

Quantum chemical insights on tuning structural stability and electronic properties of PdO nanostructures

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Abstract: Using density functional theory, the realistic structures such as cone, sheet and ring structured palladium oxide (PdO) nanostructures are optimized and simulated successfully with B3LYP/ LanL2DZ basis set. The structural stability of pure, F and Ni substituted PdO nanostructures are discussed in terms of calculated energy, binding energy and embedding energy. The dipole moment and point group of pure and impurity substituted PdO nanostructures are also reported. Electronic properties of PdO nanostructures are described in terms of HOMO-LUMO gap. The present work gives information to tailor different nanostructure of PdO using substitution impurities and to improve the electronic properties and structural stability which is suitable for oxidation catalysis, catalytic combustion of natural gas, gas sensing in fuel cell and automobiles.

Keywords: PdO; nanostructures; electron density; binding energy; embedding energy.

Introduction

The oxidation of transition metal (TM) surfaces plays a vital role in many applications which are related to oxidation catalysis, catalytic combustion of natural gas, gas sensing in fuel cell and automobiles. Oxide phases can be enhanced on TM surfaces owing to oxygen-rich conditions which lead to significant change in catalyst performance. Among TM oxides, palladium oxide (PdO) is a promising material toward the oxidation of methane. It is proven by many reports that prior catalyst studies revealed that the formation of palladium oxide is responsible for extreme activity of palladium catalysts about the catalytic combustion of methane under the lean conditions of fuel [1-4]. PdO is a p-type semiconductor with small optical band gap. Pillo et al reported energy gap value of PdO between 1.5-2 eV [5]. Rey et al [6] reported the band gap value of PdO as 2.13 and 2.67 eV using optical density measurement and photoconductivity measurements respectively. Investigation of methane adsorption on PdO (101) surfaces has been studied both experimentally and theoretically using density functional theory (DFT) [7-9]. From these studies it is inferred that methane gets strongly adsorbed on PdO (101) surface. Recent investigations are mainly focussed on intermediate oxygen phases of oxidation reactions in Pd surfaces. In the present work, the structural stability and electronic properties of PdO nanostructures with substitution impurities such as F and Ni are investigated. Moreover, the density functional theory (DFT) is an efficient method to study the electronic properties and structural stability of PdO nanostructures [10-13].

Computational methods

DFT method is used to investigate the nanostructures of PdO. The cone, sheet and ring structured PdO nanostructures are completely optimized and simulated successfully with Gaussian 09W package [14]. In the present work DFT method is facilitated with Becke's three-parameter hybrid functional in combination with Lee-Yang-Parr correlation functional (B3LYP). LanL2DZ basis set is a good choice to optimize pure and impurities substituted PdO nanostructures [15-17]. Since it is suitable for H, Li-La and Hf-Bi elements this basis set can be used to optimize PdO nanostructures. HOMO-LUMO gap and density of states (DOS) spectrum of PdO nanostructures are calculated by Gauss Sum 3.0 package [18]. The energy convergence for PdO nanostructures is achieved in the order of 10^{-5} eV.

Results and Discussion

The present work mainly focus on HOMO-LUMO gap, binding energy (BE), embedding energy (EE), calculated energy and point group (PG) of PdO nanostructures incorporating with suitable substitution impurities such as fluorine and nickel. Figure 1 (a) – Figure 1 (c) represents pure cone, sheet and ring structured PdO nanostructures respectively and each structure consists of ten Pd atoms and ten O atoms. In that order Figure 1 (d) – Figure 1 (f) denotes F substituted cone, sheet and ring structured PdO nanostructures and which have ten Pd atoms, nine O atoms and one F atom is replaced for O atom. Correspondingly, Figure 1 (g) – Figure 1 (i) refers Ni substituted cone, sheet and ring structured PdO nanostructures and they contains nine Pd atoms, ten O atoms and one Pd atom is replaced with one Ni atom.

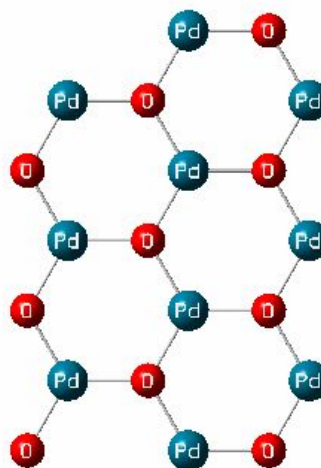
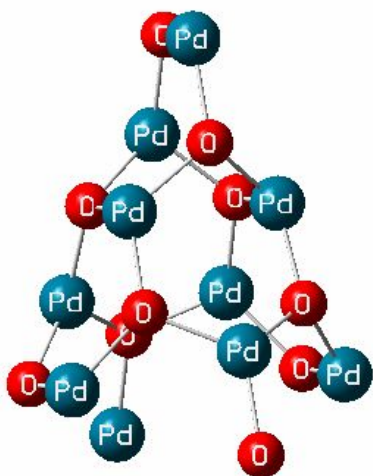


Figure. 1 (a) Pure cone structured PdO nanostructure Figure. 1 (b) Pure sheet structured PdO nanostructure

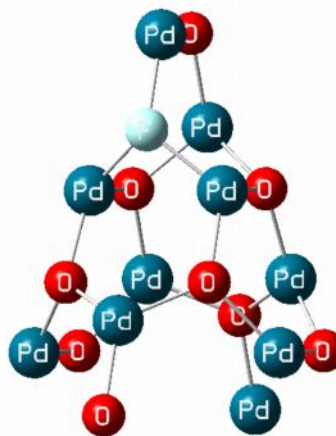
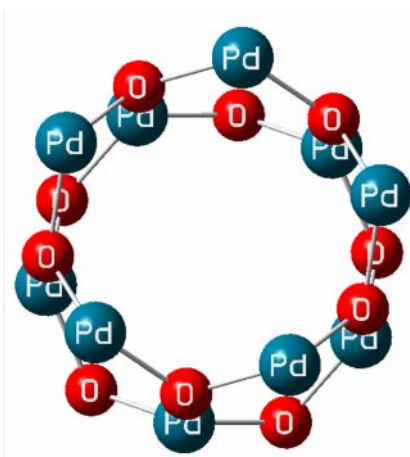


Figure. 1 (c) Pure ring structured PdO nanostructure

Figure. 1 (d) F substituted cone structured PdO nanostructure

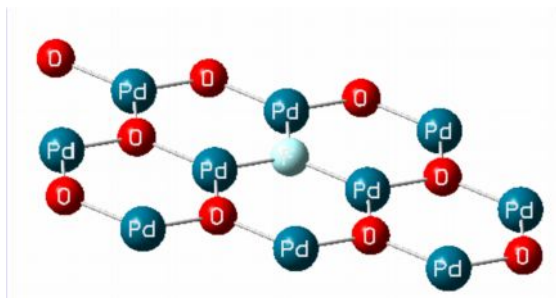


Figure. 1 (e) F substituted sheet structured PdO nanostructure

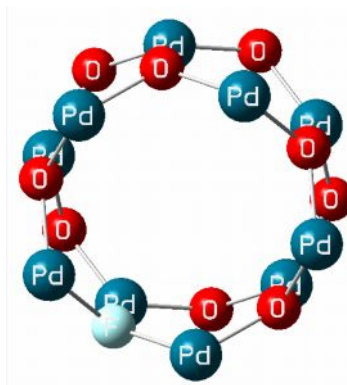


Figure. 1 (f) F substituted ring structured PdO nanostructure

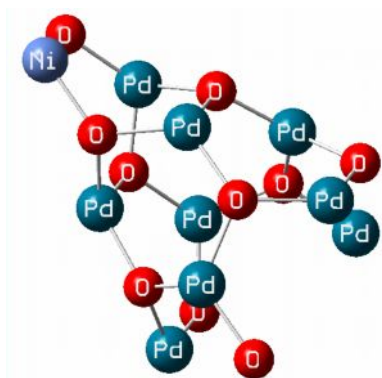


Figure. 1 (g) Ni substituted cone structured PdO nanostructure

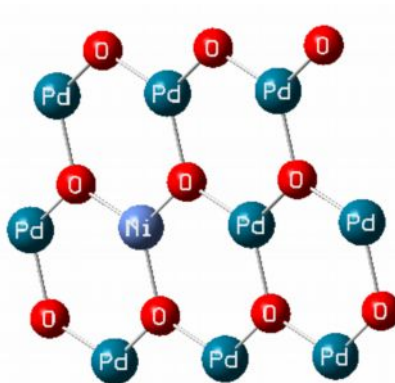


Figure. 1 (h) Ni substituted sheet structured PdO nanostructure

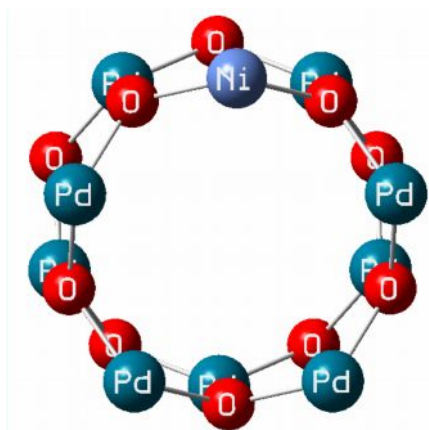


Figure. 1 (i) Ni substituted ring structured PdO nanostructure

The structural stability of PdO nanostructures can be explained by calculated energy. Table 1 shows calculated energy, point group and dipole moment (DM).

Table. 1 Energy, point symmetry and dipole moment of PdO nanostructures

Nanostructures	Energy (Hartrees)	Dipole moment (Debye)	Point Group
Pure cone structured PdO	-2005.67	15.61	C _s
Pure sheet structured PdO	-2006.29	3.65	C _s
Pure ring structured PdO	-2006.09	24.3	C ₁
F substituted cone structured PdO	-2030.58	6.75	C _s
F substituted sheet structured PdO	-2030.94	29.1	C _s
F substituted ring structured PdO	-2030.84	18.99	C ₁
Ni substituted cone structured PdO	-2048.34	0.41	C _s
Ni substituted sheet structured PdO	-2048.77	4.01	C _s
Ni substituted ring structured PdO	-2048.30	16.21	C ₁

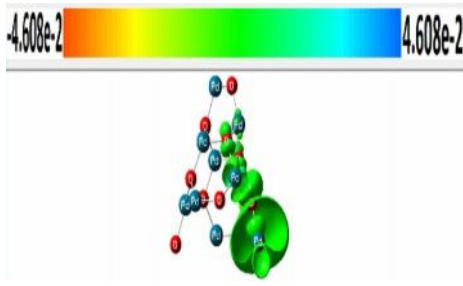
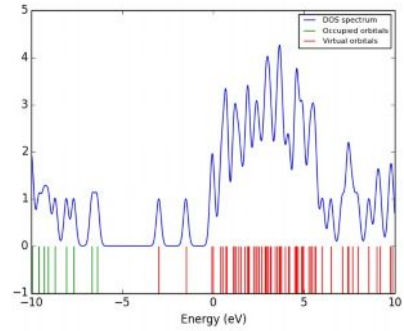
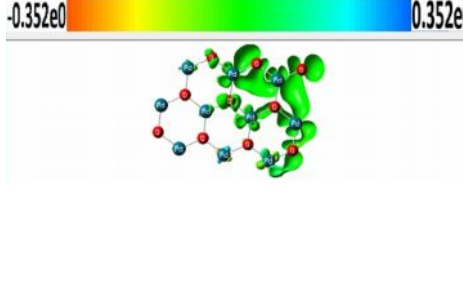
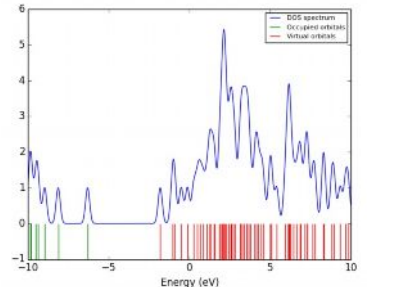
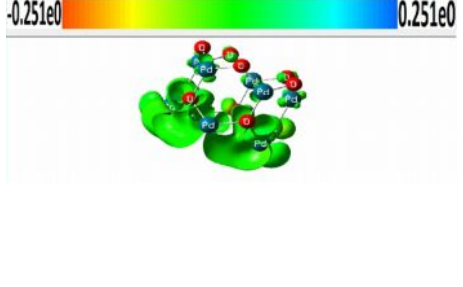
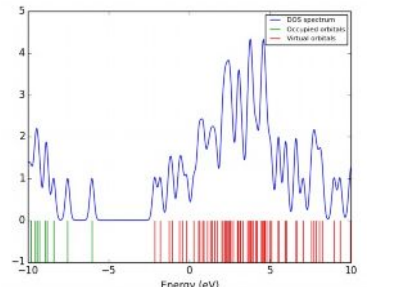
The calculated energy of pure cone, sheet and ring structured PdO nanostructures have -2005.67, -2006.29 and -2006.09 Hartrees respectively. In that order F substituted cone, sheet and ring structured PdO nanostructures have the calculated values as -2030.58, -2030.94 and -2030.84 Hartrees respectively. Correspondingly, Ni substituted cone, sheet and ring structured PdO nanostructures have the calculated values of -2048.34, -2048.77 and -2048.3 Hartrees respectively. From the observation the stability of PdO nanostructures increases owing to substitution of both impurities namely F and Ni. From all the three categories, sheet structured PdO nanostructure dominates than other two categories namely cone and ring. Since the calculated energy is slightly higher in this case and it may be concluded that the stability is more for sheet structured PdO.

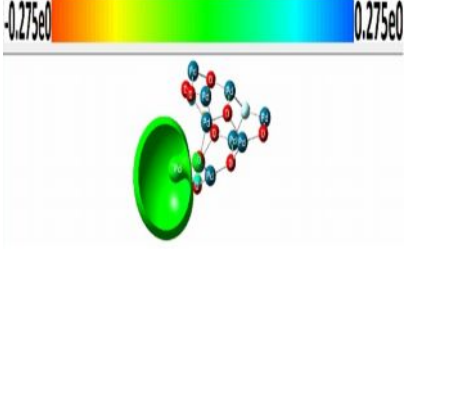
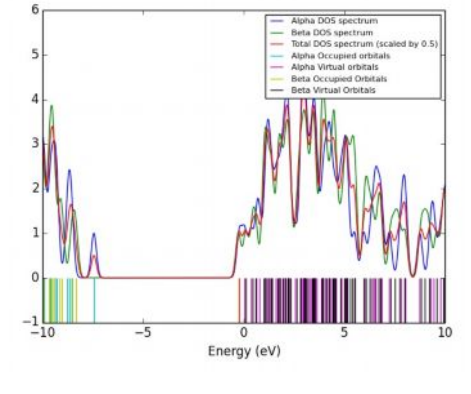
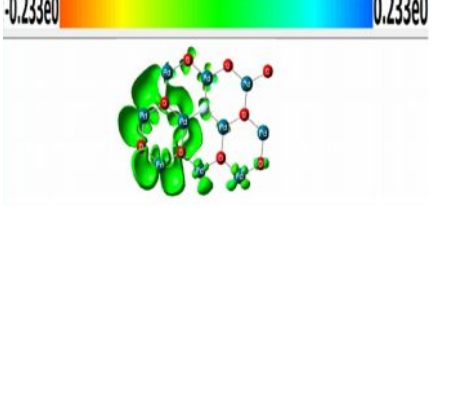
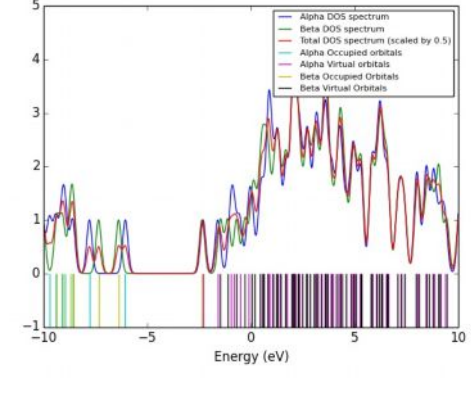
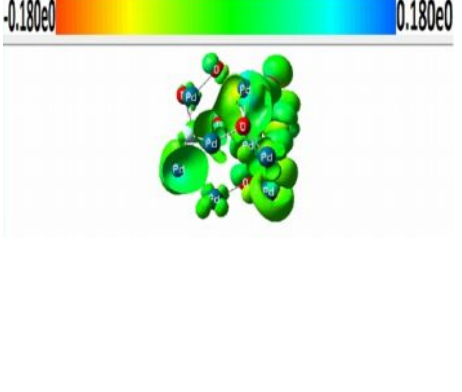
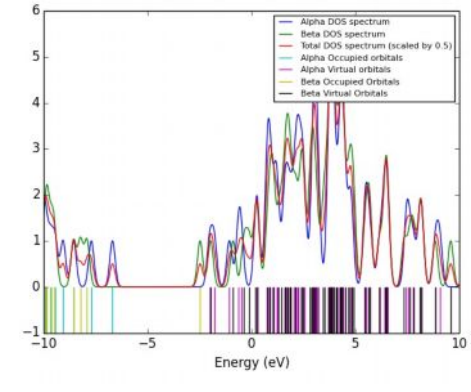
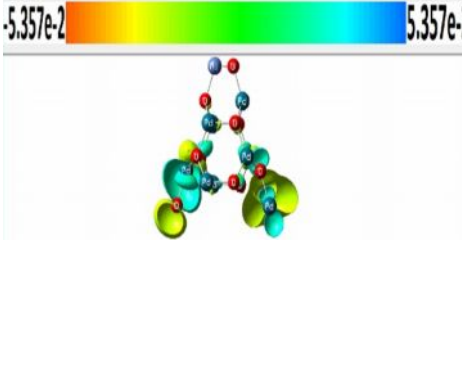
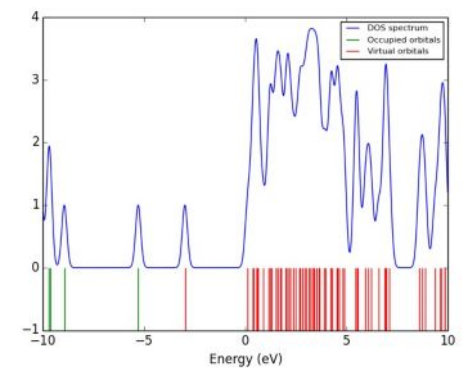
The dipole moment refers the charge distribution on PdO nanostructures. If the DM of PdO nanostructures are low value it infers that the distribution of charge is uniform. The low values of DM are recorded in the case of pure sheet, F substituted cone, Ni substituted cone and sheet structured PdO nanostructures with the values of 3.65, 6.75, 0.41 and 4.01 Debye respectively and the remaining structures of PdO nanostructures have high values of DM. The point symmetry of all the discussed PdO nanostructures is found to be C₁ or C_s.

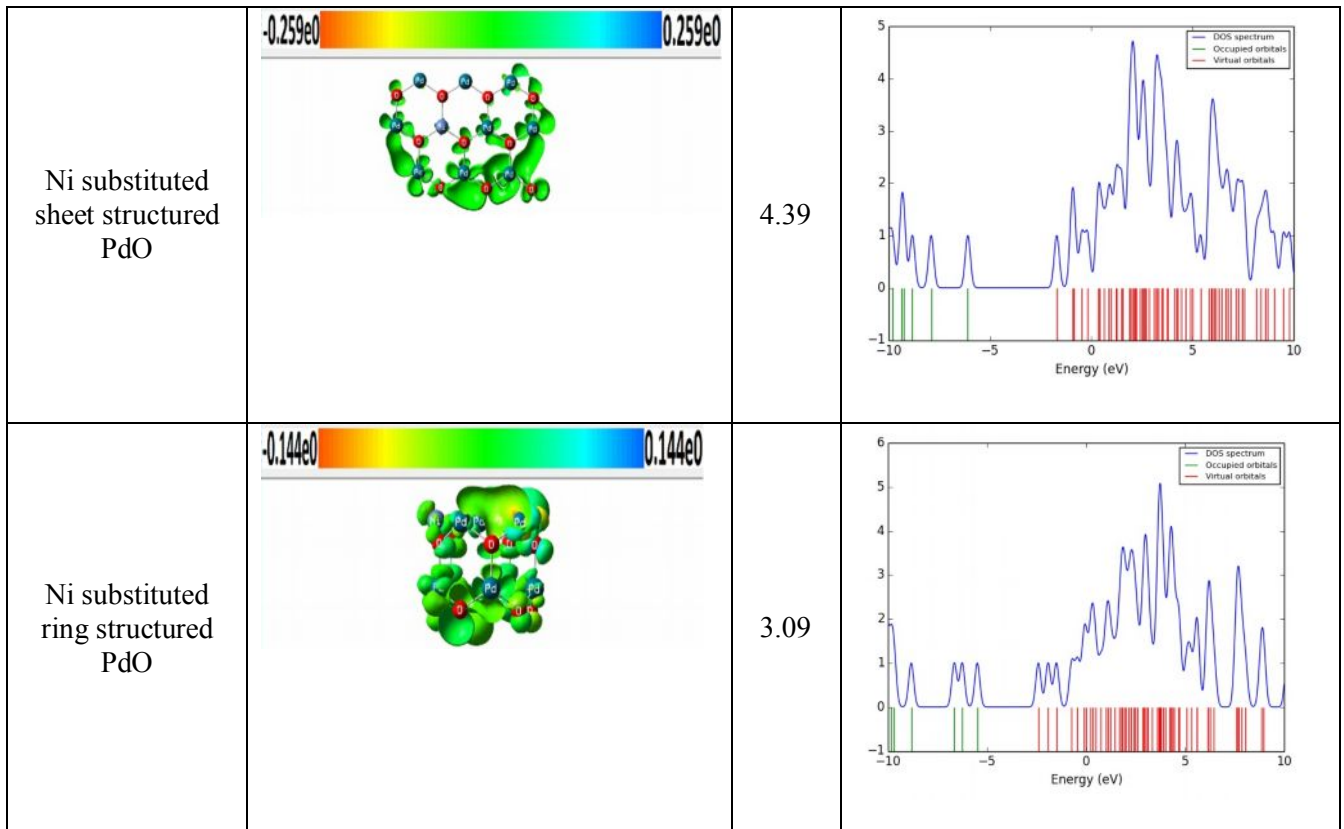
Density of states and HOMO-LUMO gap of PdO nanostructures

The electronic properties of PdO nanostructures can be illustrated by lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) [19-22]. The energy gap (E_g) value for pure, F and Ni substituted PdO nanostructures are shown in Table 2. The HOMO – LUMO gap of pure cone, sheet and ring structured PdO nanostructures have the values of 3.4, 4.5 and 3.88 eV respectively. The experiment band gap of PdO is reported as 2.67 eV. The conductance of PdO nanostructures varies owing to dimension, coordination number and bond length of Pd-O structure. The F substituted cone, sheet and ring structured PdO nanostructures has the corresponding energy gap values of 7.23, 3.75 and 4.68 eV. These energy gap variations are observed owing to electronic configuration of F atom ($1s^2 2s^2 2p^5$), O atom ($1s^2 2s^2 2p^4$) and Pd atom ($[Kr] 4d^{10}$). The high value of energy gap implies that the electrons in the valence band need more energy to transit to conduction band. F substituted cone and ring structured PdO nanostructures have comparatively high band gap value of 7.23 and 4.68 eV. Since F element is a donor impurity, it donates electrons. Obviously, PdO nanostructure belongs to p-type semiconductor, when F donor atom is substituted on PdO nanostructures the excess electrons occupies the holes in PdO. Hence the concentration of holes in PdO nanostructures rapidly decreases. In Ni substituted cone, sheet and ring structured PdO nanostructures; all have consistent value of HOMO – LUMO gap values which are 2.31, 4.39 and 3.09 eV respectively. The conductivity of PdO nanostructures gets increased owing to substitution of Ni impurities. Therefore, the concentration of holes increases in HOMO level due to substitution of Ni. From these observations, the F substituted PdO nanostructures show a reverse effect compared with Ni substituted PdO nanostructures. As a result, incorporation of impurities such as F and Ni leads to tuning of HOMO-LUMO gap between two extreme levels within the range of 2.31- 7.23 eV. Table 2 shows visualization of HOMO – LUMO gap with electron density

and density of states (DOS) spectrum. The conductivity of PdO nanostructures always depends on concentration of holes in valence band. From the observation of DOS spectrum it clearly infers that the density of charges is more in virtual orbital than in occupied orbital due to the orbital overlapping of Pd atom with O atoms in the nanostructure. The geometry of the structure also influences the density of charges in occupied and virtual orbital. Moreover, for F substitution in PdO nanostructures leads to alpha and beta spectrum that arises due to spin up and spin down electrons in the PdO nanostructure. The excess of electrons from F atom gives rise to alpha and beta orbital. In the case of Ni substitution only the amplitudes of peak maximum increases compared with its pure counterpart. Visualization of electron density also reveals that due to wide band, the density of electron is moderately seen across PdO nanostructure. The electron density mainly depends on the geometry of the structure which is observed by the green colour across PdO nanostructures. The density of electron decreases with Ni substitution, in contrast for F substituted PdO structures the electron density is more which is shown in colour bar as in the figure shown in Table 2.

Nano Structures	Visualization of Electron density (electron density in $e/\text{\AA}^3$)	E_g (eV)	HOMO, LUMO and DOS Spectrum
Pure cone structured PdO		3.4	
Pure sheet structured PdO		4.5	
Pure ring structured PdO		3.88	

<p>F substituted cone structured PdO</p>		<p>7.23</p>	
<p>F substituted sheet structured PdO</p>		<p>3.75</p>	
<p>F substituted ring structured PdO</p>		<p>4.68</p>	
<p>Ni substituted cone structured PdO</p>		<p>2.31</p>	



Binding energy and Embedding energy of PdO nanostructures

The binding energy (BE) of PdO nanostructures can be calculated by equation (1)

$$BE = [(n * E(Pd) + n * E(O) - n * E(PdO))] / n \text{ ----- (1)}$$

where E(Pd), E(O) and E(PdO) are the energy of Pd atom, O atom and pure & impurity substituted PdO nanostructures respectively and 'n' denotes the number of atoms in PdO nanostructures. BE is one of the important parameter to estimate the structural stability of PdO nanostructures [23, 24].

The binding energy of PdO nanostructures is in the range of 0.37-1.62 eV. The high value of BE implies that the nanostructure is more stable. All the PdO nanostructures are found to be more stable with more magnitude in BE, except for pure and F substituted cone structure of PdO has low value.

Embedding energy (EE) represents how far the foreign atom can be substituted on PdO nanostructures. Equation (2) is used to calculate EE

$$EE = [(n * E(Pd) + n * E(O) - n * E(PdO))] \text{ ----- (2)}$$

The embedding energy of PdO nanostructures is found to be high value in the range of 18.77 to 32.37 eV, except for pure and F substituted cone structured PdO. The corresponding EE value for pure and F substituted cone are 7.34 and 12.51 eV respectively. The low value of EE is most feasible for embedding foreign atoms in PdO nanostructures since less energy is required to substitute impurities. Figure 2 depicts both binding energy and embedding energy of PdO nanostructures.

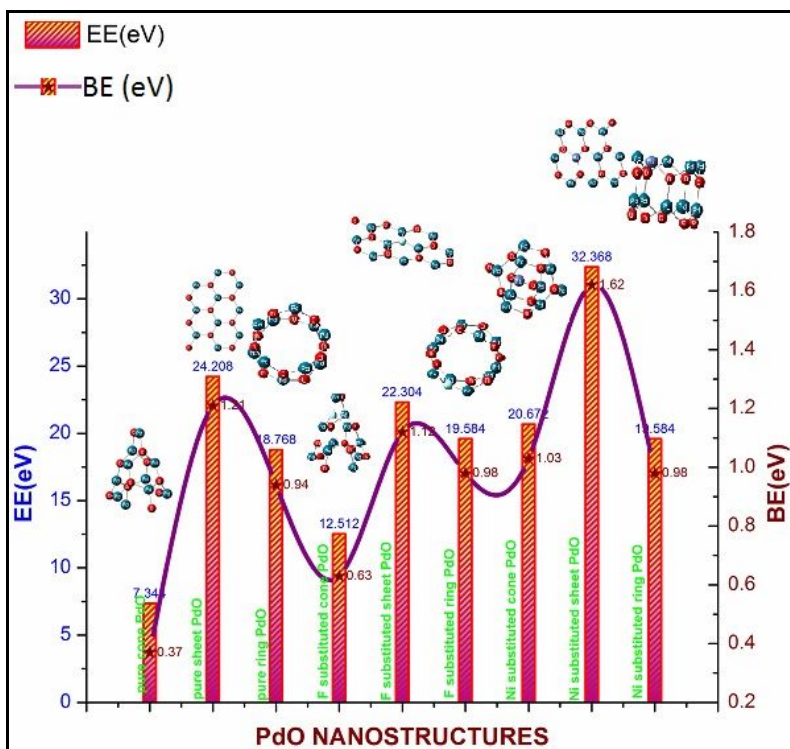


Figure. 2 BE and EE of PdO nanostructures

Conclusion

DFT method is used to optimize the realistic PdO nanostructures such cone, sheet and ring structured PdO nanostructures with B3LYP/ LanL2DZ basis set. The structural stability of pure, F and Ni substituted PdO nanostructures are described in terms of binding energy, calculated energy and embedding energy. The point symmetry group and dipole moment of pure and impurities substituted PdO nanostructures are discussed. The electronic properties of PdO nanostructures are illustrated by HOMO LUMO gap. The information provided in the present study will help in tailoring PdO nanostructures to improve its structural stability and electronic properties with impurity substitution. The proper PdO nanostructures can be synthesized with enhanced electronic properties which find its potential application as oxidation catalysis, catalytic combustion of natural gas, gas sensing in fuel cell and automobiles.

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