ab initio* simulation package (VASP version 5.4.1).<sup>36,37</sup> The projector-augmented wave (PAW)<sup>38</sup> with a generalized gradient approximation (GGA) refined by Perdew, Burke and Ernzerhof (PBE)<sup>39</sup> was used in this work. Grimme's DFT-D3 was applied for the dispersion contribution.<sup>40</sup> The  $1 \times 10^{-5}$  eV per cell and  $5 \times 10^{-3}$  eV  $\text{\AA}^{-1}$  were set as the energy- and force-convergence parameters, respectively. An energy cutoff of 400 eV and a spin-unrestricted calculation were applied in all cases. The  $\text{SiN}_4\text{G}$  slab was constructed by placing one Si at the  $\text{N}_4$  center of a  $(5 \times 5)$  slab of graphene with  $a = 12.4$   $\text{\AA}$  and  $b = 12.2$   $\text{\AA}$ . The slab was separated by 15  $\text{\AA}$  of vacuum. This size of the simulated cell is large enough to prevent interfering of adsorption interaction by its replicas. All atoms in the cell were relaxed during the calculations. After the optimized  $\text{SiN}_4\text{G}$  was obtained, the simulated cell was fixed during gas adsorption and reaction

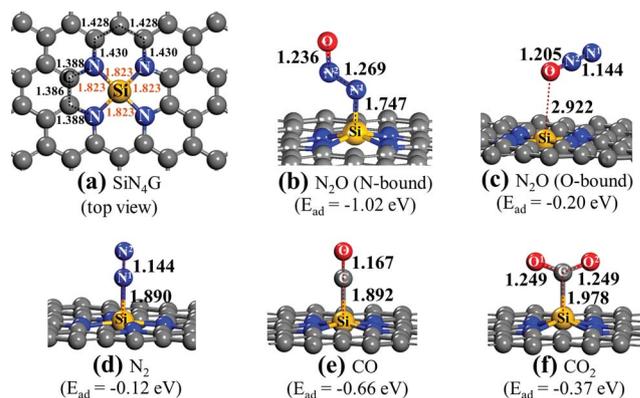


Fig. 1 Structures of (a)  $\text{SiN}_4\text{G}$ , (b)  $\text{SiN}_4\text{G}/\text{N}_2\text{O}$  (N-bound), (c)  $\text{SiN}_4\text{G}/\text{N}_2\text{O}$  (O-bound), (d)  $\text{SiN}_4\text{G}/\text{N}_2$ , (e)  $\text{SiN}_4\text{G}/\text{CO}$  and (f)  $\text{SiN}_4\text{G}/\text{CO}_2$ . Selected bond lengths ( $\text{\AA}$ ) and  $E_{\text{ad}}$  values of adsorbed gas molecules on the catalyst are given.

mechanism calculations. A top view of a center site of  $\text{SiN}_4\text{G}$  is illustrated in Fig. 1a. The isolated gas molecule was placed in the  $15 \text{\AA} \times 15 \text{\AA} \times 15 \text{\AA}$  box. The Monkhorst–Pack grids of  $5 \times 5 \times 1$  and  $1 \times 1 \times 1$  were applied for slab and isolated gas structures, respectively.

The transition state (TS) of each elementary step was calculated from the climbing-image nudged elastic band (CI-NEB)<sup>41,42</sup> and the dimer method.<sup>43,44</sup> The criterion of the force convergence threshold was  $0.025 \text{ eV \AA}^{-1}$ . Each TS structure was confirmed by its single imaginary frequency. The projected density of state (PDOS), electron density difference and Bader charge analyses<sup>45,46</sup> were elucidated in this work.

## 3. Results and discussion

### 3.1 Gas adsorption on $\text{SiN}_4\text{G}$

First, the adsorption properties of reactants and products over  $\text{SiN}_4\text{G}$  are discussed. The adsorption energy ( $E_{\text{ad}}$ ) is calculated by

$$E_{\text{ad}} = E_{\text{adsorbate-substrate}}^{\text{complex}} - E_{\text{substrate}}^{\text{isolated}} - E_{\text{adsorbate}}^{\text{isolated}} \quad (1)$$

where  $E_{\text{adsorbate-substrate}}^{\text{complex}}$ ,  $E_{\text{substrate}}^{\text{isolated}}$  and  $E_{\text{adsorbate}}^{\text{isolated}}$  are the total energies of the gas adsorbed the  $\text{SiN}_4\text{G}$  complex, bare  $\text{SiN}_4\text{G}$  surface and isolated gas, respectively. A negative  $E_{\text{ad}}$  value means stronger adsorption and greater stability of the gas-adsorbed surface complex. The calculated  $E_{\text{ad}}$  values and relevant interatomic distances of the adsorbed  $\text{N}_2\text{O}$ ,  $\text{N}_2$ , CO and  $\text{CO}_2$  on  $\text{SiN}_4\text{G}$  are given in Fig. 1.

Fig. 1a shows the top view structure of the optimized bare  $\text{SiN}_4\text{G}$  sheet. The bond distances around the core site of  $\text{SiN}_4\text{G}$  are given. The Si atom is surrounded by two five-membered rings and two six-membered rings. The four Si–N bond lengths are equivalent at 1.823  $\text{\AA}$ . According to the calculated  $E_{\text{ad}}$  values expressed in Fig. 1, the order of the binding strength of the four gas species on the catalyst is  $\text{N}_2\text{O} > \text{CO} > \text{CO}_2 > \text{N}_2$ . The linear  $\text{N}_2\text{O}$  gas strongly adsorbs on the Si atom with the N-bound mode resulting in a bent N–N–O conformation and the



calculated  $E_{\text{ad}}$  is  $-1.02$  eV (see Fig. 1b). Both N–N and N–O bonds are lengthened from  $1.146$  Å and  $1.200$  Å (free  $\text{N}_2\text{O}$  gas) to  $1.269$  Å and  $1.236$  Å, respectively. The formed coordination bond between N and Si is  $1.747$  Å. In Fig. 1c, the O-bound mode is less favorable for  $\text{N}_2\text{O}$  adsorption. In the  $\text{N}_2$  case, it shows the least binding stability with  $E_{\text{ad}} \sim -0.12$  eV as shown in Fig. 1d. It is worth to note that the attached  $\text{N}_2$  at Si site in Fig. 1d is slightly less stable than the detached  $\text{N}_2$  ( $E_{\text{ad}} = -0.17$  eV) presented in Fig. S1a of ESI.†

For CO and  $\text{CO}_2$ , their carbon atoms attach to the Si atom and their binding energies are  $-0.66$  and  $-0.37$  eV, respectively. By comparing their  $E_{\text{ad}}$  values, we can see that the CO adsorption in Fig. 1e is stronger than the  $\text{CO}_2$  adsorption in Fig. 1f. The end-on configuration of adsorbed CO over  $\text{SiN}_4\text{G}$  agrees well with literature.<sup>35</sup> The C–O bonds are activated in both CO and  $\text{CO}_2$  compared with the free molecules. The  $E_{\text{ad}}$  values from the prior work are  $-0.55$  eV and  $-0.26$  eV for CO and  $\text{CO}_2$  adsorption, respectively. Our calculated  $E_{\text{ad}}$  values are slightly stronger than those of the previous calculations because the dispersion correction is included in this work. As a result, the Si site moves along the out-of-plane direction when it chemically adsorbs molecules. On the other hand, the  $\text{SiN}_4\text{G}$  sheet is not changed when it binds with gas through physisorption interaction (see Fig. 1c).

A different order of the adsorption energies was observed in the adsorption of these gasses on Si-doped graphene (SiG) studied by Gholizadeh and Yu.<sup>15</sup> Their calculated  $E_{\text{ad}}$  values are small and are in the range of  $-0.2$  eV to  $-0.15$  eV and the adsorption strength follows the order of  $\text{SiG}/\text{CO} > \text{SiG}/\text{CO}_2 > \text{SiG}/\text{N}_2\text{O} > \text{SiG}/\text{N}_2$ . Therefore, the coordinated Si with nitrogen at the active center site in the present  $\text{SiN}_4\text{G}$  significantly enhances the adsorption ability and changes the order of these gas adsorptions. Due to the distinctly stronger interaction of  $\text{N}_2\text{O}$  on  $\text{SiN}_4\text{G}$  when compared to CO on  $\text{SiN}_4\text{G}$ , the  $\text{N}_2\text{O}$  reduction would occur first, rather than the CO oxidation. Therefore, the present results of these adsorption energies also support the claim that the reaction cycle can proceed as the two sequential steps: (1)  $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^*$  and (2)  $\text{O}^* + \text{CO} \rightarrow \text{CO}_2$ , respectively. The  $\text{CO}_2$  and  $\text{N}_2$  products can be easily desorbed due to their low binding strength. This advantage can prevent catalyst poisoning by the products and allows the active site to get ready to react with the reactant in the next cycle.

The projected density of states (PDOSs) of bare  $\text{SiN}_4\text{G}$ , and the adsorbed  $\text{N}_2\text{O}$  and  $\text{CO}_2$  on the  $\text{SiN}_4\text{G}$  structures, were analyzed and compared in Fig. 2. The Fermi level ( $E_{\text{F}}$ ) is shown by the vertical dashed line at 0 eV. Positive and negative amplitudes of PDOS correspond to the spin-up and spin-down

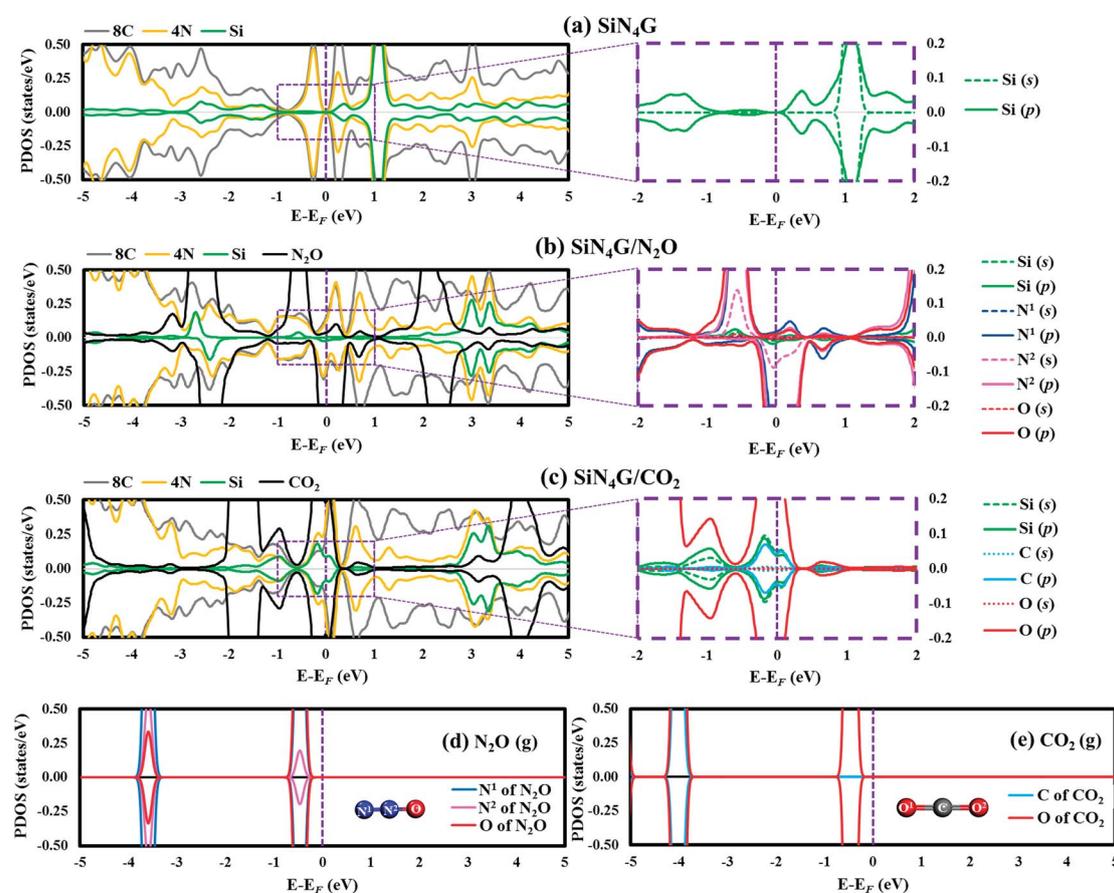


Fig. 2 PDOS plots of selected atoms in (a) bare  $\text{SiN}_4\text{G}$ , (b)  $\text{SiN}_4\text{G}/\text{N}_2\text{O}$ , (c)  $\text{SiN}_4\text{G}/\text{CO}_2$ , (d) isolated  $\text{N}_2\text{O}$  gas and (e) isolated  $\text{CO}_2$  gas. In (a) to (c), the PDOS peaks of Si, 4N, 8C and gas molecules are presented in the left panels, and the s- and p-states of selected Si and atoms of gas molecules are decomposed in the right panels. Positive and negative amplitudes of PDOS indicate the spin-up and spin-down states, respectively.



states, respectively. Fig. 2a depicts the PDOS plot of SiN<sub>4</sub>G. The hybridization of the valence states and bonding can be seen in overlapping peaks. In addition, PDOS analysis of the pyridinic-N embedded in the graphene (N<sub>4</sub>G) is depicted in Fig. S2 in ESI.† The PDOS of N<sub>4</sub>G agrees well with those reported in other literatures.<sup>47,48</sup> The PDOS peaks of the Si, the four pyridinic-N atoms (4N) and the eight neighbouring carbon atoms around the N atoms (8C) of the bare SiN<sub>4</sub>G are depicted in Fig. 2a. The right panel of Fig. 2a shows the PDOS of the decomposed s- and p-states of Si around E<sub>F</sub>, which are relevant for the reaction. SiN<sub>4</sub>G has symmetrical spin-up and spin-down peaks. The overlapped valence and conduction bands of Si and N atoms, with their adjacent carbons, can be seen in Fig. 2a. In SiN<sub>4</sub>G, the p-states of Si located close to the E<sub>F</sub> level can be found in the right panel of Fig. 2a. Furthermore, the PDOS plots of N<sub>2</sub>O and CO<sub>2</sub> adsorbed on SiN<sub>4</sub>G are also shown in Fig. 2b and c. The chemical bonds between Si and the adsorbed molecules can be observed *via* the hybridization of their PDOS peaks. To see the variation of PDOS of the adsorbed gas species, PDOS plots of isolated N<sub>2</sub>O and CO<sub>2</sub> molecules are also provided in Fig. 2d and e, respectively. For SiN<sub>4</sub>G/N<sub>2</sub>O, we found the coupling between the p-states of Si and the valence p-states the N<sup>1</sup> of N<sub>2</sub>O (g) near E<sub>F</sub> results in hybridization peaks at E<sub>F</sub> (right panel of Fig. 2b). This signifies the bonding between N<sub>2</sub>O and SiN<sub>4</sub>G. SiN<sub>4</sub>G donates an electron to N<sub>2</sub>O resulting in asymmetrical spin-up and spin-down peaks around E<sub>F</sub> (see Fig. 2b).

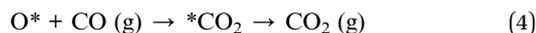
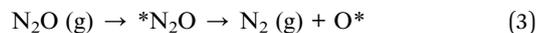
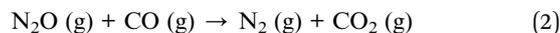
In contrast to SiN<sub>4</sub>G/N<sub>2</sub>O, SiN<sub>4</sub>G/CO<sub>2</sub> shows a symmetrical nature. The broad hybridized peaks can be observed in Fig. 2c. By comparing them with the PDOS of bare SiN<sub>4</sub>G, the reduction of the occupied valence states can be observed. The PDOS peaks of Si and the gas are decomposed into their s- and p-states and are illustrated in the right panel of Fig. 2c. The overlapping states of Si and CO<sub>2</sub> can be seen at E<sub>F</sub>. The PDOS of only one oxygen atom of CO<sub>2</sub> is presented in Fig. 2c, since the two oxygen atoms in CO<sub>2</sub> are identical to each other. According to Fig. 2c, the overlapped peaks around E<sub>F</sub> are the hybridization of the states near E<sub>F</sub> of Si in bare SiN<sub>4</sub>G (see Fig. 2a) and the states of isolated CO<sub>2</sub> (Fig. 2e).

As a result, the hybridization between the states of Si and the states of N<sub>2</sub>O and CO<sub>2</sub> results in chemical bonds between Si and those gas molecules. In addition, the Bader charge results were also calculated in this work. The changes in the valence electrons (Δe<sup>-</sup>) of the selected atoms are given in Table S1 in ESI.† Our Bader charge results demonstrate that N<sub>2</sub>O and CO<sub>2</sub> gain more electrons from SiN<sub>4</sub>G, approximately 1.03|e| and 1.06|e|, respectively. The electronegativity of O, which is greater than those of N, C and Si, also influences the direction of electron transfer in gas adsorbed SiN<sub>4</sub>G. Therefore, both the PDOS and Bader charge results support the claim that electrons are transferred from SiN<sub>4</sub>G to those adsorbed gas molecules.

### 3.2 Mechanisms

The detailed mechanism of the N<sub>2</sub>O reduction by CO is discussed in this section. The overall reaction can be described by eqn (2). There are two possible mechanisms for this reaction, which are the concerted- and stepwise-mechanisms. The

concerted mechanism presents the reaction that N<sub>2</sub>O and CO interact at once to produce N<sub>2</sub> and CO<sub>2</sub>. In the stepwise mechanism, the N<sub>2</sub>O reduction over SiN<sub>4</sub>G occurs first followed by CO oxidation over SiN<sub>4</sub>G-O\* as represented by eqn (3) and (4), respectively.



where an asterisk (\*) expresses an adsorbed intermediate on a catalyst. The energy profiles of the proposed mechanisms are compared to find the most favorable pathway. The reaction energy and the activation energy (E<sub>a</sub>) of the rate-determining step are used to determine the feasibility of using this catalyst for the N<sub>2</sub>O and CO elimination.

**3.2.1 Concerted mechanism.** The N<sub>2</sub>O reduction starts from the N<sub>2</sub>O adsorption and the N<sub>2</sub>O dissociation. As discussed above, N<sub>2</sub>O interacts with the Si active site by the N-bound mode more strongly than the O-bound mode. Thus, our proposed pathways focus on the N-bound mode of N<sub>2</sub>O adsorbed SiN<sub>4</sub>G. After N<sub>2</sub>O adsorbs at the Si active site forming INT1, the CO molecule is not able to adsorb at the same Si active site with the pre-adsorbed N<sub>2</sub>O as Langmuir–Hinshellwood (LH) manner, but rather weakly interacts with the pre-adsorbed N<sub>2</sub>O

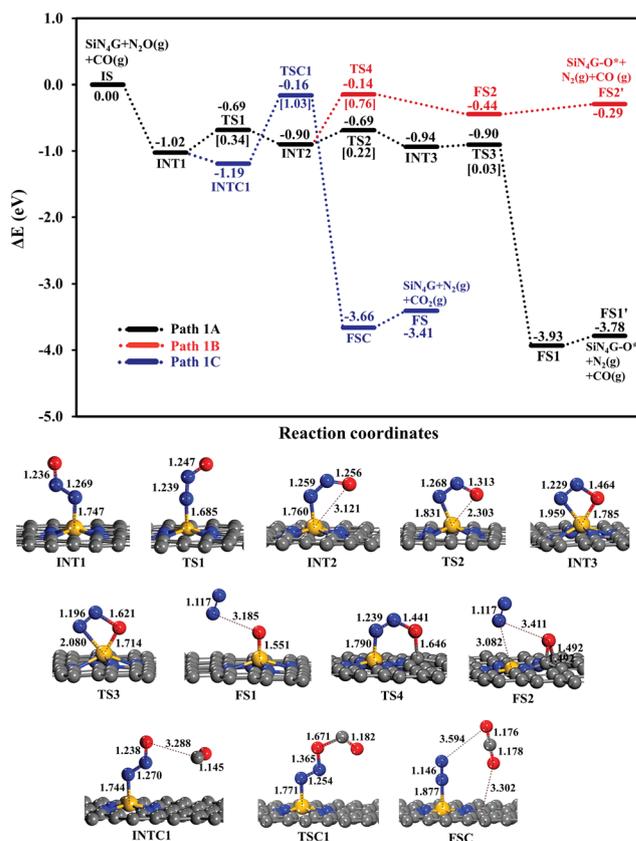


Fig. 3 Energy profiles of Path 1A (black line), Path 1B (red line) and Path 1C (blue line) with the corresponding structures.



as Eley–Rideal (ER) one with some possible configurations of very low adsorption energies ranging from  $-0.10$  to  $-0.17$  eV (see INTC1 in Fig. 3 and S1f in ESI†). These weak adsorption energies of INTC1 configurations imply that the possibility of CO involved in the reaction in the concerted mechanism is rare. Nonetheless, the energetics of concerted pathway *via* the ER mechanism has been examined. The energy profile is presented by the blue pathway in Fig. 3. The configurations in Fig. 3 present that CO interacts with the pre-adsorbed  $N_2O$  and abstracts O atom from  $N_2O$ , and then  $CO_2$  desorbs at the FSC to FS step. Although this process is exothermic, the high  $E_a$  of 1.03 eV which is required to surmount the TSC1 state and the low probability of forming INTC1 prohibit this concerted pathway.

### 3.2.2 Stepwise mechanism

**$N_2O$  reduction.** Two possible pathways of the  $N_2O$  dissociation are compared for the stepwise mechanism. The first pathway (Path 1A) represents the conversion of  $N_2O$  to  $N_2$  and leaves its O attached on the Si-site. In another possible pathway (Path 1B), the leaving O atom of  $N_2O$  is bound at the C–C bridge site of the  $SiN_4G$  catalyst.

The relative energy profile of Path 1A with structures and selected bond distances are shown as the black profile in Fig. 3. The total energies of the bare  $SiN_4G$ , isolated  $N_2O$  and isolated CO are used as a reference to calculate the relative energy ( $\Delta E$ ). The  $E_a$  value of each transition state is given in the bracket. This pathway starts from the  $N_2O$  adsorption intermediates of INT1 and INT2 with an  $E_{ad}$  of approximately  $-1$  eV. The transformation of INT1 to INT2 needs energy barrier of 0.34 eV at the TS1 state. The  $N_2O$  molecule is bent and distorted on  $SiN_4G$ , in particular for INT2 with the terminal O atom directed to the Si center. For the INT2  $\rightarrow$  TS2  $\rightarrow$  INT3 steps, a small  $E_a$  of 0.22 eV is required to enable the bonding between Si and O atoms; at TS2, the S–O distance decreases to 2.303 Å to form a bond and is 1.785 Å at INT3. The N–O bond is then broken simultaneously with a negligible  $E_a$  of 0.03 eV at TS3. Finally,  $N_2$  is produced and the O atom remains at the Si site at the final state (FS1) of this elementary step. The Si–O bond length of FS1 is 1.551 Å. The energy difference between the FS1 and FS1' describes that the  $N_2$  is easily desorbed from  $SiN_4G-O^*$  with very little energy, approximately 0.15 eV. In addition, Path 1A is a highly exothermic reaction with a reaction energy of  $-3.78$  eV.

Another possible route (Path 1B) is examined, and its energy profile with structures is depicted by the red profile in Fig. 3. This pathway proceeds through the INT2  $\rightarrow$  TS4  $\rightarrow$  FS2 steps. An  $E_a$  of 0.76 eV is required to surmount the energy barrier at TS4. Both N–O and N–Si bond lengths are elongated at TS4 in order to release  $N_2$  as a product. For the TS4 to FS2 step, the dissociated O atom binds on atop C site at TS4. Then  $N_2$  is simultaneously desorbed from Si and the dissociated O atom moves simultaneously towards the C–C bridge site, which is more energetically favorable than the top C site, at the final state (FS2). According to the relative energies, the  $SiN_4G-O^*$  structure of FS2, in which the O atom is attached to the C–C bridge site, is less stable than that of FS1, where the O atom binds with the Si site. Unlike Path 1A, this pathway is an endothermic reaction due to the less stable FS2.

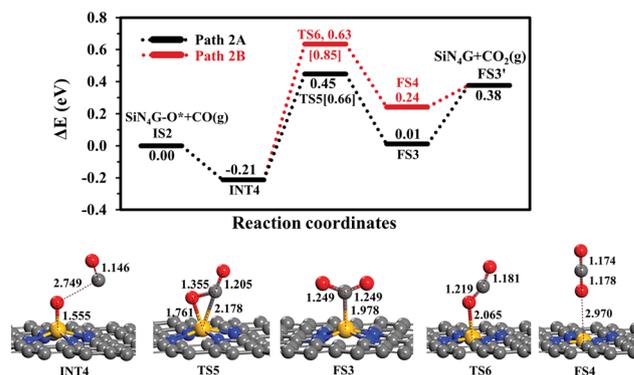


Fig. 4 Energy profiles of Path 2A and 2B with the corresponding structures.

In summary, Path 1A is more kinetically and thermodynamically favorable than Path 1B. The activation barrier of  $N_2O$  dissociation on  $SiN_4G$  for the  $N_2O$  reduction is less than that on SiG ( $E_a \sim 0.5$  eV).<sup>15</sup> Thus, the surrounding N atoms at the Si center not only improve the adsorption ability of  $N_2O$  adsorption but also enhance the activity of catalyst in the  $N_2O$  dissociation process.

**CO oxidation.** The second step is the CO oxidation, in which CO is oxidized by the pre-adsorbed oxygen from the previous step to produce  $CO_2$ , as outlined in eqn (4). The energy profile of this step and the structures are displayed in Fig. 4. Two competitive pathways, Path 2A and Path 2B, are considered. Both of these pathways start from INT4 where the CO molecule weakly interacts with  $SiN_4G-O^*$ . In Path 2A, CO interacts with  $O^*$  and then forms the  $CO_2$  product attached on the Si site with C atom. The energy barrier of the INT4  $\rightarrow$  TS5  $\rightarrow$  FS3 step is 0.66 eV and this step is slightly endothermic by +0.01 eV relative to IS2. Then  $CO_2$  is desorbed directly from FS3 to FS3'. This step requires energy approximately 0.37 eV. The PES and corresponding configurations of the direct desorption  $CO_2$  desorption process, the FS3 to FS3' step, are shown in Fig. S5 in ESI.†

In Path 2B, CO interacts with  $O^*$  and release  $CO_2$  from Si site simultaneously (see FS4 in Fig. 4). The energy barrier to surmount TS6 is 0.85 eV. For this state,  $CO_2$  needs 0.14 eV to desorb from the catalyst in FS3'. Similar to Path 2A, the  $CO_2$  desorption energy is less than the energy of breaking the O–CO bond. This step is also endothermic. Consequently, Path 2A is more favorable than Path 2B in view of energetics. The present  $E_a$  value of Path 2A is lower by approximately 0.1 eV than the reported one by Tang *et al.* in the study of CO oxidation by  $O_2$ .<sup>35</sup> In summary, the CO oxidation step is less thermodynamically and kinetically preferable than the  $N_2O$  reduction step, however, this reaction is feasible at low temperatures, which is supported by the calculated activation energy barriers and reaction energy. Finally,  $SiN_4G$  is completely regenerated and ready for the next  $N_2O$  reduction.

To conclude all the results in this work, the  $N_2O$  reduction by CO prefers the stepwise mechanism than the concerted mechanism. The energy profile of the most favorable stepwise pathway of the  $N_2O$  reduction by CO on  $SiN_4G$  is presented in



Fig. 5. A summation of the energies of bare SiN<sub>4</sub>G, N<sub>2</sub>O and CO is used as the reference energy. The calculated reaction energy of N<sub>2</sub>O + CO → N<sub>2</sub> + CO<sub>2</sub> in this work is −3.41 eV. This value is comparable to −3.5 eV reported by theoretical calculations in Si- and Fe-doped graphene<sup>45,49</sup> and −3.8 eV of the direct reaction of CO with N<sub>2</sub>O from experiment.<sup>50</sup> The N<sub>2</sub>O reduction and CO oxidation prefer Path 1A with an  $E_a$  of 0.34 eV and Path 2A with an  $E_a$  of 0.66 eV. Thus, the rate-determining step of the overall reaction is the CO oxidation. It is worth mentioning that N<sub>2</sub>O is adsorbed more strongly than CO<sub>2</sub>, as seen from their adsorption energies. The small adsorption energies of the N<sub>2</sub> and CO<sub>2</sub> products in this system indicate that the products easily desorb from the active site, which prevents them from poisoning the catalyst. Hence, the active SiN<sub>4</sub>G site can be recovered after the reaction is completed and the next reaction cycle can continue further. Overall, the SiN<sub>4</sub>G catalyst demonstrates a promising performance for the reduction of N<sub>2</sub>O by CO.

To form a better understanding of the charge property of the systems in the reaction, electron density differences of the intermediates and transition states along the most favorable pathway are also investigated. The results are given in Fig. S3 and S4 in ESI.† For bare SiN<sub>4</sub>G, the electron density difference is referenced with the isolated Si atom and N<sub>4</sub>G surface, see Fig. S3 in ESI.† The light blue and yellow regions represent the electron density increment and reduction, respectively. The electron density of Si is depleted when Si is embedded at the porphyrin-like core and is delocalized over N atoms and the Si–N bonds around the di-vacancy site. This result agrees well with the Bader charge analysis in Table S1 in ESI;† the partial charge of Si is about +2.66|e| and the coordinating N atoms show an average negative charge about −1.5|e|. Therefore, these four N atoms strongly coordinate with the embedded Si atom as confirmed by the adsorption energy of Si on N<sub>4</sub>G of −7.07 eV. This value is comparable with −7.25 eV, reported by Tang *et al.*<sup>35</sup> This strong adsorption stabilizes the catalyst and prevent the leakage of the embedded Si atoms from the catalyst, resulting in increasing the durable operation. When all adsorbed species attached on SiN<sub>4</sub>G, electrons are obviously transferred from Si

and accumulated between Si and the attached atom (see Fig. S4 in ESI†). This electron transfer supports the PDOS result.

### 3.3 Comparison with other two dimensional catalysts

Herein, the expected catalytic activity of SiN<sub>4</sub>G for the reduction of N<sub>2</sub>O by CO is considered in comparison with the Si-based graphenes or nanotubes and other metal-based catalysts from previous reports. The activation energies of the rate-limiting steps of the N<sub>2</sub>O reduction and the CO oxidation of some catalysts are compared in Table 1. The effect of the coordinating N atoms in the SiN<sub>4</sub>G on the catalytic activity of the catalyst can be described by comparing SiN<sub>4</sub>G with SiG.<sup>15</sup> SiN<sub>4</sub>G has a lower  $E_a$  in the N<sub>2</sub>O reduction step but a higher  $E_a$  in the CO oxidation step. For the entire N<sub>2</sub>O and CO<sub>2</sub> reaction, the  $E_a$  of the rate determining step is 0.5 eV in SiG, which is slightly lower than that of SiN<sub>4</sub>G. However, as mentioned in Section 3.1, the CO adsorption on SiG is slightly stronger than that of N<sub>2</sub>O, which indicates that the selectivity of SiG towards the N<sub>2</sub>O reduction is poorer than SiN<sub>4</sub>G if CO exists in the system. Thus, the presence of N atoms around the Si does not only enhance the adsorption with the reactants, but it also makes the catalyst become more selective. In SeG, the  $E_a$  of the N<sub>2</sub>O reduction is approximately 1.8 eV which is much higher than the Si doping case.<sup>15</sup> Note that for SiN<sub>4</sub>G, the adsorption CO<sub>2</sub> product is not comparative to the adsorption of the CO and N<sub>2</sub>O reactants. This characteristic is different from the SeG and SiG systems, in which reactants and products show similar adsorption energies. This means that the CO<sub>2</sub> product in the case of SeG and SiG may poison the active sites, while in the case of SiN<sub>4</sub>G the CO<sub>2</sub> is readily desorbed to get the active site ready for the next reaction cycle.

Moreover, the CO oxidation on Si-doped BN nanotubes (Si-BNNTs) and Ti-doped graphene (TiG), and the N<sub>2</sub>O reduction by CO on Al-doped graphene (AlG) and Fe-doped graphene (FeG) are facile based on their activation energies. In the Fe-doped graphene (FeG), the rate-limiting steps require 0.4 eV and 0.8 eV for the stepwise and concerted mechanisms, respectively. However, the N<sub>2</sub>O adsorption on FeG ( $E_{ad} \sim -0.4$

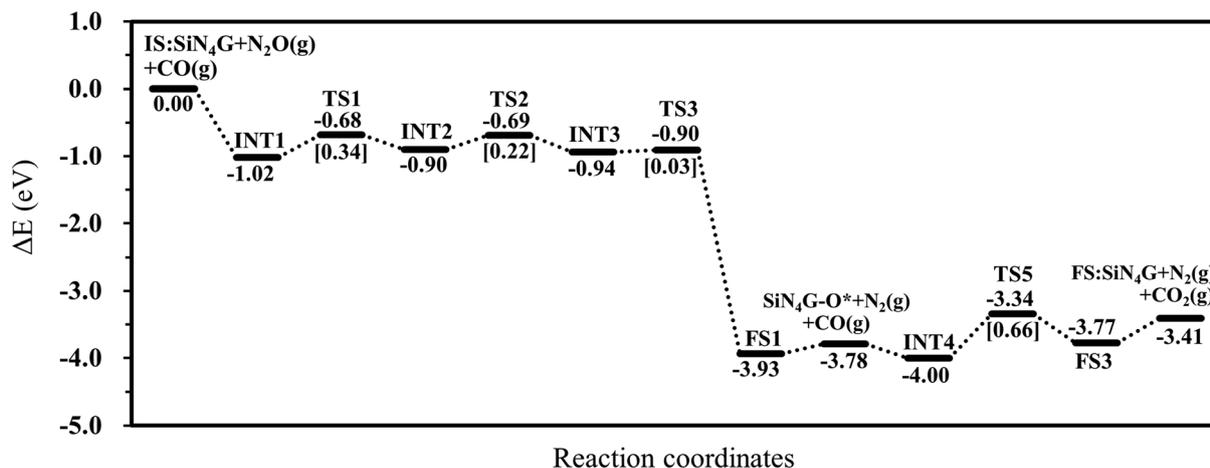


Fig. 5 Energy profile of the most favorable pathway of the N<sub>2</sub>O reduction by CO on SiN<sub>4</sub>G.



**Table 1** Comparison of the rate-limiting steps and corresponding activation energy barriers ( $E_a$ ) in eV for the  $N_2O$  and CO reactions on catalysts calculated by DFT method at 0 K

Catalyst	$E_a$ (eV)		$E_{ad}$ (eV)		
	$N_2O \rightarrow N_2 + O^*$	$CO + O^* \rightarrow CO_2$	$N_2O$	CO	$CO_2$
$SiN_4G$ (this work)	0.34	0.66	-0.97	-0.66	-0.37
$SiN_4G^{35}$		0.72		-0.55	-0.26
Mn- $N_4$ carbon nanotube ( $MnN_4CNT$ ) <sup>51</sup>		1.49		-2.20	
Si-doped graphene ( $SiG$ ) <sup>15</sup>	0.5	0.3	-0.18	-0.19	-0.18
Se-doped graphene ( $SeG$ ) <sup>15</sup>	1.8	0.7	-0.22	-0.18	-0.21
Si-doped boron nitride nanotubes ( $Si_B$ -BNNTs) <sup>13</sup>	BL <sup>a</sup>	0.08	N/A	-0.19	
Si-doped boron nitride nanotubes ( $Si_N$ -BNNTs) <sup>13</sup>	BL <sup>a</sup>	0.42	N/A	-0.16	
Silicon carbide nanotubes ((6,0)- $SiCNT$ ) <sup>17</sup>	0.71	1.01	-0.64	-0.38	
Silicon carbide nanosheets ( $SiCNS$ ) <sup>17</sup>	1.12	0.98	-0.59	-0.18	-0.14
Pd-doped graphene ( $PdG$ ) <sup>52</sup>		0.26		-1.04	-0.21
Al-doped graphene ( $AlG$ ) <sup>16</sup>	0.24	0.06	-0.81	-0.62	-0.52
Ti-doped graphene ( $TiG$ ) <sup>16</sup>	BL <sup>a</sup>	0.16	N/A	-1.03	-0.32
Fe-doped graphene ( $FeG$ ) <sup>49</sup>	0.4	0.2	-0.4	-1.5	-0.4
Pd-doped boron nitride ( $PdBN$ ) <sup>53</sup>		0.23		-1.07	-0.06
Ag-doped boron nitride ( $AgBN$ ) <sup>54</sup>		0.17		-1.04	-0.36
Co-doped boron nitride ( $AgBN$ ) <sup>55</sup>		0.16		-1.04	-0.33
$Ag_6Au_7$ cluster <sup>11</sup>	1.1	0.5	-0.2	-0.5	-0.1
$Cu_7$ cluster <sup>1</sup>	BL <sup>a</sup>	0.9	N/A		
$Cu_{12}$ cluster <sup>1</sup>	BL <sup>a</sup>	0.8	N/A		

<sup>a</sup> BL denotes a barrierless process.

eV) is less favorable than the CO adsorption on FeG ( $E_{ad} \sim -1.5$  eV).<sup>49</sup> Thus, FeG is not selective to the present reaction. As presented in Table 1, many metal-free catalysts were proposed to show better catalytic performance than pure metal cluster catalysts like Cu- and  $Ag_6Au_7$ -clusters.<sup>11,11</sup>

In conclusion, the results in this work indicate that  $SiN_4G$  is a promising catalyst because of the following reasons: (1) the durability of the catalyst indicated by the substantial adsorption strength of Si on  $N_4G$  (-7.07 eV), (2) the high reactivity and selectivity for converting  $N_2O$  and CO to less harmful products,  $N_2$  and  $CO_2$ , at low temperature, indicated by low activation barriers and large reaction energy, (3) the small adsorption energy of the  $CO_2$  product prevents catalyst poisoning, which is a problem with most of the conventional metal catalysts, and (4) a low cost for large-scale reactions in industry.

## 4. Conclusion

This work investigated the charge, density of state, energetic and structural properties for the reduction of  $N_2O$  reduction by CO on the Si-coordinated nitrogen-doped graphene catalyst,  $SiN_4G$ , by employing plane-wave-based DFT calculations. The mechanistic insight of the  $N_2O$  and CO reaction has been systematically examined. The calculation results show that the four coordinating N atoms of  $SiN_4G$  increase the reactivity of the Si active site and stabilize the adsorption state by charge transfer. The Si active site is specifically reactive to  $N_2O$  due to the strong overlap between the Si active site and the N atom of the adsorbed molecule. The reaction mechanism for the

reduction of  $N_2O$  by CO occurs through two consecutive steps:  $N_2O$  reduction followed CO oxidation. The overall reaction is thermodynamically and kinetically preferable due to its low activation barriers and exothermic characteristic. The  $N_2O$  reduction occurs easily, with a small energy barrier of 0.34 eV, while the CO oxidation is the rate determining step of the entire reaction, with an  $E_a$  of 0.66 eV and slight endothermicity. However,  $CO_2$  can be released more easily than it can be dissociated back to CO. The  $SiN_4G$  is regenerated completely after CO oxidation. Then, a new reaction cycle occurs simultaneously due to the stronger interaction between  $SiN_4G$  and  $N_2O$  when compared with the CO product. This catalyst also shows strong reaction activity when compared to proposed catalysts from the literature. In summary, this metal-free catalyst is one of many candidates for eliminating CO and  $N_2O$  at low temperature, and it is reusable for multiple reaction cycles. The mechanistic insight from this work provides a useful guidance in designing a low-cost metal-free catalyst with great catalytic performance.

## Conflicts of interest

There are no conflicts to declare.

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