

## Adsorption of carbon monoxide on graphene with high titanium coverage

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Density functional theory and molecular dynamics were used to study the adsorption of CO on a graphene layer modified with high titanium coverage ( $C_2Ti$ ) at atmospheric pressure and 300 K. We found that the CO molecule is adsorbed and dissociated.

**Keywords:** CO adsorption; graphene.

Por medio de la teoría de la funcional de densidad y de dinámica molecular, estudiamos la adsorción de Co en una capa de grafeno modificada con titanio con una cobertura muy alta ( $C_2Ti$ ) a presión atmosférica y 300 k. Encontramos que la molécula de CO queda adsorbida y disociada.

**Descriptor:** Adsorción de CO; grafeno.

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CO is a toxic gas that comes primarily from incomplete combustion of carbon containing fuels. At normal conditions it is odorless, colorless and tasteless; it is non-irritating and it is an asphyxiant. It can be deadly at high levels. One of the most attractive topics in surface science research is the adsorption of carbon monoxide on palladium and transition metals. In particular, there are theoretical and experimental studies on the adsorption of CO on Ti [001] surface [1-4].

On the other hand, it has been found that Carbon nanotubes doped with Ti can be used as a sensor device for CO molecule recognition [5]. The Ti coverage on the nanotubes used in Ref. 5 was low, one Ti atom per 32 C atoms.

In this work, we studied the adsorption of carbon monoxide on a titanium-graphene system with high metal coverage. Recently the adsorption of a water molecule on this system was studied [6]. It was found that when there is a Ti atom above the center of each carbon hexagon ( $C_2Ti$ ), the water molecule can be dissociated in two different ways forming O, H, and OH. These ways of dissociation of the water molecule are observed experimentally on the Ti [001] surface [7]. Here we considered the same metal coverage on graphene. This configuration is hexagonal and has the highest possible Ti density on the graphene layer.

As in Ref. 6 the system  $C_2Ti$  was represented using a hexagonal unit cell with  $a=b=4.875 \text{ \AA}$  and  $c=20 \text{ \AA}$ , with periodic conditions, containing four Ti atom and eight C atoms (see Fig. 1). In the c direction, we took a large enough separation to ensure that there is no interaction between adjacent Ti-graphene sheets.

We used density functional theory (DFT), with the local density approximation (LDA) and molecular dynamics (MD) within the Born-Oppenheimer approximation and the Quantum Espresso code [8]. As in Ref. 6, for exchange-correlation energies we used the Perdew-Zunger expression [9], and the norm conserving Troullier-Martins pseudopotentials [10], in the fully separable form of Kleinman-Bylander [11].

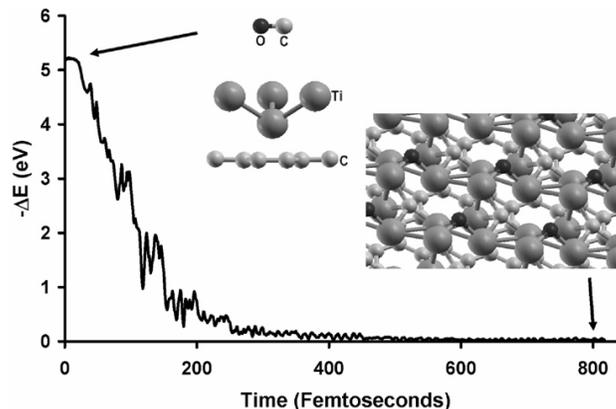


FIGURE 1. Here, the time evolution of the carbon monoxide adsorption onto Ti-graphene, with high Ti coverage ( $C_2Ti$ ) is shown. The process is at 300 K. In the final configuration we can see the dissociation of the CO molecule when adsorbed. The initial orientation of the molecule has no influence on the result. The adsorption energy is  $-5.22 \text{ eV}$ . The O atom ends up bonded to three Ti atoms and the C atom to four Ti atoms. There is some electronic charge transfer from Ti to C and O.

We considered as valence electronic states for carbon [6]:  $2s^2 2p^2$ ; for oxygen:  $2s^2 2p^4$ ; for titanium:  $3s^2 3p^6 3d^2 4s^2$ . We used the pseudopotentials given in Ref. 6. For the reader's convenience, we show here the values in  $\text{Å}$ , of the different cut-off radii  $r_l$ . For carbon:  $r_s = 0.794$  and  $r_p = 0.815$  with the  $s$  pseudopotential as the local component; for oxygen:  $r_s=r_p=0.661$ , with the  $s$  pseudopotential as the local component; for titanium:  $r_s = 0.807$ ,  $r_p = 0.750$ ;  $r_d = 1.257$ , with the  $p$  pseudopotential as the local component.

We performed non-relativistic and non-spin polarized calculations. The cut-off energy was 1100 eV and we took 40 k points within the Monkhorst-Pack special k point scheme [11]. The threshold energy convergence was  $1.2 \times 10^{-5} \text{ eV}$ .

With the oxygen and carbon pseudo potentials we obtained by energy minimization in the CO molecule, for the

length of the C-O bond 1.151 Å (the experimental value is 1.128 Å [12]).

After optimization of the titanium-graphene system ( $C_2Ti$ ), the Ti atoms are contained in two different planes [6]. The nearest Ti atom to the graphene plane is at 1.828 Å. The other plane of titanium atoms is at a distance of 3.239 Å from the graphene plane. In this way the shortest distance from a Ti atom on the lower plane to a Ti atom on the upper plane is 2.815 Å. The distance Ti-Ti is 4.22 and 2.44 Å on the upper plane and on the lower plane, respectively [6]. We have a hexagonal distribution of Ti atoms [6]. Each Ti is above a carbon hexagon. On the other hand, it is well known that the Ti [001] surface is hexagonal, with the atoms on one plane, and a Ti-Ti distance of 2.95 Å [13]. In this way, the surface for our system Ti-graphene ( $C_2Ti$ ) resembles the Ti [001] surface. The two surfaces are not identical.

From Löwdin population analysis it is found that 75% of C atoms present a net charge of -0.039 and 25% of them have a charge of +0.011. The Ti atom in the lower plane has a net charge of +0.548 and the Ti atom in the upper plane has a net charge of +0.335 [6].

In the CO molecule the C atom has a negative charge and the O atom has a positive charge. We considered three initial orientations of the CO molecule to study its adsorption on the graphene-Ti system. The first one was with the molecule line parallel to the graphene plane; the second one was with the molecule line perpendicular to the adsorption surface, with the C atom below the O atom; the third was with the molecule line also perpendicular to the graphene-Ti surface and the C atom above the O atom. We define the adsorption energy of the molecule:

$$\Delta E = E(Ti-graphene+CO) - [E(Ti-graphene) + E(CO)];$$

where  $E(Ti-graphene + CO)$  is the energy of the final configuration;  $[E(Ti-graphene) + E(CO)]$  is the energy of the initial system, which is the energy of the Ti-graphene alone with no interaction with CO, plus the energy of the CO molecule alone.

For each initial position of the CO molecule, we allowed the system to follow an evolutionary process using molecular dynamics, with a temperature of 300 K and a time step of 1 femtosecond. There were around 800 steps to reach equilibrium clearly.

The positively charged Ti atoms pull the negatively charged C atom towards the surface and repel the O atom. Thus, for the first initial position of the molecule when it is initially parallel to the surface, it rotates in such a way that the C atom gets closer to the Ti-graphene surface than the O atom. At this point the attractive force on the C atom is larger than the repulsion on the O atom by the Ti atoms. When the CO molecule is very close to the surface, the molecule interacts very strongly with the Ti atoms of the upper plane. The O atom traps electronic charge from the Ti atoms of the

upper plane, becomes negative and ends up bonded to three Ti atoms. The CO molecule is dissociated. The C atom also traps electrons, becoming more negative and it is adsorbed on the surface in such a way that the C atom is bonded to four Ti atoms. This is shown in Fig. 1.

For the second initial orientation of the molecule the C atom is below the O atom. The attractive force on the C atom is larger than the initial repulsion on the O atom by the Ti atoms. The molecule approaches the surface and it is adsorbed in the fashion we have described above.

For the third initial orientation of the molecule, the C atom is above the O atom. The molecule is initially repelled by the positive Ti atoms. Because of thermal fluctuation it becomes slightly inclined with respect to the surface and it is rotated by the action of the positive charge of the Ti atoms. In this manner the molecule approaches the surface with the C atom closer to the surface than the O atom and it is adsorbed in the way described previously.

The adsorption energy for the CO molecule is -5.22 eV. The O-Ti distances are 2.12, 1.86 and 1.86 Å, respectively. The C-Ti distances are 2.07, 1.96, 1.92 and 2.12 Å, respectively. The final C-O distance is 3.08 Å. The angles Ti-C-Ti are 109.35, 94.99, 92.27 and 157.79°, respectively; the angles Ti-O-Ti are 90.67, 103.58 and 81.37°, respectively. The angle C-Ti-O is 91.74°.

From Löwdin population analysis, the final charge of the C atom is -0.027 (the initial charge before adsorption was -0.015); the final charge of the O atom is -0.011 (the initial charge before adsorption was 0.015). It is clear that Ti atoms transfer electronic charge to the C atom and to the O atom.

There are experimental reports on the dissociative adsorption of a CO molecule on the Ti [001] surface in Ref. 4. As we expected, the way that we found, in which the CO molecule dissociates on the Ti-graphene system ( $C_2Ti$ ), is consistent with the experimental reports in Ref. 4. Thus, these two surfaces share this property. It is convenient to mention that a similar situation occurred with the adsorption of a water molecule. The same two surfaces also share the way in which a water molecule is adsorbed and dissociated [6].

Finally, we increased the temperature to 600 K, and up to 1300 K in order to find out if the adsorbed CO molecule could be desorbed. It was not desorbed. From here it is clear that it is not possible, for practical purposes, to have a renewed cycle of CO adsorption.

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