



Density-functional study of structural, electronic, and magnetic properties of N-doped Zn_nO_n ($n = 2–13$) clusters

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ABSTRACT

The structural, electronic, and magnetic properties of substitutional N-doped Zn_nO_n ($n = 2–13$) clusters have been investigated using spin-polarized density-functional theory. For both mono- and bi-doped Zn_nO_n clusters, their geometrical structures are extremely similar to those of the pristine Zn_nO_n clusters except for some local deformations. The HOMO–LUMO gaps of the doped clusters have a noticeable narrowing after N doping, due to the hybridization between N-2p and O-2p states. For the N-monodoped Zn_nO_n clusters, all isomers are magnetic with a magnetic moment of $1 \mu_B$, which is mainly contributed by the N-2p states. However, for the bidoped clusters, magnetism is quite sensitive to the geometry and to the local bonding environment. The energetically favorable states of N-bidoped Zn_nO_n clusters depend on the interactions between the two N dopants.

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1. Introduction

The study of ferromagnetism in traditional semiconductors has attracted renewed interests in the field called dilute magnetic semiconductors (DMSs) due to their potential applications in spintronic and optoelectronic devices. Among the systems of interest, ZnO-based DMSs have been extensively investigated since the theoretical prediction of room temperature ferromagnetism in Mn-doped ZnO [1]. Recently, non-magnetic dopants such as carbon [2,3] and nitrogen [4–11] have been shown to induce ferromagnetic (FM) ZnO materials as well, and have technological advantages over magnetic dopants. For example, the non-magnetic dopants can avoid troublesome problems as to whether ferromagnetic ordering arises from the magnetic ions actually substituting in the lattice or from the secondary magnetic phases or metal precipitates.

Interests of both fundamental research and potential applications of ZnO-based DMSs stimulate the synthesis and investigation of novel ZnO nanostructures doped with different dopants. A variety of ZnO nanostructures (such as nanotubes and nanowires) doped with N atoms have been investigated. For example, ZnO nanowires doped with N atoms were found that the FM state is more stable, and the induced magnetism is stronger than that in the bulk phase [8]. For N-doped ZnO nanotubes, Fang et al. [11] predicted a magnetic moment of $1.0 \mu_B/\text{cell}$ for the N substitution

on both the O and Zn sites. In addition, they indicated that the magnetic coupling between two N atoms was possible, but not robust.

As a particular state of matter, atomic cluster exhibits novel properties due to its size effect and large surface/volume ratio, and is well suited for several industrial applications such as device microminiaturization and catalysis [12]. So far, the pristine ZnO clusters have been extensively investigated for understanding their growth and size dependence of properties. Experimentally, ZnO clusters could be prepared and characterized inside mesoporous silica [13]. It is reported that ZnO clusters confined in the micropores of zeolites have unique optical properties [14,15]. On the theoretical side, the structures, energetics, stabilities, and optical properties of pristine ZnO clusters have been performed [16–25]. In these studies, there is a general agreement that the smallest Zn_nO_n ($n \leq 7$) clusters favor to form Zn–O alternating ring-like structures, and the cage or tube structures are the most stable motif as cluster size increases. Recently, our group have investigated the pure Zn_nO_n ($n = 1–13$) and Cu-doped Zn_nO_n ($n = 3, 9, 12$) clusters [26] using density functional theory. Our results for the lowest-energy structures of pure Zn_nO_n ($n = 1–13$) clusters are in complete agreement with the previous theoretical works [16–20]. Although the ZnO clusters have been extensively studied during recent years, a detailed knowledge of the physical and chemical properties for doped ZnO clusters, especially for those doped with non-magnetic atoms, is still lacking.

In this study, we report for the first time a density-functional study of the structural, electronic, and magnetic properties of

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Zn_nO_n ($n = 2-13$) clusters doped with one and two N atoms, respectively. The study of the doped ZnO clusters may offer a platform to understand finite size effect on magnetic properties and the origin of magnetism due to N doping.

2. Computational methods

In this work, all calculations were performed using the spin-polarized density functional theory (DFT) implemented in the DMOL³ program (Accelrys Inc.) [27,28]. The generalized gradient approximation formulated by Perdew, Burke, and Ernzerhof (PBE) [29] was employed to describe the exchange–correlation energy functional. Relativistic effective core potentials (ECPs) [30,31] and double numerical basis set supplemented with *d*-polarization functions (i.e., the DNP set) were selected for all atoms. Self-consistent field procedures were performed with a convergence criterion of 10^{-6} a.u. on the energy and electron density. Full geometry optimizations of the structures have been performed without any symmetry constraints. In the geometrical optimization process, we used a convergence criterion of 10^{-3} a.u. on the gradient and displacement and 10^{-5} a.u. on the total energy. The atomic charge and magnetic moment were obtained by the Mulliken population analysis. For the lowest-energy structures, the vibrational frequency calculations were performed to verify that they are real local minima of the potential energy surface of these clusters. The DOS is evaluated based on the Gaussian smearing of the each discrete energy level, with smearing width given by 0.2 eV. PDOS calculations are based on Mulliken population analysis, which allows the contribution from each energy level to a given atomic orbital to be calculated.

DFT is to date the most efficient and accurate microscopic theory for describing the electronic, magnetic, and structural properties of the ground state of electronic systems with a large number of degrees of freedom, particularly for understanding the physics of DMSSs. For example, a large number of previous studies (e.g. see Ref. [32]) have been shown that DFT is an invaluable tool for examining the ferromagnetic/antiferromagnetic nature of states of DMSSs, and for studying the effects of local doping defects and disorder on the magnetic properties. Hence, we believe that DFT can examine the magnetic properties of N-doped Zn_nO_n clusters.

3. Results and discussion

In this work, the lowest-energy structures of pristine Zn_nO_n ($n = 2-13$) clusters were taken as candidates for investigating the effect of N-atom doping. Substitutional doping of Zn_nO_n ($n = 2-13$) clusters with one and two N atoms was considered, respectively. In order to search for the most energetically favorable configurations of N-doped Zn_nO_n clusters, all possible doping sites were considered for each cluster.

3.1. N-monodoped Zn_nO_n ($n = 2-13$) clusters

In this section, we discuss the results of N-monodoped Zn_nO_n clusters. The most stable configurations of N-monodoped Zn_nO_n ($n = 2-13$) clusters are shown in Fig. 1, and the calculated results are summarized in Table 1. It is found that substitution of an O atom by N is energetically more favorable than substitution of a Zn atom in all Zn_nO_n clusters, which is very similar to N-doped ZnO bulk [10,33], thin film [8], and nanowires [8]. This is mainly because that the ionic radius of N (0.75 Å) is nearly same as that of O (0.73 Å).

We note that the geometrical structures of these doped clusters are extremely similar to those of the corresponding pristine Zn_nO_n

clusters. An O atom replaced by N only induces a little change in bond lengths. The average N–Zn bond lengths are always slightly larger than the average O–Zn bond lengths (see Table 1). This is very similar to the case of S-doped Zn_nO_n clusters [34]. It is found that, in general, the difference in bond lengths between N–Zn and O–Zn bonds gets smaller with the cluster size increasing.

The binding energies of N-monodoped Zn_nO_n ($n = 2-13$) clusters are slightly smaller than that of the corresponding pristine Zn_nO_n clusters, which may indicate that the stability of the N-monodoped Zn_nO_n clusters is weakened due to the doping processes. The stability can also be reflected by the HOMO–LUMO gap. Our results show that the HOMO–LUMO gaps of all N-monodoped clusters are smaller than that of the corresponding pristine Zn_nO_n clusters, which are consistent with the prediction of binding energies (see Table 1). Thus, the N-monodoped Zn_nO_n clusters may be less chemically stable than the corresponding pristine Zn_nO_n clusters. This feature was also found in N-doped ZnO bulk phase [33].

The calculated total magnetic moments for the lowest-energy configurations of N-monodoped ZnO clusters, as shown in Table 1, are all about 1.000 μ_B . To further investigate the origin and distribution of these magnetic moments, we calculated the magnetic moment on each atom and the distribution of spin density for N-monodoped Zn_nO_n ($n = 2-13$) clusters. The local magnetic moment on N atom is presented in Table 1, and the spin density for some representative systems is shown in Fig. 2. The magnetic moments are rather localized around the N atoms, being at least 0.756 μ_B coming from the N atom, and the others coming from the nearest-neighboring Zn atoms and the second-nearest-neighboring O atoms. When other ZnO systems are doped with one N atom [8,10,11], the N dopant also introduces a total magnetic moment of 1.000 μ_B . Fig. 3 shows the calculated density of states (DOS) of N-monodoped $\text{Zn}_{12}\text{O}_{12}$ cluster as an example since the trend of DOS for all the studied clusters is consistent. It can be seen from Fig. 3, that the density of 2*p* states of N and O atoms is overlapped significantly near the Fermi level. The 2*p* states of N atom are spin polarized (see Fig. 3b), resulting in an asymmetric spin-up and spin-down DOS and making the system magnetic. But the O 2*p* states are slightly polarized and make marginal contribution to the magnetic moment. Therefore, the observed magnetism is primarily from the 2*p* states of N atoms.

3.2. N-bidoped Zn_nO_n ($n = 2-13$) clusters

The lowest-energy and some metastable structures of N-bidoped Zn_nO_n ($n = 2-13$) clusters are shown in Fig. 4, and the calculated results are summarized in Table 2. In this section, particular attention will be paid to the magnetic coupling between the two N atoms in N-bidoped Zn_nO_n ($n = 2-13$) clusters.

The geometrical configurations of N-bidoped Zn_nO_n ($n = 2-13$) clusters are similar to those of the corresponding pristine Zn_nO_n clusters, except that the replacements induce some local deformations. It can be seen from Table 2 that the binding energy decreases as the increase of cluster size. We note that the difference in total energies between different isomers of each cluster size ($n > 7$) is very small. Moreover, the HOMO–LUMO gaps of N-bidoped Zn_nO_n ($n = 2-13$) clusters are smaller than those of the corresponding pure Zn_nO_n clusters. The HOMO–LUMO gaps in antiferromagnetic (AFM) states are always larger than those in FM states (see Table 2), which is very similar to the cases of transition metal (TM) atom-bidoped ZnO clusters [35–37]. In order to understand the reducing feature of HOMO–LUMO gap, we examined the PDOS of the N-bidoped Zn_nO_n clusters. The PDOSs of some representative systems are displayed in Fig. 5. It is found that the electronic states at the vicinity of Fermi level mainly come from *p* states and the contribution from *d* states is very small (see Fig. 5b and c). Thus, the hybridization of 2*p* states of both O and N sites should be

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