INRODUCTION

II-VI (II = Zn, Cd, Hg; VI = O, S, Se, Te) semiconductor nanomaterials have attracted a great deal of research due to their paramount potential. They have found applications in a wide variety of fields, such as photocatalysis [1], photovoltaics [2] and biology [3].

In particular, interest in Zn-based wide-gap materials has grown dramatically. Due to their high excitation binding energies, they are excellent candidates for optoelectronic applications. Moreover, they are particularly amenable for biomedical applications since they are abundant, highly stable and environmentally friendly materials.

To fully exploit the potential of semiconductor nanosstructures, a deep understanding of the processes occurring in the nanoscale is mandatory. Unfortunately, the tiny size and small scales inherent in nanomaterials are really challenging for the experimental characterization techniques and computational modeling has emerged as a valuable tool.

The present theoretical work is devoted to the modeling of ZnX (X = O, S, Se, Te) nanomaterials by first principles. Following our previous works on ZnO [4,5] and ZnS [5], realistic wurtzite-like models have been set and H2X molecules have been employed to passivate the surface unsaturated sites. Special attention has been paid to the electronic and optical properties. The role of the anion vacancies on the visible emission of ZnX nanomaterials has also been investigated.

RESULTS & DISCUSSION

QUANTUM DOTS

The passivation of the unsaturated sites stabilizes the wurtzite polymorph. Moreover, it avoids the occurrence of midgap states arising from the dangling bonds, opening the bandgap on the whole set of QDs studied.

The HOMO and the LUMO are related to anion valence p and Zn 4s orbitals, respectively.

The LUMO, despite having the same nature of higher lying orbitals, is quite separated from the rest of the conduction band states.

The calculated TDDFT gaps are in excellent agreement with the experimental absorption onsets of similar size nanocrystals.

Irrespective of the material, the LUMO is the arriving state of the low lying excitations, which could explain the broad excitation profiles and narrow emission spectra inherent in semiconductor QDs.

Model and Method

Several models have been built up from bulk wurtzite: quantum dots, nanowires and nanofilms. In order to minimize both the dipole and the energy of the nanomaterials, we saturate the polar surfaces by dissociating H2X molecules and adsorbing H and HX ions on the unsaturated X and Zn sites, respectively.

All geometries have been fully optimized using the GGASBE functional in combination with a STO DZ basis set.

Since GGA functionals severely underestimate the bandgap of II-VI semiconductors, the hybrid B3LYP functional has been used, in conjunction with the GTO da2-SVP basis set, to perform the electronic structure and TDDFT calculations. The B3LYP functional has been modified to contain 27.5% HF exchange. Solvation effects have been included by means of PCM. Water has been chosen as solvent.

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As in NWs, for NF1 and NF2 the HOMO is mainly localized in the slab borders, further corroborating that the stabilization of the cluster does not mandatorily imply the absence of midgap states.

The HOMO-LUMO gap shrinks only slightly with the increasing slab size, mainly due to the stabilization of the LUMO. It seems that the optical gap is quite insensitive to the surface extension. The binding energy of the d band is quite stable as well. However, the maximum of the TDDFT spectra redshifts with the increasing size of the model.

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REFERENCES