A DFT study for adsorption of CO and H₂ on Pt-doped ZnO nanocluster

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Received: 30 November 2019 / Accepted: 24 March 2020 / Published online: 1 April 2020

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Abstract

Using density functional theory calculations, we studied structural, electronic and adsorption properties of CO and H₂ adsorption on the Pt-doped (ZnO)₁₂ nanoclusters. The more suitable position for the Pt atom is its lateral doping on the nanocluster surface. The lower energy gap for the Pt-doped (ZnO)₁₂ nanoclusters denotes that their conductivity is higher in comparison with the bare nanocluster. The results showed quite a reasonable increase in CO and H₂ gas molecules adsorption energies on the nanoclusters compared with the pristine (ZnO)₁₂ due to Pt doping. The sensitivity of the electronic and adsorption properties to the number of molecules was calculated as well. Upon CO adsorption on the Pt-doped (ZnO)₁₂ nanoclusters energy, it is better when no more than two molecules can be attached to one Pt atom, while H₂ adsorption provides at least three hydrogen molecules on Pt atom. Also, changes in electronic spectra of nanoclusters under the influence of adsorbed CO and H₂ molecules imply a decline in conductivity in such systems. These investigations proved that the Pt-doped (ZnO)₁₂ nanoclusters can be proposed as an approachable candidate in gas sensors for detecting CO and H₂ gas. Also, the calculation results of H₂ adsorption on Pt-doped (ZnO)₁₂ nanoclusters can help in consideration of the possibility of hydrogen storage media creation.

Keywords DFT calculation · Adsorption properties · Pt-doped (ZnO)₁₂ nanoclusters · Electronic properties · Bandgap

1 Introduction

Today, zinc oxide (ZnO) is one of the most important semiconductors for various applications in nanodevices due to its unique properties like wide bandgap (3.44 eV at 4.2 K), large exciton binding energy (60 meV) at room temperature, transparently in the visible region, non-toxicity, biocompatibility [1]. This is confirmed by the intensive research of ZnO over the last decade [2, 3]. Also, ZnO has the richest family of its nanostructures including nanowires, nanotubes, nanoribbons, nanobelts, nanorings, nanoclusters, etc. These ZnO nanostructures have been often utilized as gas sensors for the detection of different gases such as NH₃, NO, F₂, O₂ and CO [4–7]. Usually doping ZnO with metal ions is used to modify its electronic and optical properties [8–13]. Also doping of non-metal ions and

vacancy-defect formation is used for sensing applications to overcome low sensitivity of the substrate materials to manipulate their geometry in order to improve the electronic properties and the electron transport [1].

Within a wide variety of nanostructures, fullerene-like nanoclusters need special attention, because their unique properties make them useable for different applications including photocatalysis, solar cells, gas sensors, or hydrogen storage [14–16]. Previous studies show that (ZnO)₁₂ nanoclusters are the most stable hollow structure for the small cluster [17, 18] and have been successfully synthesized [19]. Earlier adsorption properties of (ZnO)₁₂ nanoclusters with small gases using density functional theory method [20, 21] were investigated and as a result, it was established that energy bandgaps of gas adsorbed (ZnO)₁₂ nanoclusters depends on the adsorbate gases.

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Hadipour et al. investigated the electronic and sensing properties of CO adsorption on Al-doped $(\text{ZnO})_{12}$ nanoclusters [12]. Research results have shown that Al-doped $(\text{ZnO})_{12}$ nanocluster can detect CO molecules because of the significant bandgap and resistivity decrease in unlike to bare nanocluster. They established decreases of bandgap by increases the numerosity of Al atom as well. Saeed Aslanzadeh in his work reviewed the sensitivity properties of the transition metal-doped $(\text{ZnO})_{12}$ nanoclusters for CO detection [11] and found that among all doped atoms, Cr-doped $(\text{ZnO})_{12}$ nanocluster is the most suitable sensor for CO detection. The study [22] describes experimentally investigated photoluminescent and adsorption properties of ZnO nanopowders with surface-doped of noble metals, and it was found that the sensor's sensitivity to gases increases. However, there are no theoretical studies dedicated to the investigation of microscopic interactions between gas molecules and ZnO nanoclusters, although a detailed understanding of how adsorbates can transform electronic structures of doped ZnO nanoclusters is headed. In this study, we present density functional theory calculations of the structural and electronic properties of Pt-doped ZnO nanoclusters with CO and H_2 adsorbates. The purpose of this work is to understand how the electronic structure of Pt-doped ZnO nanocluster changes under the influence of adsorbed gas molecules on the nanocluster surface. The influence of the number of adsorbed gas molecules on the electronic properties of Pt-doped nanoclusters is also very important.

2 Computational details

All calculations including geometry optimization, energy spectra, the density of states (DOS) calculations and adsorption configuration of CO and H_2 gas molecules were accomplished on the bare and Pt-doped $(\text{ZnO})_{12}$ nanoclusters using density functional theory (DFT), which was implemented in Quantum-Espresso package [23]. Density functional GGA (PBE) was used to describe the exchange–correlation energy of the electronic subsystem [24] with Hubbard corrections (GGA + U) within the Cococcioni and Gironcoli approach [25].

Unfortunately, for strongly correlated materials including ZnO, standard DFT with GGA (PBE) functional will underestimate the bandgap. This is explained by the fact that in such systems the Zn d -states form a narrow band that placed in the middle of the valence band like other tetrahedral coordinate bonded semiconductors. These Zn d -states mix with the O p -states and create the top of the valence band. The composing shifts upward to the top of the valence band, decreasing the bandgap. Using Hubbard U correction to the Zn d -orbitals is an efficient

and computationally low-cost way to correct for the serious underestimation of the bandgap and also set right the incorrect energy position of the d -states of the Zn atoms. The bandgap of ZnO calculated with one U parameter stay about 50% lower than the experimental value [8]. To accurately describe the electronic spectrum, two Hubbard corrections were selected the studied objects: for d -orbitals Zn (U_d) and p -orbitals O (U_p). This method has been successfully applied in the investigation of the electronic properties of structures ZnO of different dimensions [26–29]. Using $U_d = 10$ eV and $U_p = 7$ eV, we received bandgap (E_g) for bulk ZnO 3.4 eV perfectly consistent with experimental data [30]. All investigated nanostructures were put in a cubic unit cell with a thickness of a vacuum slab of 15 Å on all sides to avoid any effects of periodicity. Structural lattice parameters were relaxed by quasi-Newton ionic optimization applying the Broyden, Fletcher, Goldfarb, Shanno (BFGS) algorithm [31–34]. These parameters were optimized while the forces were declined smaller than 0.01 eV/Å per atom.

As a model object $(\text{ZnO})_{12}$ nanocluster was selected, which constructed with eight hexagons and six tetragons and has the T_h symmetry, its optimized structure is depicted in Fig. 1a. The results show that is two different Zn–O bond length within nanocluster: the short bond is 1.90 Å between two hexagons and long bond is 1.98 Å between a hexagon and a tetragon that is within the experimental data for Zn–O bonds [35, 36] and earlier ab initio calculations [11–13].

For all considered $(\text{ZnO})_{12}$ nanoclusters: pure and decorated of Pt atoms, energy band structure and density of states (DOS) was calculated. The energy bandgap is defined as the difference between the energy of the highest occupied states and the energy of the lowest unoccupied states. To identify the genetic origin of energy band states, total and partial DOS distributions were plotted. This is very quick and easy to analyze which atoms or orbitals are affected by the specific peaks in the DOS. The Gaussian smearing of 0.2 eV width has been applied to the DOS.

For pure $(\text{ZnO})_{12}$ nanocluster calculated bandgap is 4.11 eV (Fig. 1b) which is in a good agreement with previous theoretical studies, where B3LYP functional was used [11, 12]. Figure 1c represents partial DOS for $(\text{ZnO})_{12}$ nanocluster which indicates that the top of the valence band is formed by O $2p$ -orbitals while the bottom of the conduction band is composed of Zn $4s$ -orbitals. Zn d -orbitals locate around the energy mark -7 eV.

For Pt-decorated and Pt-doped structures, we considered four different positions of locating Pt atoms in the structure of $(\text{ZnO})_{12}$ nanocluster: Pt atom substituted by Zn atom; Pt atom substituted by O atom; Pt atom located above the tetragon surface and Pt atom located above

Fig. 1 Optimized structure (a), band structure (b) and partial DOS (c) of $(\text{ZnO})_{12}$. Bond lengths are in Angstroms (Å)

the hexagon surface. The formation energy of Pt-doped $(\text{ZnO})_{12}$ nanoclusters, when there is a substitution of surface Zn or O atoms by Pt atom is considered, is estimated pursuant to the following equation:

$$E_f = E_{\text{NC} + \text{Pt}} + E_X - E_{\text{NC}} - E_{\text{Pt}},$$

where $E_{\text{NC} + \text{Pt}}$ and E_{NC} correspond to the total energies of the Pt-doped and undoped $(\text{ZnO})_{12}$ nanocluster, respectively, E_X and E_{Pt} are total energies of free Zn or O and Pt atoms, respectively. The optimized free O, Zn and Pt atoms energies were calculated in the same unit cell as $(\text{ZnO})_{12}$ nanocluster. When the Pt atom is placed above the surface of $(\text{ZnO})_{12}$ nanoclusters, the equation to determine E_f can be rewritten as:

$$E_f = E_{\text{NC} + \text{Pt}} - E_{\text{NC}} - E_{\text{Pt}},$$

where $E_{\text{NC} + \text{Pt}}$ and E_{NC} correspond to the total energies of the Pt-decorated and bare $(\text{ZnO})_{12}$ nanocluster, respectively.

Positive formation energy denotes the replacement process is endothermic, while negative formation energy denotes the replacement process is exothermic.

Adsorption properties are defined by adsorption energy:

$$E_{\text{ad}} = E_{\text{NC} + \text{Pt} + \text{gas}} - E_{\text{NC} + \text{Pt}} - E_{\text{gas}},$$

where $E_{\text{NC} + \text{Pt} + \text{gas}}$, $E_{\text{NC} + \text{Pt}}$, respectively, describe total energies of Pt-doped $(\text{ZnO})_{12}$ nanoclusters with or without gas molecules adsorbed on their surfaces, and E_{gas} corresponds to the total energy of free gas molecules. The relaxed isolated gas molecules were calculated in the same unit cell as $(\text{ZnO})_{12}$ nanocluster. The received negative adsorption energy implies that the adsorption process is exothermic.

3 Results and discussion

3.1 Structural geometry Pt-doped $(\text{ZnO})_{12}$ nanoclusters

We considered as noted above four placement positions of Pt atoms on the surface of $(\text{ZnO})_{12}$ nanoclusters, optimized structures which depict in Fig. 2: Pt atom substituted by Zn atom ($(\text{ZnO})_{12} + \text{Pt}(\text{Zn})$, Fig. 2a); Pt atom substituted by O atom ($(\text{ZnO})_{12} + \text{Pt}(\text{O})$, Fig. 2b); Pt atom located above the tetragon surface ($(\text{ZnO})_{12} + \text{Pt}(4)$, Fig. 2c); Pt atom located above the hexagon surface ($(\text{ZnO})_{12} + \text{Pt}(6)$, Fig. 2d). Changes in the geometry of structure are observed for all Pt-doped nanoclusters after structural relaxation. In the case, $(\text{ZnO})_{12} + \text{Pt}(\text{Zn})$ were formed by three Pt–O bonds, one of which has a length of 2.15 Å and two have a length of 2.16 Å. The calculated bandgap is 1.56 eV as can be seen from Table 1. To illustrate how the Pt atom changes the electronic structure of the $(\text{ZnO})_{12}$ nanoclusters were plotted DOS of the Pt-doped $(\text{ZnO})_{12}$ nanoclusters. The total DOS for $(\text{ZnO})_{12} + \text{Pt}(\text{Zn})$ displays the appearance of two new

Fig. 2 Optimized structure, total DOS and partial DOS for **a** $(\text{ZnO})_{12} + \text{Pt (Zn)}$, **b** $(\text{ZnO})_{12} + \text{Pt (O)}$, **c** $(\text{ZnO})_{12} + \text{Pt (4)}$ and **d** $(\text{ZnO})_{12} + \text{Pt (6)}$ configurations. Bond lengths are in Angstroms (Å)

Table 1 Energy bandgaps (E_g , eV) and formation energy (E_f , eV) of pristine and Pt-doped $(\text{ZnO})_{12}$ nanoclusters

System	E_g	E_f
$(\text{ZnO})_{12}$	4.11	
$(\text{ZnO})_{12} + \text{Pt (Zn)}$	1.56	−0.22
$(\text{ZnO})_{12} + \text{Pt (O)}$	2.11	1.39
$(\text{ZnO})_{12} + \text{Pt (4)}$	1.21	−2.45
$(\text{ZnO})_{12} + \text{Pt (6)}$	0.58	−1.99

states near 1.59 and 2.92 eV compared to DOS of the bare nanocluster and indicates a decrease in the bandgap by 2.55 eV (Fig. 2a).

In the case of $(\text{ZnO})_{12} + \text{Pt(O)}$, three Pt–Zn bonds were formed, one of which has a length of 2.52 Å and two have a length of 2.59 Å, E_g is 2.11 eV. DOS also demonstrates emerging of two new states near the 2.13 and 2.89 eV comparing with DOS of the bare nanocluster indicating narrowing the bandgap by 2.0 eV (Fig. 2b). For $(\text{ZnO})_{12} + \text{Pt(4)}$, Pt atom forms two bonds with neighboring Zn atoms and the length of which is nearly 2.75 Å. The bandgap, in this case, is 1.21 eV. Total DOS displays a decrease in energy band gap due to the appearance of three new states at 1.17, 2.2 and 3.31 eV related to Pt states on a surface $(\text{ZnO})_{12}$ (Fig. 2c). For $(\text{ZnO})_{12} + \text{Pt(6)}$ configuration, we are seeing that Pt atom does not form any bonds with neighboring atoms and Pt atom is placed at a distance above 2.82 Å (Fig. 2d) after structural optimization and E_g is 0.58 eV. The DOS indicates that states of Pt atom dominate in the bandgap, which leads to a significant narrowing of the bandgap (Table 1). Also, considering the states below the Fermi level on the DOS of Pt-doped $(\text{ZnO})_{12}$ nanoclusters, we observed the shift of the main peaks down the energy scale compared with its bare analog. This is mainly due to the hybridization of Pt *d*-states and O *p*-states.

Formation energy was calculated for all placement positions of Pt atoms on the surface of $(\text{ZnO})_{12}$ nanoclusters and is presented in Table 1. As seen from Table 1, three replacements position produce exothermic process, while substitution of O atom leads to the endothermic process. Consequently, the most favorable placement position is configuration when a Pt atom placed above the tetragon surface. Hence, further calculations are made for this position of Pt atom on the surface of $(\text{ZnO})_{12}$ nanocluster.

3.2 CO molecules adsorption on Pt-doped $(\text{ZnO})_{12}$ nanoclusters

Previous theoretical calculations of the adsorption of a CO molecule on the surface of nanostructures show a stronger interaction with a bare cluster at C orientation of molecule CO that O orientation [7, 21]. Similar results were obtained with the adsorption of CO molecule on the surface of $(\text{ZnO})_{12}$ -doped nanoclusters by atoms of different metals [11, 12, 20]. Therefore, we also investigated the CO adsorption on the Pt-doped nanocluster surface, depending on the orientation of the molecule. Figure 3 presents optimized structures Pt-doped $(\text{ZnO})_{12}$ nanoclusters with different orientations of CO molecule. Bond length Pt–O in $(\text{ZnO})_{12} + \text{Pt (4)} + \text{OC}$ is 2.23 Å that longer than Pt–C $(\text{ZnO})_{12} + \text{Pt (4)} + \text{CO}$ which is 1.95 Å and indicates weaker interaction between Pt–O than Pt–C. Particular atomic DOS for $(\text{ZnO})_{12} + \text{Pt (4)} + \text{OC}$ (Fig. 3a) shows the appearance of the states near 1.55 and 2.61 eV that leads to more narrowing of the width of bandgap than $(\text{ZnO})_{12} + \text{Pt (4)} + \text{CO}$ (Fig. 3b). A weaker interaction of the O orientation of the CO molecule also confirms the lower value of the adsorption energy in this case than for C orientation (see Table 2).

Fig. 3 Optimized structure, total DOS and partial DOS for **a** $(\text{ZnO})_{12} + \text{Pt} + \text{OC}$, **b** $(\text{ZnO})_{12} + \text{Pt} + \text{CO}$ and **c** $(\text{ZnO})_{12} + \text{CO}$ configurations. Bond lengths and bond distances are in Angstroms (Å)

Table 2 Energy bandgaps (E_g , eV) and adsorption energy (E_{ad} , eV) after CO adsorption on pristine and Pt-doped $(\text{ZnO})_{12}$ nanoclusters

System	E_g	E_{ad}
$(\text{ZnO})_{12} + \text{CO}$	4.17	-0.19
$(\text{ZnO})_{12} + \text{Pt} + \text{CO}$	1.98	-3.54
$(\text{ZnO})_{12} + \text{Pt} + \text{OC}$	1.49	-0.74
$(\text{ZnO})_{12} + \text{Pt} + 2\text{CO}$	2.27	-4.65
$(\text{ZnO})_{12} + \text{Pt} + 3\text{CO}$	0.6	-3.41

For comparison with sensing properties of Pt-doped $(\text{ZnO})_{12}$ nanoclusters, we also considered adsorption CO on undoped $(\text{ZnO})_{12}$ nanocluster. Structure after optimization is presented in Fig. 3c. Bond length Zn-C is 2.21 Å which is bigger than bond length Pt-C. Bond C-O inside of gas molecule is 1.14 Å that is smaller than this bond in the doped system, while C-O bond length in $(\text{ZnO})_{12} + \text{Pt} (4) + \text{CO}$ is 1.16 Å that approximately the same as for a free CO molecule. E_g $(\text{ZnO})_{12} + \text{CO}$ is 4.17 eV and slightly changed in comparison with E_g bare $(\text{ZnO})_{12}$ (Fig. 3c) that also is in correlation with previous theoretical results [11, 12]. This indicates that the interaction between the nanocluster and CO does not have a significant effect on the electronic structure of Pt-doped $(\text{ZnO})_{12}$.

The adsorption energy of the $(\text{ZnO})_{12} + \text{Pt} (4) + \text{CO}$ is -3.54 eV and indicates the overflow of the exothermic absorption process. Its absolute value is bigger than for $(\text{ZnO})_{12} + \text{CO}$ (see Table 2) and assumes that Pt-doped nanoclusters have energy preferable adsorption properties. The bond length between C atom of CO molecule and Pt atom of doped nanocluster is 1.95 Å and is shorter than the bond length between C and Zn atoms in bare

nanocluster which together with larger adsorption energy value indicates stronger bonding of CO molecule with Pt-doped nanocluster. The good adsorption properties at CO adsorbed on Pt-doped nanoclusters are also confirmed by the experimental data [22]. Adsorption of the CO molecule on the Pt-doped nanocluster leads to an increase in the bandgap to 1.98 eV of the doped nanocluster. Thus, the interaction between CO molecule and doped nanocluster produces a modification of electronic properties Pt-doped $(\text{ZnO})_{12}$. Partial DOS of CO molecule in $(\text{ZnO})_{12} + \text{Pt}(4) + \text{CO}$ (Fig. 3b) compared with DOS of Pt-doped $(\text{ZnO})_{12}$ (Fig. 2c) represents that *p*-states of CO molecule lead to a change of the Pt atom states energy position and to an expansion of the bandgap.

Also, we have carried out additional studies of the influence of the amount of adsorbed CO molecules on the Pt atom in order to establish the sensitivity of such systems. The optimized structures of such systems are displayed in Fig. 4 and the results of adsorption and electronic properties in Table 2.

When two molecules of CO are on Pt atom (Fig. 4a), adsorption of the second CO molecule changes the site of the first CO and there is an increase in the bond length between the CO molecules and the Pt atom up to 2.07 and 2.01 Å, respectively. Also, the C-O bond length of the second molecule is 1.15 Å. The adsorption energy for two molecules of CO is -4.65 eV which is more than in the case of one molecule of CO adsorbed on nanocluster that implies higher sensitivity of Pt atom to two CO molecules. Also, it was observed increases to 2.27 eV of energy band gap of $(\text{ZnO})_{12} + \text{Pt}(4) + 2\text{CO}$ compared with $(\text{ZnO})_{12} + \text{Pt}(4) + \text{CO}$ that testifies to change the electrical conductivity. Total DOS shows that the presence of two molecules of CO on

Fig. 4 Optimized structure, total DOS and partial DOS for **a** $(\text{ZnO})_{12} + 2\text{CO}$ and **b** $(\text{ZnO})_{12} + \text{Pt} + 3\text{CO}$ configurations. Bond lengths and bond distances are in Angstroms (Å)

Pt atom indicates the appearance of two states around to 2.28 and 3.37 eV, but disappearing of the state near the valence band top that leads to expanding of bandgap which is easily visible when comparing Figs. 4a and 3b.

The presence of a third CO molecule in the structure (Fig. 4b) changes the position of the other two and the bond length between the Pt atom and the CO molecules increases to 2.19, 2.07 and 2.16 Å, respectively. The bond length between the Pt atom and the Zn and inside the CO molecule also increases. Total DOS (Fig. 4b) displays the appearance of additional CO-states in the forbidden zone of nanocluster electron spectra (Fig. 4a) leading to bandgap constriction to 0.6 eV. After adsorption of the third CO molecule, we observe a change of adsorption energy to -3.41 eV. Such decreasing of adsorption energy absolute value indicates that the electronic properties of the Pt-doped $(\text{ZnO})_{12}$ are less sensitive to this amount of adsorbed CO molecules. So, we can conclude that the preferable state is adsorption of no more than two CO molecules on a single atom of Pt in $(\text{ZnO})_{12}$ nanocluster.

3.3 H_2 molecules adsorption on Pt-doped $(\text{ZnO})_{12}$ nanoclusters

Next, we analyze the H_2 molecule adsorption on the Pt-doped $(\text{ZnO})_{12}$ nanoclusters. The results of adsorption and electronic properties of all studied systems are presented in Table 3.

To determine the effect of Pt atom on the adsorption properties of nanoclusters initially were performed calculation H_2 adsorption on undoped $(\text{ZnO})_{12}$ nanoclusters,

Table 3 Energy bandgaps (E_g , eV) and adsorption energy (E_{ad} , eV) after H_2 adsorption on pristine and Pt-doped $(\text{ZnO})_{12}$ nanoclusters

System	E_g	E_{ad}
$(\text{ZnO})_{12} + \text{H}_2$	4.18	-0.02
$(\text{ZnO})_{12} + \text{Pt} + \text{H}_2$	1.55	-2.93
$(\text{ZnO})_{12} + \text{Pt} + 2\text{H}_2$	1.52	-2.75
$(\text{ZnO})_{12} + \text{Pt} + 3\text{H}_2$	2.50	-3.43
$(\text{ZnO})_{12} + \text{Pt} + 4\text{H}_2$	1.36	-2.37

optimized geometry and DOS of which represented on Fig. 5a. Next, we placed one H_2 molecule to Pt-doped $(\text{ZnO})_{12}$, the optimized structure of which presented in Fig. 5b. The two H–Pt bond lengths are about 1.78 Å; the Pt–Zn bond lengths are 2.57 and 3.69 Å. Compared to the Pt–Zn bond length in the nanocluster without of the H_2 molecule, the adsorption of the hydrogen molecule practically become stronger the one Pt–Zn bond but reduce the other Pt–Zn bond. The bond length inside of the H_2 molecule is 0.86 Å. The calculated adsorption energy of this complex (-2.93 eV) implies exothermic adsorption. This value is higher compared with adsorption of H_2 molecule on the bare $(\text{ZnO})_{12}$ nanocluster (-0.017 eV) denotes that Pt-doped $(\text{ZnO})_{12}$ is more sensitive to H_2 molecule. Before and after adsorption, the energy bandgap increases from 1.21 to 1.55 eV, respectively. DOS plot for Pt-doped $(\text{ZnO})_{12} + \text{H}_2$ indicates that appear states at 1.54 and 2.94 eV compared to DOS of H_2 adsorbed on undoped $(\text{ZnO})_{12}$ (Fig. 5a) derived from s -states of H_2 and d -states of Pt atom. Such interaction between impurity states and molecule states

Fig. 5 Optimized structure, total DOS and partial DOS for **a** $(\text{ZnO})_{12} + \text{H}_2$, **b** $(\text{ZnO})_{12} + \text{Pt} + \text{H}_2$, **c** $(\text{ZnO})_{12} + \text{Pt} + 2\text{H}_2$ and **d** $(\text{ZnO})_{12} + \text{Pt} + 3\text{H}_2$ configurations. Bond lengths and bond distances are in Angstroms ($\text{\AA}$)

leads to a reduction in the bandgap (see Table 3) for Pt-doped $(\text{ZnO})_{12} + \text{H}_2$ comparing to undoped nanocluster, but H_2 states provide an increase in E_g compared with Pt-doped $(\text{ZnO})_{12}$ before adsorption.

Further, we studied the augment of the second hydrogen molecule to the complex. The optimized structure and DOS are represented in Fig. 5c. Adding a second H_2 molecule has not changed the placement of the first H_2 molecule and H–H bond inside of the second molecule is $0.77 \text{ \AA}$ that is shorter than the bond length in first H_2 molecule ($0.87 \text{ \AA}$). The Pt–H bond lengths for first and second H_2 molecules, respectively, elongated to 1.79 and $2.19 \text{ \AA}$. When two hydrogen molecules adsorbed on Pt-doped $(\text{ZnO})_{12}$, the Pt–Zn bond lengths are 3.75 and $2.59 \text{ \AA}$, thus clear that the second H_2 molecule contributes to an even greater weakening the interaction between the Pt atom and $(\text{ZnO})_{12}$. The adsorption energy of this complex is -2.75 eV . Upon the adsorption of the second H_2 molecule, the E_g slightly reduce compared with adsorption of one H_2 molecule and is 1.52 eV . Consequently, the conductivity of Pt-doped $(\text{ZnO})_{12}$ nanocluster is slightly increased when two hydrogen molecule is adsorbed. The total DOS depicted in Fig. 5c is similar to the case of adsorption one molecule on Pt-doped nanocluster. As a result, the second molecule makes no significant contribution to the electronic structure of this system.

Finally, we verified the incorporation of the third H_2 molecule to the Pt-doped $(\text{ZnO})_{12}$ nanocluster, the optimized structure of which is displayed in Fig. 5d. The presence in the system of the third H_2 molecule causes a change in the location of the other two. The average Pt–H bond lengths for three molecules are 2.01 , 1.91 and $1.92 \text{ \AA}$, while H–H bond inside of H_2 molecules is 0.80 , 0.82 and $0.81 \text{ \AA}$. After adding the third H_2 molecule to the system, the Pt–Zn bond lengths are 2.72 and $4.39 \text{ \AA}$, indicating

that the interaction between Pt and $(\text{ZnO})_{12}$ nanocluster is even more weakened. However, unlike the adsorption of two molecules, the adsorption energy increases with the addition of the third molecule of H_2 to -3.43 eV . This value is also bigger than at one H_2 molecule adsorbed on Pt-doped $(\text{ZnO})_{12}$ nanocluster demonstrating a higher sensitivity of such a system. The total DOS shows when three molecules are adsorbed on Pt-doped nanocluster, there is a shift up the energy scale of the bands (Fig. 5d) corresponding to the interaction between the s -states of the H_2 molecule and d -states of impurity. Comparison of Fig. 5d with Fig. 5c and 5b shows that such displacement leads to a widening of the energy bandgap (see Table 3). Also, the increase in bandgap indicating significant jump down conductivity of Pt-doped $(\text{ZnO})_{12}$ nanocluster. Further studies show that with increasing the number of H_2 molecules on Pt-doped $(\text{ZnO})_{12}$ nanocluster leads to a decrease in adsorption energy absolute value (see Table 3) and indicates that the most energetically preferable state is three H_2 molecules adsorbed on a single Pt atom of the Pt-doped $(\text{ZnO})_{12}$.

4 Conclusions

Within DFT, we carried out the investigation of the structural, electronic and adsorption properties of Pt-doped $(\text{ZnO})_{12}$ nanocluster with CO and H_2 gas molecules. Studies show that the most energetically favorable position is the surface doping of the Pt atom on the tetragon surface of bare $(\text{ZnO})_{12}$. Also, this placement leads to the smaller energy gap of the Pt-doped $(\text{ZnO})_{12}$ nanocluster and denotes that the doping improves the conductivity of nanocluster. We predicted that CO and H_2 adsorbed on Pt-doped $(\text{ZnO})_{12}$ leads to increase in adsorption energy

compared with undoped analogs. The electronic properties of Pt-doped (ZnO)₁₂ are responsive to the amount of adsorbed CO molecules. The calculation results show that energy preferable is a situation when no more than two CO molecules can be present on a single atom of Pt. The CO adsorption on Pt-doped (ZnO)₁₂ implies a decrease in conductivity with increasing gas molecules number. The interaction strength between Pt atom and nanocluster is reducing upon adsorption of the H₂ molecule. When two H₂ molecules adsorbed on doped nanocluster there is a slight narrowing of the bandgap, while adsorption of three molecules causes a sharp increase in the bandgap. Thus, a jump in electrical conductivity will be observed. The sensitivity of the adsorption properties to the number of adsorbed hydrogen molecules is also investigated, and results show that at least three H₂ molecules can be adsorbed on a single Pt atom.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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