Ab initio study of the effect of metal doping on electronic properties of $(ZnO)_n$ (n= 96, 120) nanoclusters

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Introduction

Zinc oxide (ZnO) is a wide-gap semiconductor with a plethora of useful and interesting properties, like: direct and wide band gap, high exciton binding energy (60 meV) at room temperature, amphoteric chemical properties, non-toxicity, large piezoelectric constants (Dai, Dunn and Park 2010), transparency in the visible region of the spectrum, sensitivity of surface conductivity to the presence of absorbed species, biocompatibility, photoconductive, photoluminescent, gas sensing properties, considerable resistance to weathering and irradiation, which makes it a promising material to use in a variety of micro-, nano-, optoelectronic devices. Zinc oxide has one of the most diverse family of nanostructures, including nanotubes, nanoparticles, nanobelts, nanowires, nanorings, nanoribbons, nanoclusters etc. These nanostructures are often candidates for creating UV emitters and switches, solar cells, creating ultrathin displays etc. From this cornucopia of nanostructures, fullerene-like nanoclusters deserve special attention due to their unique set of characteristics that get them used in a variety of applications, including but not limited to photocatalysis, hydrogen storage, new generation gas sensors. Our previous studies describe structural and electronic properties of $(ZnO)_{12}$ nanoclusters as well as "magic" nanoclusters $(ZnO)_n$, n=(34, 60, 96, 120) [1, 2, 3]. This study presents the results of theoretical calculations of the structure and electronic properties of metal doped (Co, Cu, Ni) nanoclusters $(ZnO)_n$ (n = 96, 120) within the density functional theory, using the generalized gradient approximation (GGA + U) with Hubbard corrections.

Methods of calculation

Ab initio calculations within density functional were performed, which have been successfully used for studying properties of nanoscale structures such as nanotubes and nanowires. For structural models, the optimization (relaxation) of the geometry (finding the equilibrium of ions coordinates, in which the full electronic energy of the system is minimal) was carried. Optimization was calculated using the effective algorithm of delocalized internal coordinates. The convergence of the relaxation procedures deemed reached when the magnitude of forces acting on atoms was less than 0.05 eV/Å.

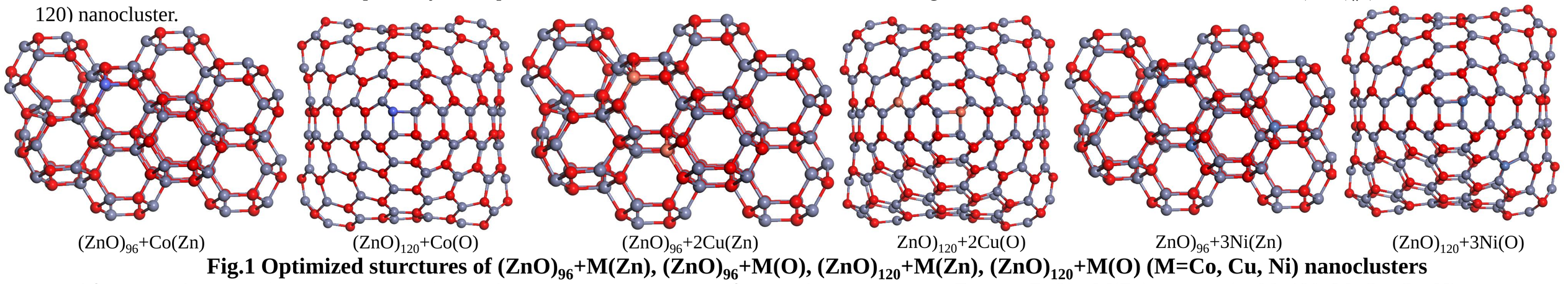
For describing the exchange-correlation energy of the electronic subsystem, the generalized gradient approximation with Hubbard corrections (GGA)+U in a parameterization of Perdew, Burke, and Ernzerhof was used. Unfortunately, for strongly correlated materials including ZnO, standard DFT with GGA (PBE) functional will underestimate the bandgap. To accurately describe the electronic spectrum, two Hubbard corrections were selected the studied objects: for d-orbitals Zn (Ud) and p-orbitals O (Up). Electronic functions of electrons were divided in the basis of atomic orbitals, including d-orbitals. Core electrons had been described using effective potential with regard to relativistic corrections. Integration in the first Brillouin zone was conducted in the Monkhorst-Pack k-point set.

Results

The first task in this research, was figuring out the best placement position for the doping atoms. We considered two main configurations of the placement of Co, Cu and Ni atoms on the surface of the optimized $(ZnO)_{96}$ and $(ZnO)_{120}$ nanoclusters (Fig. 1): zinc atoms were substituted by Co, Cu and Ni atoms, oxygen atoms were substituted by Co, Cu and Ni. The formation energy for the metal doped nanocluster in these configurations was calculated using the following formula:

$$E_f = E_{NA} + E_X - E_N - E_A,$$

Where E_{NA} and E_N represent the total energies of the M-doped (M = Co, Cu, Ni) and undoped $(ZnO)_n$ (n = 96, 120) nanocluster, respectively, E_X and E_A are total energies of free Zn or O and M = Co, Cu, Ni atoms, respectively. The optimized free O, Zn and M = Co, Cu, Ni atoms energies were calculated in the same unit cell as $(ZnO)_n$ (n = 96, 120) nanocluster.



$(ZnO)_{96}$+Co(Zn) $(ZnO)_{120}$+Co(O) $(ZnO)_{96}$+2Cu(Zn) $ZnO)_{120}$+2Cu(O) $ZnO)_{96}$+3Ni(Zn) $(ZnO)_{120}$+3Ni(O)

Fig.1 Optimized sturctures of $(ZnO)_{96}$+M(Zn), $(ZnO)_{96}$+M(O), $(ZnO)_{120}$+M(Zn), $(ZnO)_{120}$+M(O) (M=Co, Cu, Ni) nanoclusters

After relaxation procedure, we observed changes in the structural geometry of all studied nanosystems. For the $(ZnO)_n$+M(Zn) systems (n=96, 120; M=Co, Cu, Ni) as well as $(ZnO)_n$+M(O) (n=96, 120; M=Co, Cu, Ni) systems, we observed significant drop in the energy gap value (E_g) compared to the pristine nanoclusters. Formation energy (E_f) was calculated for both placement positions researched in this study. Formation energy values (E_f) and energy gap value (E_g) for $(ZnO)_{96}$ and $(ZnO)_{120}$ nanoclusters doped with metals are presented in Table 1. The negative values for the formation for $(ZnO)_n$+M(Zn) indicate the exothermic character of the doping process while the positive formation energy value is corresponds to the endothermic process. Because of that, for our study the most favorable placement position for our doping atoms is configuration when a metal atom M (M=Co, Cu, Al) replaces the Zn atom.

Table 1 Band gap (E_g (eV)) and formation energy (E_f (eV)) of pristine and metal doped $(ZnO)_{96}$ and $(ZnO)_{120}$ nanoclusters

Isomer	$(ZnO)_{96}$ +Co(Zn)	$(ZnO)_{96}$ +Co(O)	$(ZnO)_{96}$+ 2Co(Zn)	$(ZnO)_{96}$+ 2Cu(O)	$(ZnO)_{96}$+ 3Co(Zn)	$(ZnO)_{96}$+ 3Co(O)	$(ZnO)_{96}$ +Cu(Zn)	$(ZnO)_{120}$ +Cu(O)	$(ZnO)_{96}$+ 2Cu(Zn)	$(ZnO)_{120}$ +2Cu(O)	$(ZnO)_{96}$+ 3Cu(Zn)	$(ZnO)_{120}$ +3Cu(O)	$(ZnO)_{120}$ +Ni(Zn)	$(ZnO)_{120}$ +Ni(O)	$(ZnO)_{120}$+ 2Ni(Zn)	$(ZnO)_{120}$ +2Ni(O)	$(ZnO)_{120}$+ 3Ni(Zn)	$(ZnO)_{120}$ +3Ni(O)
E_g, eV	2,65	3,14	2,44	3,31	2,17	3,67	2,46	2,75	2,29	2,88	2,17	3,13	2,87	3,15	2,56	3,42	2,26	3,74
E_f, eV	-0,35	1,73	-0,84	4,12	-1,36	6,48	-0,57	2,21	-1,23	4,53	-1,94	7,12	-0,43	1,93	-0,92	4,11	-1,49	6,52

Conclusions

Using Density functional theory with the GGA+U method, we carried out a study of the structural and electronic properties of metal doped (Co, Cu, Ni) $(ZnO)_{96}$ and $(ZnO)_{120}$ nanoclusters. Optimization of structure geometry, as well as the band structure research, was performed. In our study we showed that the most energetically favorable position for the surface doping of the nanocluster is the replacement of the zinc atom with the doping atom. This type of placement causes the reduction of the energy gap of the metal doped nanoclusters and indicates that the doping improves the conductivity of the nanoclusters.

References

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