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Novel two-dimensional ZnO_2, CdO_2 and HgO_2 monolayers: a first-principles-based prediction

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In this paper, the existence of monolayers with the chemical formula XO_2, where X= Zn, Cd, and Hg with hexagonal and tetragonal lattice structures is theoretically predicted by means of first principles calculations. Through cohesive energy calculation and phonon dispersion simulation, it has been proven that the two-dimensional XO_2 monolayers proposed are energetically and dynamically stable suggesting their potential experimental realization. Our detailed study demonstrates that these novel newly predicted materials are half-metals and dilute magnetic semiconductors as well as they exhibit magnetism in the ground state. The half-metallic character could find many applications in electronic and spintronic devices. Research into the magnetic properties revealed here can enrich theoretical knowledge in this area and provide more potential candidates for XO_2 2D-based materials and Van der Waals heterostructures.

1 Introduction

The discovery of the first atomically thin two-dimensional (2D) material Graphene[1]- with magnificent properties, which have never been observed before, has triggered tremendous pure scientific and technological interest. A huge number of researchers has devoted enormous efforts in exploration of the monolayer carbon and in development of novel 2D materials beyond Graphene such as MXenes,[2–6], honeycomb-like Xenes (X= Pb, Sn, Ge, and Si)[6,7], perovskites[8], and so on. The 2D materials family has potential applications in nanoscale electronic and optoelectronic devices[9], and and photocatalytic hydrogen productions[10]. Among 2D materials, some behave like insulators, others as[11], semiconductors[12], metals[13], semi-metals[14], half-metals[15,16], or superconductors[17]. II-VI group semiconductors or group II-chalcogenide materials with the general formula of AX (where A is referred to Zn, Cd, Hg, and X to O, S, Se, Te elements) have brought many advantages, and they can be utilized in different fields including photovoltaics[18–20], light-emitting diodes[21–24], photocatalytic hydrogen production and photoelectrochemical water splitting[25–27], optical gain[28–32], CO_2 reduction to CO[33–37] and so on, due to their unique electronic, optical, mechanical properties, and long-term stability. Experimentally, there have been several synthesis methods have been developed for group-II chalcogenide compounds, including colloidal approach[38], colloidal ALD[39], chemical bath deposition[40], CVD[41]. Their unique properties have been revealed by a lot of theoretical cal-culations and analytical methods[42–47].

Nanoscaled ZnO, CdO, and HgO oxide compounds, have been a subject of many investigations both experimentally and theoretically (based on DFT calculation[48–52] due to their exceptional physical and chemical properties. In general, they are wide-bandgap semiconductors with potential applications from the ultraviolet to the deep blue spectral region similar to III-nitrides and Ga_2O_3[53]. They have a tendency to be inherent n-type semiconductors and p-type doping poses a serious issue in these materials. In addition to aforementioned oxide compounds, the transition metal peroxides such as zinc peroxide (ZnO_2), cadmium peroxide (CdO_2), and mercury peroxide (HgO_2) could be new candidates for 2D structures still unknown properties. It should be noted that bulk trigonal and cubic ZnO_2 structures have been depicted magnetic and non-magnetic properties, respectively. Trigonal ZnO_2 structure has a band gap of about 4 eV with insulating

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properties, while cubic ZnO_2 structure depicts a semiconductor with a band gap of 2.157 eV. For the bulk CdO_2, both cubic and monoclinic structures have been depicted non-magnetic properties. Both CdO_2 structures show an indirect semiconductor with a bandgap of 1.268 and 2.36 eV for cubic and monoclinic structures, respectively. Finally, for the bulk HgO_2 with orthorhombic and monoclinic structures, both have been depicted as non-magnetic materials, with an indirect bandgap of 0.308 and 0.212 eV, respectively. The ZnO_2 structure has two oxygen atoms which are linked by a single bond. It has gathered large scientific interest because of the high electronegativity due to the excess of oxygen, especially on a nanoscale level.

Nanostructured ZnO_2 has been successfully utilized in contamination removal from water by UV irradiation[55] as well as in detoxification of mustard gas[56]. The ZnO_2 powder used in many areas, including cosmetics, wear resistance, oral surgeries, and so on[56]. However, while the photocatalytic properties of different 2D metal oxides structures[57–60] have been studied until now, the photocatalytic properties of metal peroxides and related composite materials require detailed investigation. A. G. El-Shamy[61] reported on photocatalytic and tunable photoluminescence performance of carbon quantum dots (CQDs) and ZnO_2 nanocomposites. The results have depicted a larger photocatalytic activity of the CQDs/ZnO_2 nanoparticles than pristine TiO_2, and ZnO_2 structures, against Rh.B, Mo, and MB degradation degradation than of the pristine TiO_2, and ZnO_2 structures. CdO_2 is a semiconductor with a bandgap of 2.33 eV. It can be synthesized with different methods[62–64] and utilized in fields such as photocatalyst[65], a precursor for CdO n-type semiconductor synthesis[66], and as an additive material in the rubber and plastic industry[64]. Several theoretical studies (first-principle calculations) have been implemented to understand the CdO_2 structure. For example, A. Zaoui and M. Ferhat,[67] reported a thermodynamically and mechanically stable a cubic CdO_2 semiconductor structure with bandgap of 2.9 eV. Nanostructured mercury compounds have been used in different applications[68–71].

The origin of 1H and 1T phase configuration goes back to MoS_2 different phases, including 1H, 2H, 1T, and so on. Among these phases, two of them are favorable from a structural point of view: 1H-MoS_2 possesses a very rich physics and chemistry. The 1T-MoS_2 structure is a metastable phase, and the most significant distinction between the H and T phase is that 1T-MoS_2 structure depicts metallic properties, while 1H and 2H is an insulator or a semiconductor[72]. By following the phase structural differences modeling and synthesis, scientists started to develop other structural materials in different phases both theoretically and experimentally, such as semimetal 1H-SnS_2[73], metallic H-TaS_2[74], and H-$TaSe_2$[75], semiconductor 1T-$PtSe_2$[76], semiconductor 1T-$HfSe_2$[?] , and so on. Obviously, to have different electronic properties of the same materials, it is better to synthesize the material in different phases. XO_2 structures are also following the phase structural differences, which depict different electronic properties behavior. As the same as a 1H-MoS_2 monolayer, our 1H-XO_2 structures can be considered as the pristine structures for other XO_2 related structures.

However, there is no a single study on nanostructured HgO_2 in the literature. Theoretically, DFT modeling of HgO_2 can stimulate new research on understanding ructure mercury peroxide compounds. In this paper, the stability as well as structural, electronic and magnetic properties of XO_2 (X= Zn,Cd,Hg) monolayers with hexagonal (1H) and tetragonal (1T) structures have been investigated by means of the first-principle calculations. XO_2 monolayers with 1H and 1T structures are found to be dynamically stable. Our calculation results demonstrate that the XO_2 monolayers are half-metal and exhibit magnetism in the ground state, i.e. they could open a new door in technology and applications.

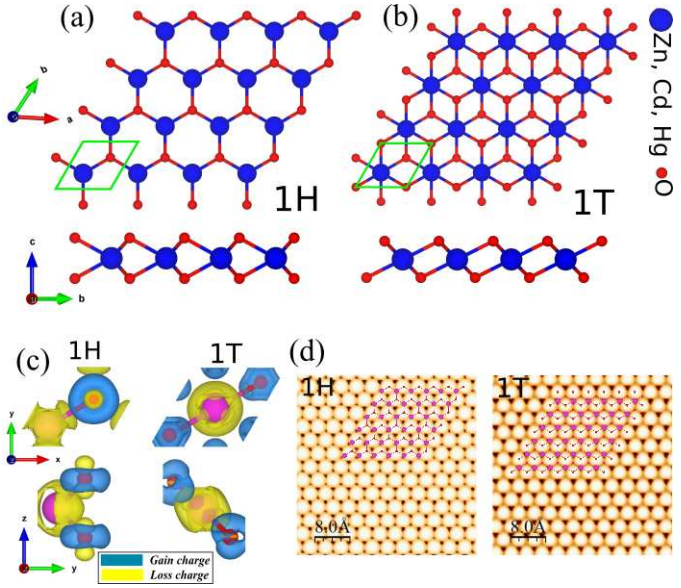

Fig. 1 Atomic structures of XO_2 (X= Zn,Cd,Hg) monolayers (a) -1H and (b) -1T phases, with a primitive unit cell indicated by a green parallelogram. (c) Difference charge density of CdO_2-1H and -1T monolayers. (d) Simulated STM images of CdO_2-1H and -1T monolayers. The inset structure represents repeating the unit cell.

2 Method

The structural optimization and electronic properties were performed by the plane-wave basis projector augmented wave (PAW) method in the framework of density-functional theory (DFT). The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof(PBE)[77,78] exchange-correlation functional was used for exchange and correlation contributions as implemented in the Vienna *ab-initio* Simulation Package (VASP)[79,80]. Analysis of the charge transfers in the structures was determined by the Bader technique[85]. The kinetic energy cut-off for plane-wave expansion was set to 500 eV and the energy was minimized until its variation in the following steps became 10^{-8} eV. To get the optimized structures, the total Hellmann-Feynman forces were reduced to 10^{-7} eV/Å. $21\times21\times1$ Γ centered k-point sampling was used or the primitive unit cells by using Monkhorst-Pack[86]. Monolayers have been modeled with vacuum region 20 Å to avoid interaction between neighboring slabs. The vibrational properties were obtained from the small displacement method as implemented in the PHON code[87]. Simulated scanning tunneling microscopy (STM) images were obtained using the Tersoff-Hamann theory[83]. The STM simulated images were graphically presented using the

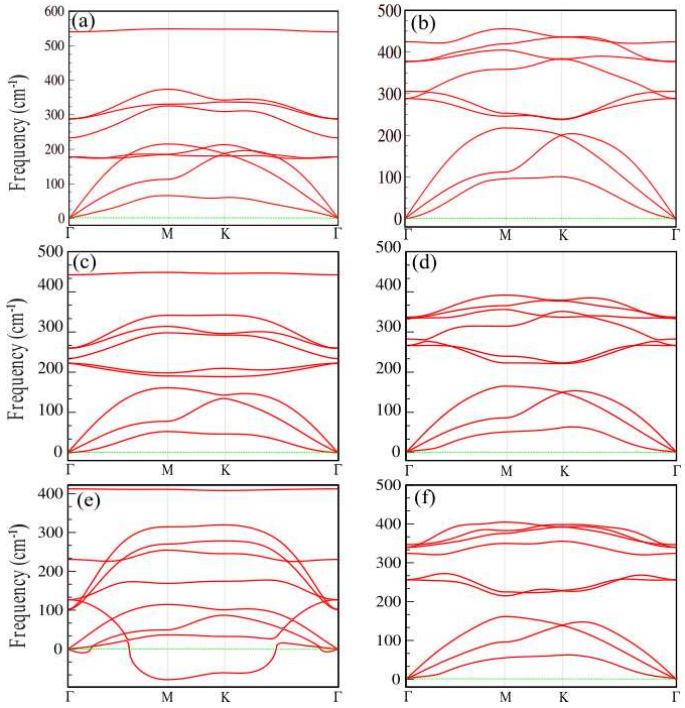

Fig. 2 Phonon band dispersion of (a) ZnO_2-1H, (b) ZnO_2-1T, (c) CdO_2-1H, (d) CdO_2-1T and (e) HgO_2-1H and (f) HgO_2-1T monolayers.

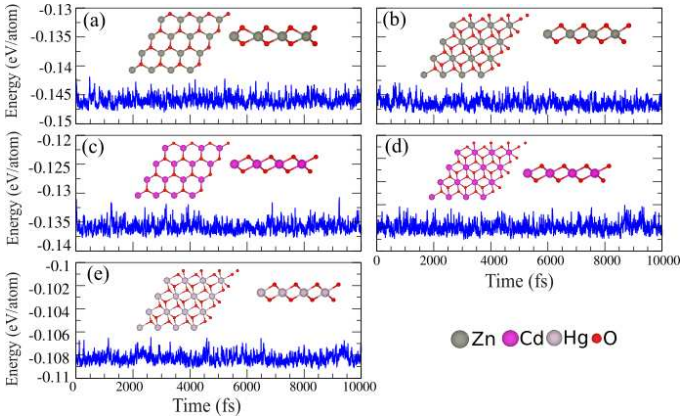

Fig. 3 Ab initio molecular dynamics (AIMD) for the (a) ZnO_2-1H, (b) ZnO_2-1T, (c) CdO_2-1H, (d) CdO_2-1T and (e) HgO_2-1T monolayers at room temperature. The top and side views of the structures after 5 ps of simulation indicated as inset.

WSxM software[84]. The training set was prepared by conducting ab-initio molecular dynamics (AIMD) simulations over $2 \times 2 \times 1$ supercells with $2 \times 2 \times 1$ k-points. AIMD simulations were carried out at 50 and 600 K, each for 1000 time steps. Half of the AIMD trajectories are selected to create the training sets.

3 Monolayer of XO_2 (X= Zn,Cd,Hg)

3.1 Structural properties

The honeycomb structures of the XO_2 monolayers exhibit space group P_{3m1}, as shown in Figs. 1(a) and (b), respectively. The hexagonal primitive unit cell is formed by four atoms and the vectors $\vec{a} \neq \vec{b}$ are the translational unit cell vectors. Before gaining insight into the electronic properties, we first calculate the geometrical structure, with full optimization of all the atoms and determine the crystal lattice parameters. The calculated lattice constants of the ZnO_2 are equal to 3.08 Å (1H) and 3.11 Å (1T), while the bond lengths d_1 and d_2 are determined to be 2.07 Å (1H) and 2.11 Å (1T), respectively. The two angles of the Zn-O-Zn bonds in the ZnO_2-1H (1T) lattice are 96.21° (79.84°) and 61.47° (100.13°) , i.e. slightly deviating from 120° and indicating the in-plane anisotropy of the lattice. In the CdO_2-1H (-1T), we found that the lattice parameters increase to 3.44 (3.40) Å, while the bond lengths are d_1=2.27 (2.23) Å and d_2=2.20 (2.82) Å. In addition, the bond angles are same θ_1=98.44° and θ_2=58.05° for each CdO_2-1H layer as well as the thickness of the CdO_2 is determined to be 2.55 Å. Notice that in the case of HgO_2-1T structure, the lattice parameter is determined to be 3.00 Å. We found out that the bond lengths are 2.24 and 2.89 Å, while the bond angles are calculated 80.21 and 99.80°, respectively. The difference charge density of CdO_2-1H and -1T is depicted in Fig. 1(c), where the blue and yellow regions represent the charge accumulation and depletion, correspondingly. The difference charge density ($\Delta\rho$) is defined as follows:

$$\Delta\rho = \rho_{XO_2} - \rho_X - \rho_O \tag{1}$$

where ρ_{XO_2}, ρ_X and ρ_O represents the charge densities of the XO_2 and isolated atoms, respectively. From the difference charge density, we found out that the negatively charged O atoms are surrounded by positively charged X atoms. We discover that each O atom gains about 1.33 e, and 1.27 e from the adjacent Zn and Cd atoms in ZnO_2-1H and CdO_2-1H structures, respectively. Meanwhile, in the $1T$ structure of ZnO_2, CdO_2 and HgO_2, each O atom gains about 1.40, 1.32 and 1.22 e from the adjacent Zn, Cd and Hg atoms. The charge redistribution is due to the different electro-negativity of Zn (1.65), Cd (1.69), Hg (2.00) and O (3.44). Simulated STM image of the CdO_2-1H (left) and -1T (right) is illustrated in Fig. 1(d), which overlayed with its structure. From the theoretically predicted STM images, it is easy to recognize and correlate them with the corresponding atomistic structure. One can see the the O atoms are brighter than the Cd ones. Cohesive energy, which is defined as the energy required to separate condensed material into isolated free atoms, is one of the most important physical parameters for quantifying the energetic stability of materials. The cohesive energy per atom was calculated using the following equation:

$$E_{coh} = \frac{E_{tot} - E_X - 2E_O}{n_{tot}} \tag{2}$$

where E_X and E_{Bi} represent the energies of isolated single X (Zn, Cd and Hg) and O atoms, n_{tot} is the total number of unit cell, respectively; E_{tot} represents the total energy of the XO_2 monolayer. The cohesive energy of ZnO_2-1H and -1T, are found to be -2.88 and -3.00 eV/atom, respectively, which indicates that the formation of $1T$ is more favorable than $1H$. In addition, the calculated cohesive energy of CdO_2-1H (-2.55 eV/atom) and CdO_2-1T (-2.62 eV/atom) indicates the magnetic ground state of the $1T$ is more favorable. Notice, the cohesive energy of HgO_2-1T is

Table 1 The structural, electronic and magnetic parameters of XO_2-1H and -1T monolayers. The corresponding structural, electronic and magnetic parameters including lattice constant **a**; the bond lengths between X-O atoms $d_{1,2}$; the bond angles between X-O atoms $\theta_{1,2}$; the thickness layer (t); the cohesive energy per atom, (E_{coh}); the charge transfer (ΔQ) between atoms; the magnetic moment per unitcell M_{tot}; Electronic states (ES) are specified as half-metal (HM) and Dilute magnetic semiconductor (DMS). The band gap (E_g) of PBE functional in the up-spin channel.

	a (Å)	d_1 (Å)	d_2 (Å)	t (Å)	$\theta_{1,2}$ (°)	E_{coh} (Å)	ΔQ (eV/atom)	Φ (e)	ES (eV)	M_{tot} (μ_B)	E_g (eV)
ZnO_2-1H	3.08	2.07	2.11	2.57	96.21,61.47	2.88	1.33	7.72	HM	2	0
ZnO_2-1T	3.11	2.03	2.60	2.57	79.84,100.13	3.00	1.40	7.46	DMS	2	0.25
CdO_2-1H	3.44	2.27	2.20	2.57	98.44,58.05	2.55	1.27	7.26	HM	2	0
CdO_2-1T	3.40	2.23	2.82	2.57	100.138,78.67	2.62	1.32	7.24	DMS	2	0.05
HgO_2-1T	3.00	2.24	2.89	2.57	80.21,99.80	2.03	1.22	7.21	DMS	2	0.21

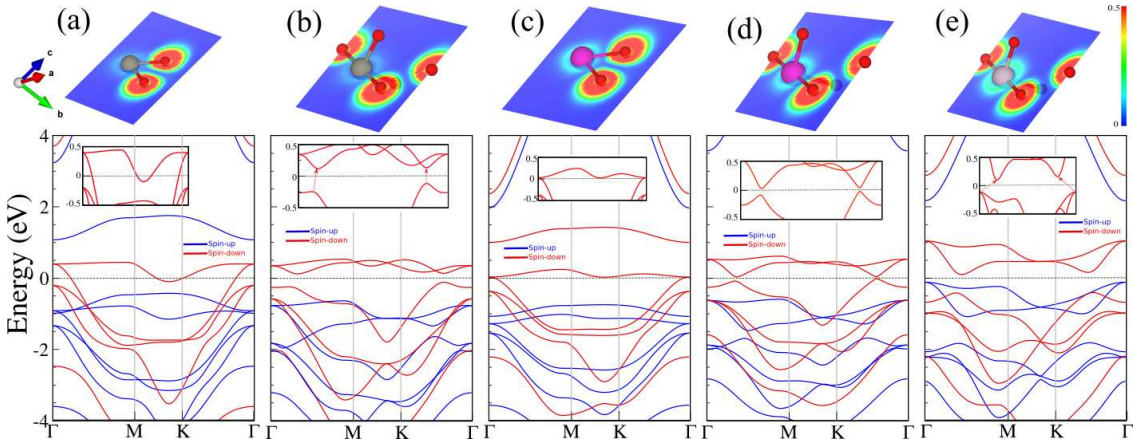

Fig. 4 Electronic band structure of (a) ZnO_2-1H, (b) ZnO_2-1T, (c) CdO_2-1H, (d) CdO_2-1T and (e) HgO_2-1T. Contour plot of the electron localization function (ELF), are shown in the top of panels. Red (blue) color indicate high (low) electron density. The zero of energy is set to Fermi-level.

obtained -2.03 eV/atom The more negative values for cohesive energies suggest that the energetically more stable monolayer, and the structures represent more stability when the atoms get lighter. Now we examine the dynamical and thermal stability of XO_2 monolayer by evaluating the phonon dispersion relation and AIMD trajectories at 500 K, respectively. The dynamical stability is verified by calculating the phonon band dispersions, as presented in in Figs. 2(a-f). Apparently, phonon branches are free from any imaginary frequencies indicating the dynamical stability of all the XO_2 monolayers, except HgO_2-1H, as depicted in Fig. 2(e). It demonstrates the instability of the HgO_2-1H monolayer. Ab initio molecular dynamics (AIMD) and for the studied monolayers at room temperature is shown in Figs. 3(a-e). The top and side views of the structures after 5 ps of simulation as insets is shown in Fig. 3. Analysis of the AIMD trajectories also shows that the structure could stay intact at 300 K, with very stable energy and temperature profiles, proving the thermal stability of the XO_2 monolayer.

3.2 Electronic and magnetic properties

The electronic band structure of the XO_2 monolayers are depicted in Figs. 4(a-e). The contour plot of the electron localization function (ELF), are shown in the top of panels, which red and blue colored indicate high and low electron density, respectively. Notice, that ZnO_2-1H exhibit a half-metallic behavior with valence bands in the $\downarrow$ spin channel, crossing the Fermi level and has 2 μ_B magnetic moment. While ZnO_2-1T, shows semiconducting characteristics in both of $\uparrow$ and $\downarrow$ spin channels, i.e., it is a dilute. The direct band gap of ZnO_2-1T in the $\downarrow$ spin channels is calculated to be 0.21 eV, while the valance band minimum (VBM) and conduction band maximum (CBM) are located along the K-Γ points. Notice that, we can see a direct band gap with a value of 0.27 meV, which is located along the Γ-M points. The magnetic moment of the ZnO_2-1T is determined to be 2 μ_B in the ground state. Similarly ZnO_2, CdO_2 exhibit HM and DMS in the $1H$ and $1T$ phases structures and our results show that the magnetic moment of the CdO_2-1T and -1H is 2 μ_B in the ground state. In the $\downarrow$ spin channels of the CdO_2-1T, we can see a narrow direct band gap of 50 meV, while the VBM and CBM are located between the K and Γ points. Pay attention, we found a narrow direct band gap with a value of 110 meV, which are located between the Γ and M points. In the case of HgO_2-1T, the $\uparrow$ and $\downarrow$ spin channels are splitted, result in show a DMS and induce 2 μ_B magnetic moment in the ground state. The indirect band gap of the HgO_2-1T in the $\downarrow$ spin channels is calculated to be 0.25 eV, while the VBM and CBM is located along the Γ-M points. Notice that, a direct band gap of 0.35 eV, is shown in the along K-Γ points.

Since these monolayers are semiconductor in the $\uparrow$ and $\downarrow$ spin channels, the HSE06 functional was also used to study the electronic band structures, shown in Fig. S2. Based on the acquired band structure by HSE06 method, the ZnO_2-1H and ZnO_2-1T monolayers exhibits a half-metallic characteristic. Our results

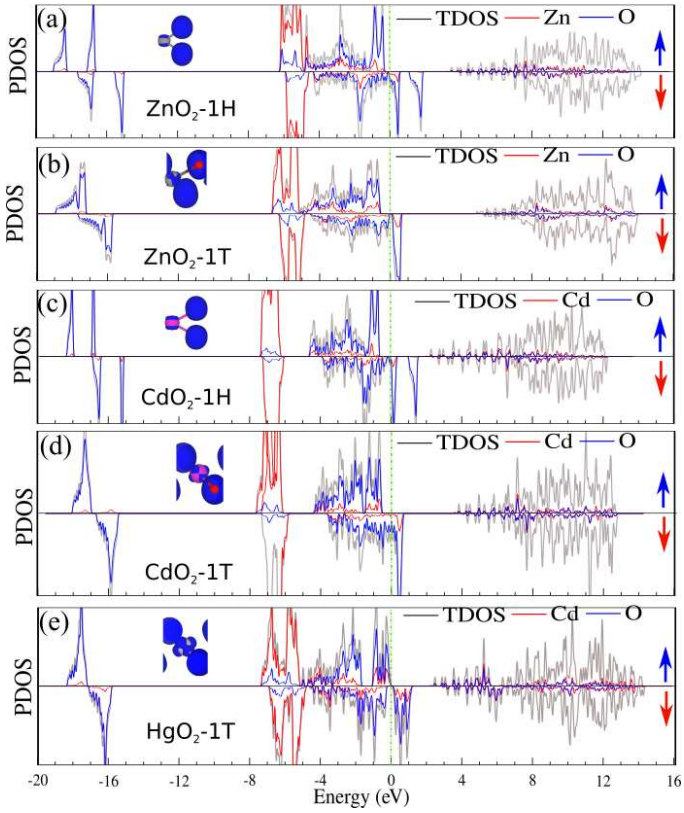

Fig. 5 DOS and PDOS of (a) ZnO_2-1H, (b) ZnO_2-1T, (c) CdO_2-1H, (d) CdO_2-1T and (e) HgO_2-1T. Difference spin density are shown in the insets. The blue and yellow regions represent the ↑ and ↓ spin states, respectively. The zero of energy is set to Fermi-level.

shows that CdO_2 shows DMS and half-metallic behaviors in the 1*H* and 1*T* phases structures, respectively. In the case of HgO_2-1T, the ↑ (↓) spin channels is semiconductor (metal), result in shows a half-metallic in the ground state.

In order to explain the origin of the electronic states, the density of states (DOS) and projected DOS (PDOS) is shown in Fig. 5. The contribution of different atomic orbitals indicated in Fig. S1 in the supplementary information (SI). Evidently, that the metallic character of the ZnO_2-1H and CdO_2-H comes from the O atoms in the ↓ spin channel, while and Zn and Cd atoms do not show any contribution (see Fig. 5). From DOS and PDOS of the ZnO_2-1T and CdO_2-T, we can see that the VBM originates from the O-$p_{x,y}$ orbitals (↑ spin channels), while the CBM consists of O-p_z orbital states (↓ spin channels). Unlike the ZnO_2-1T, we found that the VBM and CBM of HgO_2-1T originates from the O-p_z (↑ spin channel) The difference spin density is calculated from the difference spin density between ↑ and ↓ spin channels. In order to analyses the magnetism, the difference spin density of the XO_2, is illustrated in the inset of Fig. 5. One can conclude that the magnetism mainly originates from the O atoms in XO_2.

Due to the weak screening of the Coulomb interaction in 2DM, it is expected that the Hubbard U will be larger than in three-dimensional materials, thus the energy band gap may be expected to be enhanced significantly. We investigate effects of correlation by varying the value of the Hubbard U, since the accurate value of U has not been determined for ZnO_2-1H and CdO_2-H monolayers. The electronic band structure of ZnO_2-1H and CdO_2-H monolayers as a function of Hubbard U, is shown in Figs. S3(a,b). We see from the Fig. S3(a) that the ZnO_2-1H still maintains the DHM feature even when considering the effect of the Hubbard U. With increase of Hubbard U, the 3d orbitals of Zn atom states do not change near Fermi-level, indicating the robustness of energy bands against the correlation effect in Zn-3*d* electrons. The correlation effects on the electronic properties of CdO_2-H significant and we can see that the CdO_2-H still maintains the DMS character. Notice, the band gap increasing in the ↓ spin channel is a result of a cooperative effect of electron correlation for the CdO_2-H. Our results show that the band gap (↓ spin channel) of CdO_2-H increases from 1.25 eV for U = 1 eV to 2 eV for U = 8 eV, and therefore DMS remains for U = 1-8 eV.

4 Conclusion

In summary, we have investigated the structural, dynamical stability, thermal stability, electronic and magnetic properties of novel 2D materials- XO_2 (X=Zn, Cd, Hg) - by using first-principles calculations. Our computational results have proven the energetic and dynamic stability of this new class of 2D materials with amazing properties. Thus, our study could trigger the search for methods of synthesis of ZnO_2, CdO_2 and HgO_2 monolayers and exploration of their high application potential. Research into the magnetic properties revealed here can enrich theoretical knowledge in this area and provide more potential candidates for XO_2 2D-based materials and Van der Waals heterostructures.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon request

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