

Structural and electronic properties of CO molecule adsorbed on the TiO₂ supported Au overlayers: Insights from density functional theory computations

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Abstract

We have examined the adsorption behaviors of carbon monoxide (CO) molecule on TiO₂ anatase supported Au overlayers. The results of density functional theory (DFT) calculations were used in order to gain insights into the effects of the adsorption of CO molecules on the considered hybrid nanostructures. We have investigated different adsorption geometries of CO over the nanoparticles. CO molecule is preferentially adsorbed on the surface of Au atoms with significant adsorption energies. It was found that the CO molecule moves preferentially towards the Au atoms when it was positioned at the top Au sites of the nanoparticle. Here, we have focused on the adsorption of CO on the studied system, and the major point is that the charge is transferred from the CO molecule to the nanoparticle. The results suggest that the oxygen atom has a little mutual interaction with the surface Au atoms. We have summarized the results of density functional theory calculations including adsorption energies, Mulliken charge analysis and electronic density of states. Charge analysis based on Mulliken charges reveals a substantial charge transfer from the CO molecule to the TiO₂ supported Au overlayers. With the inclusion of van der Waals (vdW) interactions, the results show an increase in the adsorption energy values. TiO₂ supported Au overlayers have strong sensing capability for the detection of CO molecules, indicating the higher adsorption ability of these modified nanostructures. The goal of this study was to report on results that provide new insights, or significantly expand our understanding of the structural and electronic properties of novel TiO₂ supported Au overlayers for chemical sensing of CO molecules.

Keywords: Density functional theory (DFT); CO; Interaction; PDOS; TiO₂ supported Au overlayer.

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INTRODUCTION

Metal oxide field effect transistors such as TiO₂ have gained more and more attentions in the last decades due to their unique properties such as high catalytic efficiency, non-toxicity and wide band-gap [1]. TiO₂ has been generally used in a wide range of technological applications such as gas sensor devices, photo-catalysis, dye-sensitized solar cells and removal of air pollutants [2-5]. There exist three main crystallographic polymorphs of TiO₂ in the nature, namely anatase, rutile, and brookite [6]. The large band gap of TiO₂ (3.2 eV)

limited its photocatalytic activity, making the adsorption of the solar light by a little percentage (3-5 %). Nonmetal doping of TiO₂ is a convenient solution in order to enhance the optical sensitivity of TiO₂ to the visible region [7, 8]. Au nanoparticles supported with metal oxide field effect transistors have fascinated remarkable attentions because of the outstanding catalytic activities of these materials [9, 10].

Recently, gold has been demonstrated to be a noble metal with activity lower than the other metals in many reactions, until Haruta et

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al. suggested that gold particles can increase CO combustion and various catalytic reactions [10]. Multicomponent structures composed of the gold particles and supporting metal oxides (Oxide-supported gold particles) have been found to be more active than the pristine gold and TiO₂ particles [11, 12]. Also, the enhanced activity of gold nanoparticles supported on many different metal oxides has been addressed in some works [13, 14]. In the past decades, the supported Au nanoparticles as effective catalysts have attracted numerous attentions. This enhanced activity of oxide-supported Au overlayers has been extensively reported for a large number of important reactions, such as epoxidation of propene [15], reduction of NO_x molecules [16], and dissociation of SO₂ molecule [17]. Thus, a hybrid structure of TiO₂ with Au nanoparticle has been accepted to be a promising candidate in applications such as CO oxidation in low temperatures [18, 19].

A large number of important experimental studies have been published, describing the reactivity and adsorption ability of Au nanoparticles. For example, Goodman and co-workers [20] investigated size and effects of the band structure and measure the onset of the reactivity. Their aim was to explain while the Au particles become as thin as two monolayers at which point they subject to a variation from a metallic to a nonmetallic state. Previously, several DFT calculations of O₂ adsorption and CO+O₂ reaction at different Au particles and clusters have been published. Landman *et al.* [21] studied the changes in the structure and properties of the Au particles as an effective factor. O₂ and CO₂ adsorptions and their reactivity with modified gold nanoparticles supported by different surfaces of TiO₂ have been examined in detail [22]. Additionally, there is a large number of computational studies devoted to the multicomponent N-doped TiO₂ anatase and Au nanoparticles, describing the important electronic and structural properties of these nanostructures. Liu *et al.* [23] investigated the NO adsorption on the undoped and N-doped TiO₂ anatase nanoparticles. Habibpour *et al.* performed a computational study of the electronic, spectroscopic and chemical properties of Cu_n (n=2-8) nanoclusters for CO adsorption [24]. The adsorption behaviors of ammonia molecule on the N-doped TiO₂ anatase nanoparticles have been also investigated in our previous study [25].

The importance of oxide supported overlayers and their structural and electronic were mainly discussed in some published works [26, 27]. The enhanced capability of N-doped TiO₂ anatase nanoparticles for the removal of toxic NO₂ molecules from the environment has been also reported in our previous work [28].

Detection of toxic gas molecules is an important subject to environmental protection and public health. In this regard, numerous efforts have been done to provide a safe environment because of increasing toxic gas emissions that are considered as criteria for environmental pollution by incomplete natural gas combustion. CO adsorption on the TiO₂ anatase supported Au overlayers is an efficient strategy for the removal of harmful CO molecules. In this study, the interactions of CO molecules with TiO₂/Au hybrid nanostructures were investigated by density functional theory (DFT) calculations. The electronic structures of the complex systems were analyzed in view of the projected density of states (PDOSs) and Mulliken population analysis. The aim of this study is to report on insights that provide new findings, or significantly expand our understanding of the properties of materials or phenomena associated with the design of novel TiO₂/Au overlayer based sensors for CO detection in the environment.

EXPERIMENTAL

Density functional theory

This work has been performed within the framework of Density Functional Theory (DFT) method [29, 30]. The calculations were carried out with the Open source Package for Material explorer (OPENMX3.8) [31], which has been demonstrated to be an efficient software package for nanoscale materials simulations based on DFT, pseudo atomic orbitals and Norm-conserving pseudo potentials [32, 33]. DFT has already been widely used to study oxide surfaces and the adsorption of different molecules on these surfaces with sufficient accuracy. The cutoff energy of 150 Ry was set in our calculations. The selected PAOs were constructed by using basis sets of (3-s, 3-p, 1-d) for the titanium atom, (3-s, 3-p, 2-d, 1-f) for the gold atom, (2-s, 2-p) for oxygen, carbon and nitrogen atoms within the chosen cutoff radii set to the values of 7 for Ti, 9 for Au, 5 for O, C and N (in Bohrs). In the calculations, the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof form (PBE) was

used for exchange-correlation energy functional [34]. The open-source program, XCrysDen, was used in the display of the figures of adsorption configurations [35]. Our considered simulation box contains 88 atoms (16 Au, 48 O and 24 Ti atoms) of pristine TiO₂ anatase supported Au overlayers. Grimme's DFT-D₂ method was also employed in order to include the effects of long range van der Waals (vdW) interaction [36]. The charge exchange between the CO molecule and nanoparticle was described based on Mulliken charge analysis. Mulliken charges originate from the Mulliken population analysis and deliver a means of calculation partial atomic charges from calculations performed by theoretical chemistry techniques. The method was developed by Robert S. Mulliken. The Mulliken charges are charges based on the local electron density (charge density) and depend strongly on the basic set and the functional used. So it is necessary to use the same functional and basis set in the calculations in order to make an accurate comparison and description of the results. Thus, the Mulliken charges are seriously sensitive to the considered basis sets. Technically, a comprehensive basis set for a molecule can be covered by putting a large set of functions on a single atom. In the Mulliken scheme, all the considered electrons should be assigned to this given atom. Thus, it is impossible to define a complete basis set limit for this method, since the exact value depends on the way the limit is approached. This also means that the charges are ill defined, as there is no exact answer. Consequently, the method does not possess the convergence of the charges for the considered basis set, and various basis set choices significantly give rise to various results.

The adsorption energy is estimated based on the following formula:

$$E_{ad} = E_{(composite+adsorbate)} - E_{composite} - E_{adsorbate} \quad (1)$$

where, $E_{(composite+adsorbate)}$ is the total energy of the TiO₂ supported Au overlayer with adsorbed CO molecule, $E_{composite}$ is the energy of the TiO₂ supported Au overlayer, and $E_{adsorbate}$ is the net energy of free CO molecule. Based on this formula, the adsorption energies of the stable configurations are negative; the more negative the adsorption energy, the higher tendency for adsorption. The adsorption energy is estimated as the difference between the total energy of the adsorption system (TiO₂ supported Au + CO) and

the energies of the bare TiO₂ supported Au and CO molecule. For this purpose, we have relaxed the structures of TiO₂ supported Au nanoparticle and CO molecule, separately and obtained the energies of the intrinsic components. If the adsorption energy is negative, the adsorption process is energy favorable. In the case of positive results, the process is not favored from the energetic point of view.

The density of states (DOS) of a system defines the number of states per interval of energy at each occupied energy level. A high DOS at a given energy level represents that there are many states that can be occupied by electrons. A DOS of zero means that no states are available for occupation at that energy level. The Gaussian broadening method for evaluating DOS was used. Also, we can select DOS or PDOS in our calculations. When we select the calculation of PDOS, we should select atoms for which the projected DOS is obtained. In the case of Gaussian broadening method, the value of Gaussian parameter is set to 0.2 eV, which determines the width of Gaussian. In fact, the projected DOS represents the DOS of the considered atoms in the system under study.

Modeling TiO₂/Au nanocomposites

We have constructed a TiO₂ anatase nanoparticle containing 72 atoms by using a 3×2×1 supercell of TiO₂ anatase. The unit cell data are available at "American Mineralogists Database" webpage [37], reported by Wyckoff [38]. Two dangling oxygen atoms were considered in the nanoparticle in order to set a 1:2 atomic number ratio between the titanium and oxygen atoms. The optimized structure of pristine TiO₂ nanoparticle was shown in Fig. 1.

The considered Au nanoparticles were supported by TiO₂ nanoparticle in order to model a TiO₂ supported Au overlayer. TiO₂/Au hybrid system containing 88 atoms was shown in Fig. 2. Gas-phase CO has a linear geometry with C-O bond length of 1.128 Å, based on GGA method. The relevant structure was represented in Fig. 3.

RESULTS AND DISCUSSION

Adsorption configurations of CO molecule on TiO₂ supported Au overlayers

Adsorptions of CO molecule on the active Au sites of Au particles overlaid on the pristine TiO₂ anatase nanoparticles were discussed in detail. Fig. 4(a-c) represents optimized geometry

configurations of CO molecules adsorbed on the TiO_2 supported Au overlayers. Configurations A and B represent the orientation of the carbon and oxygen atoms of the CO molecule towards the TiO_2 supported Au overlayers, respectively. Besides, configuration C means that the carbon atom of the CO molecule bridges two Au atoms of the nanoparticle. In this case, a double contacting point was observed on the TiO_2 supported Au. In all complexes displayed in this figure, we can see different orientations of CO molecule towards the TiO_2 supported Au. We commented on the most stable adsorption configurations based on the energy point of view. In configuration A, CO molecule is positioned towards the top Au sites of TiO_2 supported Au overlayer by its carbon atom. This means the carbon atom of CO molecule interacts with the TiO_2 supported Au overlayer, and the binding site is located on the active top Au atom. It was found that the carbon

atom of CO molecule moves towards the Au site of the nanocomposite, forming chemical bond. Configuration B represents the interaction of CO molecule with the top Au site of nanocomposite by its oxygen atom. The oxygen atom of CO does not interact with the nanocomposite anymore, whereas the interaction between the carbon and Au atoms is strongly favored. Configuration C denotes a bridge geometry, in which the carbon atom of CO molecule interacts with two surface Au atoms. Two binding sites were found to be located on the Au atoms in this configuration, as shown in Figure 4C. In this configuration, we can see a stronger interaction between the CO and nanocomposite than the other configurations. As can be seen, in this configuration, there is a double contacting point between the nanocomposite and CO molecule, while configurations A and B represent a single interaction point between the nanocomposite and CO.

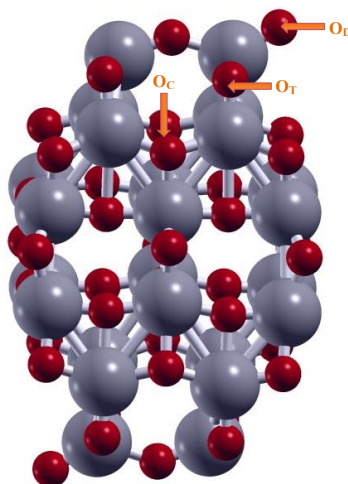


Fig. 1: Optimized structure of an undoped TiO_2 anatase nanoparticle constructed from the $3 \times 2 \times 1$ unit cells. Labels O_C , O_T and O_D indicate threefold coordinated (central oxygen), twofold coordinated oxygen and dangling oxygen atoms, respectively.

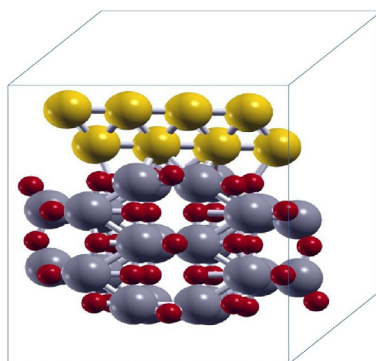


Fig. 2: Schematic representation of TiO_2 anatase supported Au overlayer in a large cubic supercell.

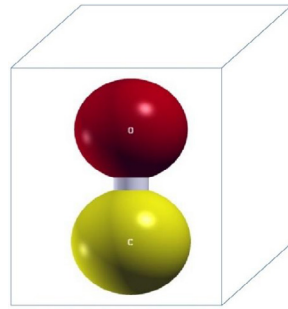


Fig. 3: Schematic representation of a carbon monoxide (CO) molecule.

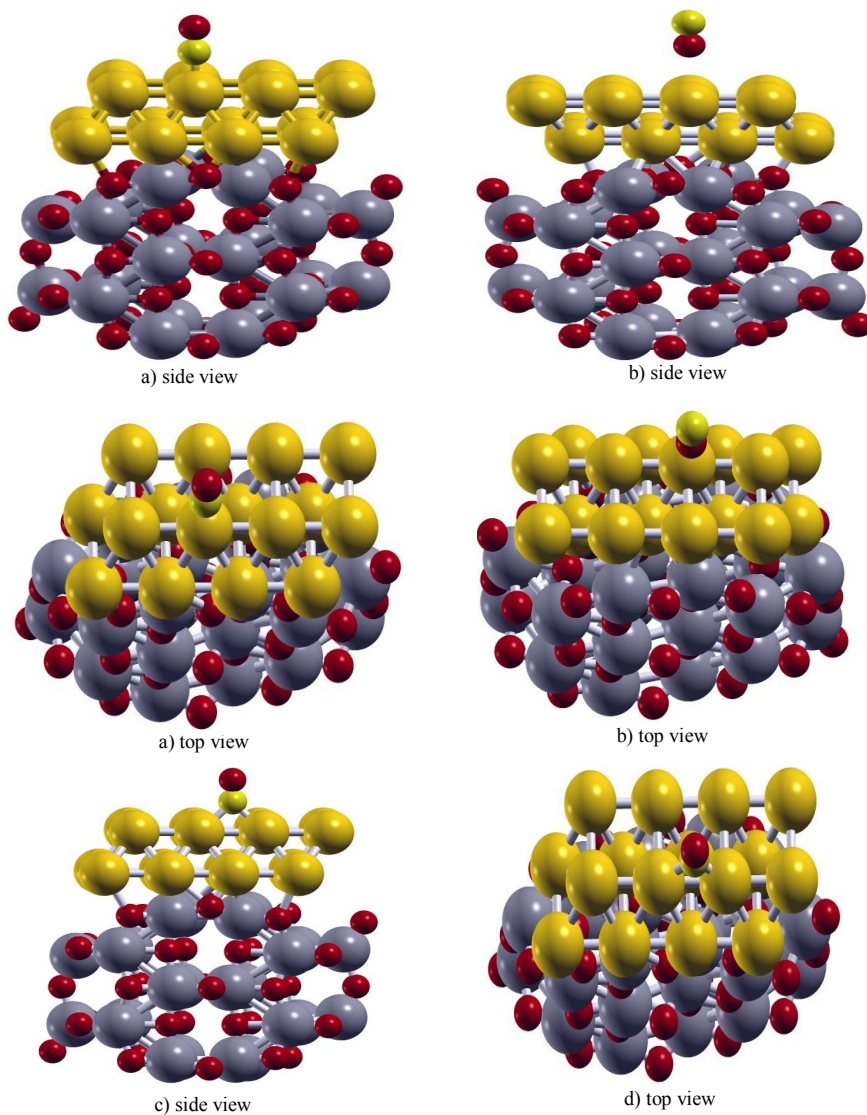


Fig. 4: Optimized structures of CO molecules adsorbed on TiO_2 supported Au overlayers, (a) CO molecule adsorbed on the top Au site by its carbon atom; (b) CO molecule adsorbed on the top Au site by its oxygen atom; (c) The carbon atom of the CO molecule connected to the Au sites of the TiO_2 supported Au overlayer, bridging two surface Au atoms; (d) Top view of the carbon atom of CO bound to the top Au sites, the carbon atom binds to the active surface Au atoms.

Adsorption energy analysis

Adsorption energy analysis was conducted in order to fully investigate the interaction of CO molecule with considered TiO_2 supported Au overlayers. Table 1 lists the adsorption energies calculated based on standard DFT and van der Waals corrected approaches. Of the three configurations, configuration C has the highest adsorption energy value, indicating that the adsorption of CO molecule on TiO_2 supported Au overlayer is energetically more favorable than the adsorption in configurations A and B. It means that the bridge configuration of the carbon atom of CO towards the Au site is the most stable adsorption configuration. The higher (more negative) the adsorption energy, the higher tendency for adsorption and consequently more powerful adsorption. Also, the adsorption energy of configuration A is higher (more negative) than that of configuration B, representing that the adsorption of CO molecule in configuration A is more favorable in energy than the adsorption in configuration B. Therefore, the carbon site adsorption of CO is found to be more stable than the oxygen site adsorption, which indicates that the carbon site adsorption is strongly favored from the energetic point of view.

By considering these results, we found that configuration C, which provides two binding sites between the carbon and Au atoms, is the most energy favorable configuration after the adsorption process. The effects of long range van der Waals interaction were included in order to correct and modify the adsorption energies. It is well known that the inclusion of vdW interactions gives rise to a significant increase in the adsorption energy values. The adsorption energies calculated from DFT-D2 methods are significantly larger than those obtained from DFT-PBE calculations. All the calculated adsorption energies are largely increased when the effects of vdW interactions are taken into account (Table 1). The inclusion of the vdW interactions increases the accuracy of the calculations by improving adsorption energies and greatly enhances the accordance of the calculated results with the experimental and computational data.

By considering these results, it can be concluded that the metal oxide supported Au overlayers can act as efficient candidates for the removal of toxic atmospheric pollutants from the environment. Based on these novel

multicomponent heterostructures, we can design and develop highly sensitive devices for toxic gas detections. It should be noted that the working principle of the constructed devices depends intensely on the induced charge transfer between the adsorbent and adsorbed molecule. Therefore, Au nanoparticle is conducive to the adsorption of CO molecule on the TiO_2 supported Au overlayers, since it strengthens the interaction of CO with considered nanoparticles. Unfortunately, there exist no detailed experimental or theoretical data about the adsorption of gas phase CO molecule on TiO_2 supported Au overlayers so far.

Projected density of states (PDOSs) and Mulliken charge analysis

Fig. 5a-e show the projected density of states (PDOSs) for the adsorption of CO molecule on the TiO_2 supported Au overlayers. Figs. 5a-5b represents the PDOSs for configurations A and B, respectively. In Fig. 5a, there is significant overlap between the PDOSs of the Au and C atoms, indicating the formation of new chemical Au-C bond between these two atoms, while in configuration B, there is a small overlap between the PDOSs Au and C atoms. Figs. 5c-5e show the PDOSs of the C and Au atoms for configuration C (bridge configuration), representing large overlaps between the PDOS spectra of these two atoms. This means that the Au atom of nanoparticle and C atom of CO molecule form a chemical bond after the adsorption process. This formation of chemical bond indicates that CO molecule was chemisorbed on the TiO_2 supported Au nanoparticle. Based on the magnitude of the PDOS overlaps between the interacting atoms, we can evaluate the strength of the formed chemical bonds. In panels (a, c and d), we can see strong overlaps between the PDOSs of the Au and C atoms in comparison with the other panels, representing significant coordination of the C atom to the surface Au atoms. This strong interaction between the contacting atoms would provide a useful strategy in order to describe the sensing capabilities of the sensor materials.

Fig. 6(a-e), show the PDOSs for the Au atom and different s and p orbitals of the carbon atom, indicating the highest overlap between the p^1 orbital of carbon atom and Au atom (panel b).

In other words, p^1 orbital of carbon atom has significant interaction with the Au atom. Fig. 7a-e displays the PDOSs of the carbon atom of CO molecule and five d orbitals of the Au atom.

Table 1: Calculated adsorption energies and Mulliken charges of CO molecule adsorbed on TiO₂ supported Au overlayers.

Configuration	Adsorption energy (eV)		Mulliken charge (e)
	GGA-PBE	DFT-D2	
A	-3.16	-5.04	-0.292
B	-3.06	-5.24	-0.041
C	-3.86	-5.66	-0.348

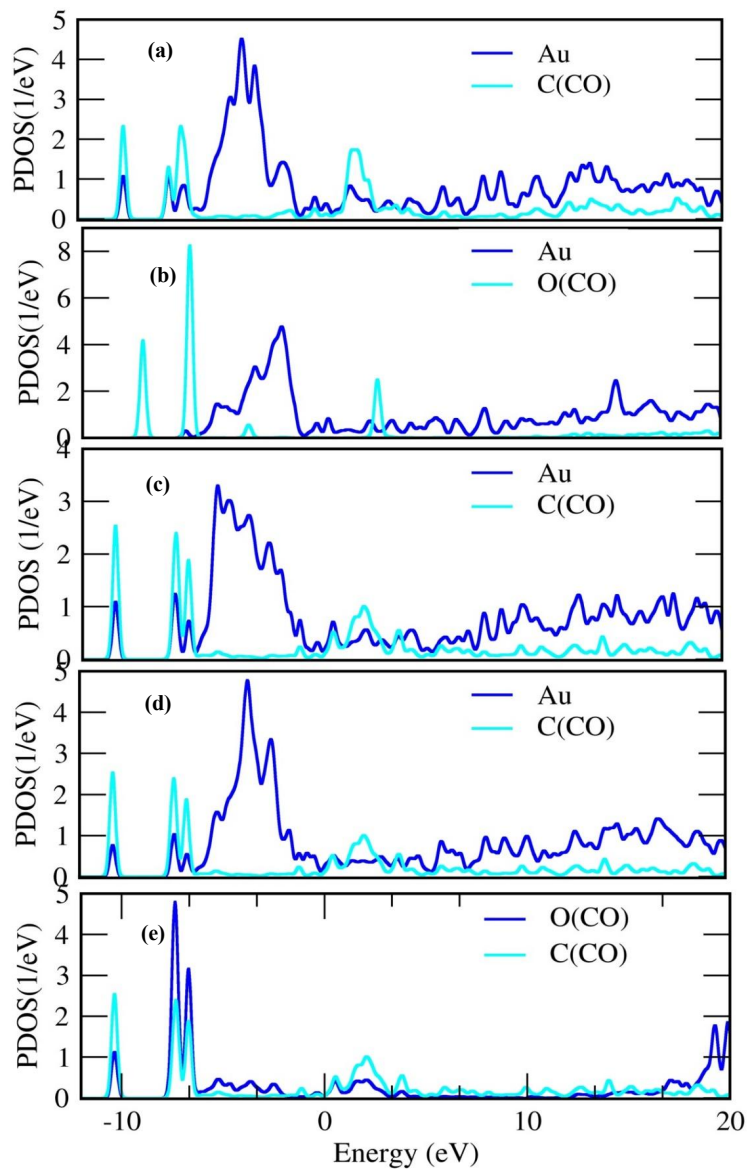


Fig. 5: Projected density of states of CO molecule adsorbed on TiO₂ anatase supported Au overlayers. (a): PDOSs of Au and C atoms for configuration A, (b): PDOSs of Au and O atoms for configuration B, (c): PDOSs of Au and C atoms for configuration C, (d): PDOSs of Au and C atoms for configuration C, (e): PDOSs of O and C atoms of the CO molecule for Configuration C.

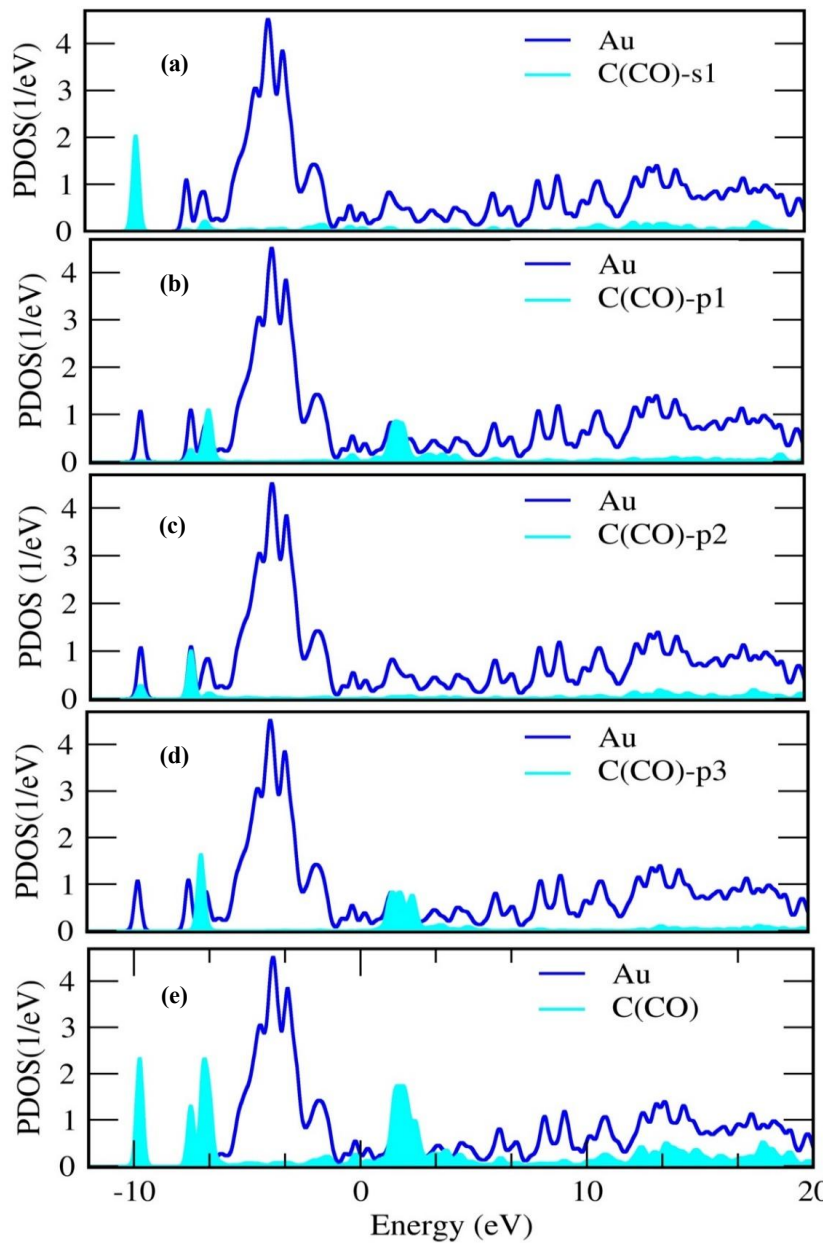


Fig. 6: Projected density of states of Au and three p orbitals of carbon for CO molecule adsorbed on TiO₂ anatase supported Au overlayers (Configuration A). (a) PDOS of the Au and s₁ orbital of the carbon atom; (b) PDOS of the Au and p₁ orbital of the carbon; (c) PDOS of the Au and p₂ orbital of the carbon; (d) PDOS of the Au and p₃ orbital of the carbon; (e) PDOS of the Au and carbon atom of the CO molecule.

Fig. 7b represents the higher overlap between the d² orbital of Au atom and carbon atom of CO molecule, compared with the other d orbitals. The PDOSs of the different s and p orbitals of Au atom and carbon atom of CO molecule were shown in Fig. 8a-e. As can be seen from Fig. 8a, the s¹ orbital of the Au atom has a large PDOS overlap with the carbon atom of CO molecule, implying the

significant interaction between the s¹ orbital of Au and carbon atom. However, these variations in the electronic structure of the studied TiO₂ supported Au overlayers would affect the electronic transport properties of the nanocomposites and this feature can provide an efficient method to improve the sensing capabilities of oxide supported Au overlayers for CO detection.

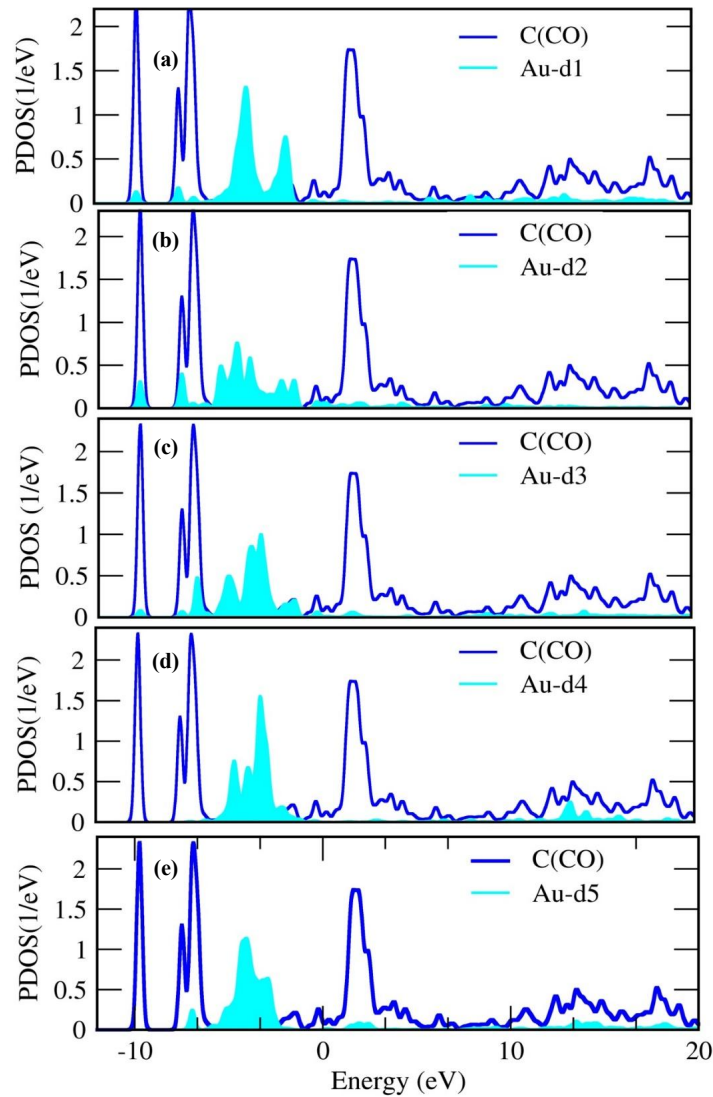


Fig. 7: Projected density of states of carbon and five d orbitals of Au for CO molecule adsorbed on TiO₂ anatase supported Au overlayers (Configuration A), (a) PDOS of the carbon and d¹ orbital of Au; (b) PDOS of the carbon and d² orbital of Au; (c) PDOS of the carbon and d³ orbital of Au; (d) PDOS of the carbon and d⁴ orbital of Au; (e) PDOS of the carbon and d⁵ orbital of Au.

Charge transfer analysis

In order to fully examine the charge transfer between the CO molecule and TiO₂ supported Au overlayers, Mulliken charge analysis was conducted based on the Mulliken atomic populations. The results were listed in Table 1.

The charge difference for the particle *i* after and before adsorption, was calculated using the following equation:

$$\Delta C_i = C_{i(\text{in complex})} - C_{i(\text{in vacuum})} \quad (2)$$

where, C_i is the value of Mulliken charge of the *i*. Subscript “*i*” denotes the TiO₂ supported Au

overlayer or CO molecule. The charge difference, ΔC , is a measure of the amount of charge shifted to, or, from the studied nanocomposites from, or, to the CO molecule. For configuration A, CO adsorption induces a considerable charge transfer of about $-0.292 |e|$ (e , the electron charge) from CO molecule to the nanocomposite, suggesting that the TiO₂ supported Au overlayer accepts electrons from the CO molecule. This gives rise to the variations on the conductivity of the nanocomposite, being a useful property to help in development of sensors and remover devices based on TiO₂ and Au particles for CO detection.

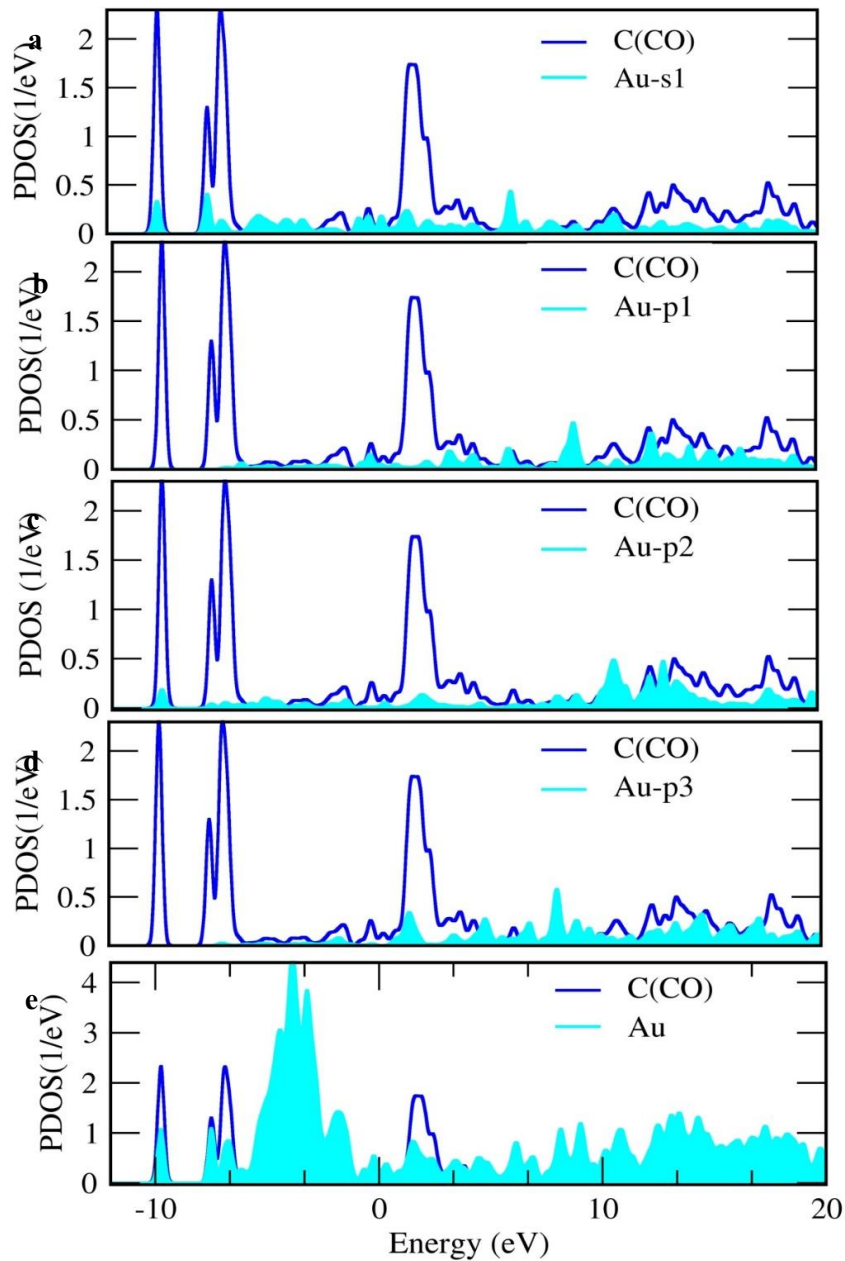


Fig. 8: Projected density of states of carbon and three p orbitals of Au for CO molecule adsorbed on TiO₂ anatase supported Au overlayers (Configuration C), (a) PDOS of the carbon and s¹ orbital of Au; (b) PDOS of the carbon and p¹ orbital of Au; (c) PDOS of the carbon and p² orbital of Au; (d) PDOS of the carbon and p³ orbital of Au; (e) PDOS of the carbon and Au atoms.

CONCLUSIONS

We carried out density functional theory calculations on the structural and electronic properties of TiO₂ anatase supported Au overlayers for the adsorption of toxic CO molecules in the environment. The results suggest that the carbon atom of CO molecule strongly interacts with the surface Au atom. The oxygen atom of CO has a weak

mutual interaction with the TiO₂ supported Au overlayer. The adsorption energy results indicate that the CO adsorption in configuration C (bridge configuration) is more energetically favorable than the adsorption in other configurations. The adsorption energy values are increased when the effect of vdW interaction are included. We commented on the electronic PDOSs of the

TiO₂ supported Au overlayers to understand the electron transport process between the adsorbent and adsorbed molecules. The large overlaps between the PDOSs of the carbon and Au atoms represent the formation of new chemical bonds between these two atoms. Our calculated results thus suggest a theoretical basis for TiO₂ supported Au overlayers to be effectively utilized in gas sensing applications and give an explanation to help in the design and improvement of modified sensors for CO detection.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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