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Said Hamad, Scott Marcus Woodley, Richard Catlow. Review on experimental and computational studies of ZnS nanostructures. *Molecular Simulation*, 2009, 35 (12-13), pp.1015-1032. 10.1080/08927020903015346 . hal-00530454

HAL Id: hal-00530454

<https://hal.science/hal-00530454>

Submitted on 29 Oct 2010

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Journal:	<i>Molecular Simulation</i> / <i>Journal of Experimental Nanoscience</i>
Manuscript ID:	GMOS-2009-0017.R1
Journal:	Molecular Simulation
Date Submitted by the Author:	18-Apr-2009
Complete List of Authors:	Hamad, Said; Institute of Materials Science of Seville, CSIC - University of Seville Woodley, Scott; University College London, Computational Materials Chemistry, Department of Chemistry Catlow, Richard; University College London, Computational Materials Chemistry, Department of Chemistry
Keywords:	ZnS, nanoparticles, clusters, global minimisation, nanotubes

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Manuscripts

Review on experimental and computational studies of ZnS nanostructures.

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We review the experimental and computational studies of nano-particulate ZnS, a system that has received much attention recently. We describe in detail how the nano-particle structures evolve with increasing size. The results of the computational studies reveal intriguing families of structures based on spheroids, which have the greater stability for clusters with less than 50 ZnS pairs. More complex structures are predicted for larger nano-particles.

Keywords: ZnS, nanoparticles, clusters, nanotubes, global minimisation.

1. Introduction

The rapid growth of nanotechnology during the last decade has spawned an increasing interest in the search of methods to control the properties of nanoscale materials. Quantum size effects become large in materials with sizes in the range of the nanometre, which makes the properties of these materials dependent to a great extent on their size and structure^{1,2}. It is therefore of key importance to understand the kinetic and thermodynamic factors that determine the size and structure of nanoparticles. Since the study of kinetic processes is complex, there have been great efforts directed towards the study of the thermodynamic factors that control the arrangement of the atoms or molecules that form the nanoparticles. The basic idea behind these efforts is the assumption that the nanoparticle will adopt the structure that minimises its energy. When dealing with crystals in the macroscopic scale, it is possible to obtain the morphology of a given crystal by employing the Wulff construction³, which yields the equilibrium shape of a crystal knowing the energies of the surfaces that might appear in the crystal. This approach is not appropriate for nanoparticles; but we can still assume that the most likely structure that a given nanoparticle will adopt is that which minimises its energy. Thus, in order to predict the structure of a nanoparticle we can employ global minimisation techniques, which yield the most stable structures. In this article, we review the use of computational techniques in the study of an important semiconductor compound, ZnS, paying particular attention to the global optimisation techniques that provide information about the most stable nanostructures.

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2. Experimental studies on ZnS nanostructures

ZnS belongs to the family of II-VI semiconductor compounds, which have a large number of applications in nanotechnology, as it is relatively easy to tailor the optical and electronic properties of the materials by controlling the shape of the nanostructures⁴. The shape of II-VI nanoparticles might be controlled by several methods: one is by manipulating the growth kinetics, injecting precursor molecules into a hot surfactant, which yields either monodisperse, nearly spherical quantum dots (QDs) or nanorods with different aspect ratios⁵. This ability to produce QDs routinely with controlled sizes and optical properties has found many applications in biological imaging⁶⁻⁹ and their photosensitizing properties are being investigated for their potential applications in cancer treatments^{10,11}, where UV irradiation might be absorbed by QDs and transferred selectively to cancer cells. The materials are also being studied for their potential uses in new electronic devices: a single CdSe QD can be optically excited in close proximity to a silver nanowire¹², which induces the QD to emit radiation coupled directly to guided plasmons in the nanowire, causing the wire's end to light up.

ZnS, which is amongst the most studied II-VI compounds, is a wide band-gap (3.7eV) semiconductor and is one of the most important materials in optoelectronic applications, due to its good photoluminescent¹³ properties; it is also used as a photocatalyst¹⁴. It can adopt two crystal structures¹⁵, namely sphalerite (cubic or zinc blende phase) and wurtzite (hexagonal phase). Sphalerite is the most stable form at room temperature, while the less dense wurtzite is stable above 1020°C at atmospheric pressure and is metastable (as a macroscopic phase) under ambient conditions. Of course, the stability of the two phases is influenced by the morphology of the material: thermodynamic analysis, which makes use of surface energy data, shows that smaller

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wurtzite nanoparticles are more thermodynamically stable than sphalerite¹⁶. For particles as small as 7nm the temperature for the transformation from sphalerite to wurtzite is only 25°C. The origin of the change in the order of stability of the two crystal structures is the free energy γA (the product of the surface free energy and the surface area). For macrocrystalline phases, this term is negligible and the stability is determined by the difference in energy between the two phases. But for nanostructures the surface to bulk ratio is large enough to make the term significant. In this case, the difference between the surface energies of the two phases plays a key role. Changing the surface energies therefore induces changes in the crystallinity of the nanoparticles¹⁷. This change in surface energies might be achieved, for example, by changing the solvent in which the particles are immersed. When 3nm ZnS nanoparticles synthesised in methanol are dried out, they adopt a very disordered structure. But when water is adsorbed on the surface, they undergo a reversible water-driven structural transformation¹⁸ to the sphalerite phase, as shown in Figure 1.

Using the appropriate synthesis conditions, it is possible to tune the morphology of ZnS structures in order to create nanobelts¹⁹ (Figure 2a) with the wurtzite polymorph, which is the more desirable polymorph for its optical properties. Due to their high aspect ratio, ultrafine ZnS nanobelts²⁰ are being extensively studied as field emitters and highly useful in novel nanoscale electric and optoelectronic devices²¹. Other exotic structures such as nanosheets²² (Figure 2d) and nanoflowers²³ (Figure 2b), which show optical properties that can be finely tuned, might also be obtained by solution synthesis routes. Low cost thermal evaporation routes yield ZnS multiangular branched nanostructures²⁴ with needle-shaped tips (Figure 2c), which show good optical properties with potential application in the fabrication of displays. Self-aggregation/assembly methods are very valuable tools for building materials with desired nanostructures. Their use allows the creation of two coexisting levels of nanostructural order, by synthesising monodisperse (2.8nm) ZnS nanoparticles in a one step colloidal precipitation method²⁵, which spontaneously aggregate

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and self-assemble to form dense nanospheres of 100-120nm sizes with optimal optical properties (Figure 2f). Since temperature influences strongly the rates of nucleation, growth and diffusion, it plays a crucial role in self-assembly methods, as shown by Yin et al.²⁶, who found that high temperatures (1500°C) were needed to form single-crystalline ZnS nanotubes with hexagonal cross-sections (Figure 2e). The use of lower temperatures resulted in the formation of solid nanowires. In some cases it is possible to form complex structures with ordered features that range from the nanoscale to the microscale. Vapour deposition processes can be tuned to form hierarchical structures, in which ZnS helices several micrometers long are formed by two structures: a spine with helical shape²⁷, from which a secondary structure of Y-shape branches (all with the same size) grows towards the axis of the helix, rotating as they follow the geometry of the helix (Figure 2g). The existence of hierarchical order in nanostructures often leads to the emergence of unexpected properties, such as the ability to withstand ultra-high stress and strain as shown by hierarchically hollow CdS nanoparticles²⁸.

Determining the atomic structure of nanomaterials is essential to understanding the processes that take place during their use in nanotechnological applications and much effort is being devoted to that goal. Structure determination of nano crystals by X-ray diffraction is inherently difficult as they often show an appreciable degree of disorder²⁹. Two methods that are commonly used to elucidate the structure of nanomaterials are transmission electron microscopy (TEM) and extended X-ray absorption fine structure (EXAFS). Neither, however, provides enough information to determine uniquely the structure of the materials. As Urban stated in a recent review³⁰ of TEM studies of nanomaterials: “understanding the results is generally not straightforward and only possible with extensive quantum-mechanical computer calculations”. This combination of computer modelling and experiment is the basis of what has been named “complex modelling”. Billinge and Levin³¹ suggested “complex modelling” as a powerful method

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1 to solve the structure of nanomaterials, employing experimental and modelling techniques in a
2 self-consistent computational framework³¹. Similar techniques have been successfully applied to
3 solve crystalline structures with very complex unit cells, such as those of metal-organic
4 frameworks (MOFs)³²⁻³⁴. In the study of clusters with only a small number of atoms or molecules,
5 the use of experimental techniques has been very limited so far, and computational techniques are
6 the main source of information about their structures and properties. In the next section we will
7 focus on the studies carried out on ZnS clusters, with particular emphasis on the different
8 computational techniques that have been employed to elucidate their structure and properties.
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3. Computational studies on ZnS nanostructures

Early theoretical studies

In 1989 Lippens and Lannoo³⁵ reported one of the first theoretical studies of ZnS nanoparticles (although, at that time, they were referred to as crystallites instead of nanoparticles). They employed tight binding approximations to calculate the band gap of small CdS and ZnS crystals with sizes between 1nm and 6nm (20-25000 atoms). The calculations strongly overestimated the band gaps, although they provided a correct description of the size effect of small semiconductor crystallites. Another line of research investigated chemisorption processes on ZnS surfaces, which were modelled employing cluster approaches. In 1992 Muilu and coworkers³⁶ carried out Hartree-Fock calculations of the adsorption of ZnCl₂ and Zn(CH₃)₂ on the polar (111) zinc-blende surface of ZnS and ZnSe, in which the surfaces were modelled as single and double layer (ZnS)_n clusters, with n=3-15. These simplistic models provided information about the preferential sites for adsorption. Later on, they used the translational symmetry of two-electron integrals to make possible the study of larger (n=3-240) clusters³⁷, obtaining a linear dependence of the cohesive energy on the surface to bulk ratio. The study of nanoparticles was too demanding for the computational resources available at that time. But the discovery of carbon fullerenes³⁸ and hollow metallo-carbohedrenes^{39,40} prompted extensive calculations on clusters, which were much smaller and therefore more easily tractable with *ab initio* techniques. For example, Smalley and co-workers used DFT calculations to study M₈X₁₂ clusters⁴¹ (M=Ca, Ti, Zn, Sc and Al, X=B, C and N), which are hollow-cage structures where all the atoms are three-coordinated. The overall shape is generated by 12 pentagons, which are joined to form a dodecahedron with T_h symmetry. One of the first studies of II-VI compounds clusters was carried in 1994 by Behrman et al.⁴² Employing Born-Mayer interatomic potentials, they performed Molecular Dynamics (MD) simulations of (ZnO)₁₅, with the initial structure being a fragment of the most stable bulk phase at

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1 ambient conditions for ZnO (the hexagonal, wurtzite structure). During the simulation, the four-
 2 coordinated atoms lost one bond, and after 10ns the cluster was a spheroid in which all the atoms
 3 were three-coordinated, formed by the arrangement of 4- and 6-atom rings. The (ZnO)₁₂ cluster
 4 were three-coordinated, formed by the arrangement of 4- and 6-atom rings. The (ZnO)₁₂ cluster
 5 was also studied, and it was suggested that it might be a magic cluster, due to its particularly
 6 symmetric structure⁴². A recent review of computational studies of ZnO clusters can be found in
 7 reference⁴³. After this MD study, the existence of fullerene-like clusters has been predicted and
 8 observed experimentally for many materials, such as ZnS⁴⁴, ZnO⁴⁵⁻⁴⁸, group IIa-VIa clusters⁴⁹,
 9 AgI⁵⁰, BN^{51,52}, B⁵³, FeC⁵⁴, GaP⁵⁵, AlN⁵⁶ or other group III-V^{57,58} clusters.

21 Nanoparticles capped with organic ligands

22 Another relevant field of solid state science in which the study of small clusters was of key
 23 importance, in the early 1990's, was the study of II-VI quantum dots capped with organic ligands.

24 In 1993 Herron et al.⁵⁹ synthesised a single crystal in which the building unit (Figure 3) was a
 25 Cd₃₂S₁₄ cluster capped with organic molecules, namely Cd₃₂S₁₄(SC₆H₅)₃-DMF₄. These materials
 26 have been useful to understand the dependence on cluster size of properties such as the band gap,
 27 since the periodicity of the crystals allows the knowledge of the exact geometry of the clusters⁶⁰,
 28 which can then be directly related to the properties studied. Bertoncetto et al.⁶¹ studied ligand
 29 capped ZnS₄, Zn₄S₁₀, Zn₁₀S₁₆ and Zn₁₀S₂₀ clusters, by coupling DFT to UV electronic and X-ray
 30 photoelectron spectroscopy. They found that the only cluster that reasonably mimics both the
 31 structural arrangement and electronic structure of the bulk ZnS sphalerite phase is Zn₁₀S₁₆. We
 32 have noted the big influence that even small quantities of adsorbed water molecules have on
 33 relatively large (>3nm) ZnS nanoparticles, causing them to change their crystallinity order⁶²⁻⁶⁴. It is
 34 therefore obvious that the presence of capping organic molecules in small (typically smaller than
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2 2nm) nanoparticles will be one of the main factors involved in the growth and stability of these
3 small bulk-like nanoparticles⁶⁵, and that the growth processes that govern their formation will be
4 different from those of non-capped nanoparticles. The physical properties of these capped
5 nanoparticles are also affected by the presence of the ligands, as recently shown for capped Zn₈S₁₅
6 nanoparticles⁶⁶. Tight Binding DFT calculations show that even passivation with small ligands (-H
7 and -OH) has an important effect on the electronic and optical properties of ZnSe nanoparticles⁶⁷.
8 MD simulations of the self-assembly of capped CdTe nanoparticles⁶⁸ have provided an atomistic
9 view of the template-free, spontaneous self-organisation of the nanoparticles to form free-floating
10 particulate sheets, in a process reminiscent of those happening in biological systems.
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23 **Aqueous ZnS clusters**

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25 Metal-sulphide (including ZnS) nanoparticles are present in aquatic sulfidic systems, where
26 they can control the mobility and bioavailability of pollutants such as zinc, mercury and silver⁶⁹.
27 They also act as intermediates of mineralization reactions⁷⁰. The initial stages of nucleation and
28 growth of ZnS nanoparticles in aqueous solutions has therefore been a subject of extensive
29 experimental research⁷¹⁻⁷⁶, but theoretical studies are very scarce. One of the main centres of
30 attention has been the study of the predominant Zn complexes in water. UV-VIS and titration
31 experiments⁷² show that initially neutral clusters (stoichiometry 1 Zn : 1 S) are formed, and when
32 additional sulphide is added, the stoichiometry changes to 2 Zn : 3 S. Gel electrophoresis suggests
33 that these clusters are negatively charged. The clusters might be interpreted to be Zn₄S₆(H₂O)₄⁴⁻
34 clusters. The experiments did not provide information about the structure of these clusters,
35 although Luther et al.⁷² carried out classical molecular mechanics calculations of the condensation
36 of two hydrated Zn₃S₃(H₂O)₆ rings to form one Zn₄S₆(H₂O)₄⁴⁻ cluster, and observed that the latter
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1 cluster could have the structure of a fragment of sphalerite. But no other cluster structures were
2 studied, so there is no comparison between the stability of the sphalerite-like clusters and any other
3 non-bulk-like cluster. The existence of the structural units of the crystal is not a prerequisite for the
4 formation of the corresponding crystal. For example, glycine molecular crystals, where the
5 metastable α polymorph grows from water solution instead of the most stable polymorph, γ , which
6 had been attributed to the presence of glycine dimers⁷⁷ (characteristic of the α polymorph) in water
7 solution, a simplistic view which has been recently refuted^{78,79}.

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16 Tiemann et al.⁷⁵ employed *in situ* stopped flow UV absorption spectroscopy to study the
17 first stages of the nucleation and growth of ZnS in aqueous solution. They found that the growth of
18 the clusters in solution is very fast. The clusters initially formed are negatively charged even in
19 neutral pH conditions. During the first 60ms there is a substantial decrease in particle
20 concentration⁷⁶, indicating that there is a high degree of particle coalescence. The size of the
21 smaller particles observed in these experiments^{75,76} (at 1.8ms) is between 7Å and 8Å. MD
22 simulations provide an atomistic picture of the cluster formation of ZnS from Zn^{2+} and S^{2-} ions in
23 water solution⁸⁰. The clusters are negatively charged, since they tend to have more S than Zn
24 atoms (see Figure 4a). There might be a thermodynamic driving force for this effect, as Zn^{2+} ions
25 form very stable hexa-aquo complexes ($\text{Zn}^{2+}(\text{H}_2\text{O})_6$), while S^{2-} ions do not interact strongly with
26 water. The formation of a Zn-S bond is a very exothermic event, and therefore the bonds in the
27 clusters are not easily broken, which is in accordance with the experimentally observed preference
28 of coalescence over Ostwald ripening⁷⁶ and with previous EXAFS studies⁸¹. Figure 4b shows a
29 schematic view of one of the growth sequences of a system with a 1.25M concentration at room
30 temperature. There are two clusters formed in different parts of the unit cell. The clusters are
31 initially planar, formed by 4-atom and 6-atom rings, but as they grow they become more spherical.
32 The largest cluster formed after 6ns of simulation, $(\text{Zn}_9\text{S}_{11})^4$, is shown in Figure 4c. It is an open

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2 bubble-like structure, which has no water molecules inside. The simulations therefore suggest that,
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4 after the formation of planar clusters, closed bubble-like clusters with no water molecules inside
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6 will be formed.
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9 This growth model is valid for very small clusters, since larger nanoparticles have bulk-like
10 structures. Zhang et al.⁸² performed MD simulations of water adsorption processes of ZnS
11 nanoparticles (3nm and 5nm), coupled with temperature-programmed desorption (TPD)
12 experiments. The results from both techniques show that each surface Zn atom can adsorb 2.5
13 water molecules, while each S atom can adsorb 0.5 water molecules⁸². Their simulations show that
14 water-water interactions are not as strong on the curved surfaces of the nanoparticles as on the flat
15 surfaces of bulk crystals, which provided a theoretical reason why more water molecules can be
16 adsorbed by ZnS nanoparticles (and with higher binding energy) than by bulk ZnS surfaces.
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25 Huang et al.⁸³ carried out a study of the adsorption of water, ammonia and other Lewis
26 base molecules on ZnS clusters, employing BLYP/dnp calculations. Although the molecules
27 induce a certain amount of structural rearrangement, there is no rupture of Zn-S bonds, and all
28 molecules are chemisorbed. Their results suggest that the stronger the basic nature of the adsorbed
29 molecule, the stronger the interaction with the ZnS clusters. This effect might be used to stabilize
30 small ZnS clusters and nanoparticles, reducing particle aggregation.
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38 Chemical vapour deposition (CVD) is one of the techniques employed in the fabrication of
39 electronic devices. Sarifi and Achenie⁸⁴ investigated the clusters formed in the initial stages of
40 growth in CVD processes by means of B3LYP/6-311+G(d,p) calculations. They considered
41 different structures of clusters with one Zn, one S and two H atoms to study the initial, transition
42 and final states of the reaction $Zn+HSH \rightarrow ZnS+H_2$. Despite the small size of the model system,
43 they found very good agreement between their enthalpy and free energy of reaction data and those
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obtained from experiments. This method could be used to study the formation of other ZnS clusters (including water molecules), which would provide very valuable information on the kinetics of ZnS cluster growth.

Small ZnS clusters.

Matxain et al.⁸⁵ made one of the first attempts to obtain the most stable structures of ZnS clusters. They did not employ global minimisation techniques but made use of chemical intuition to create a set of stable (ZnS)_n clusters (n=1-9). The clusters were optimised within the density functional theory (DFT) framework, using the hybrid 3-parameter B3LYP functional⁸⁶, and the effective core potentials (ECP) and shared-exponent basis sets of Stevens et al.⁸⁷ (SKBJ) to model the core electrons. They found that there are two competing factors involved in the stabilisation of (ZnS)_n clusters: (i) in the most stable configuration, the S-Zn-S angles are as close as possible to 180°; (ii) stabilisation of the system is enhanced by higher coordination. As a result, the global minima for the smaller clusters (n=1-5) are planar, ring structures, whereas for n=6-9 the most stable clusters are three-dimensional spheroidal structures. Once the structure of the most stable clusters was found, they studied electron excitation energies for the three smallest clusters⁸⁸, employing three different methods: configuration interaction singles (CIS), time-dependant density-functional theory (TDDFT) and multi-reference configurational interaction (MR-CI). The latter method was used as reference with which to compare the results obtained with the other two methods, due to the lack of experimental data. They found that both CIS and TDDFT methods need to include several polarisation functions in the basis sets in order to yield correct electron excitation energies. The less computationally demanding calculations that yielded results comparable to those of MR-CI calculations are TDDFT calculations employing the MPW1PW1

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functionals⁸⁹ and the ECP-SKBJ basis sets mentioned above, augmented with 1 sp, 2 d and 2 f functions. This type of calculations was later employed⁹⁰ to study larger (ZnS)_n clusters (n=1-9). The electronic excitations occur typically from nonbonding p orbitals of S atoms, which are perpendicular to the molecular plane in the smaller, ring-like clusters and normal to the spheroid surfaces for the larger clusters⁹⁰. The electronic excitation energies of the spheroid clusters lie within the visible range of the spectrum. They also found that a reasonably good approximation to the electronic excitation energies of the largest could be obtained by calculating the difference between the B3LYP Kohn-Sham energies of the orbitals. The energies obtained with this method⁹⁰ are within 10% of those calculated employing TDDFT.

One consequence of the hollow structure characteristic of these clusters is the possibility of enclosing different atoms, which could induce changes in their physical properties, as happens in the case of fullerene clusters. No experimental studies on this subject have been published so far, although DFT techniques have been used to study the properties of small ZnS and ZnO clusters^{91,92} doped with Mn, Li, Na, K, Cl and Br.

The clusters discussed so far are stoichiometric (i.e. they have the same number of Zn and S atoms). Chuchev and Belbruno⁹³ carried out an investigation on small, nonstoichiometric Zn_nS_m and Zn_nS_m⁺ clusters (1≤n,m≤4), using B3LYP/CEP-121G calculations. Their results provide an energetic basis for the observed excess sulfur clusters in mass spectrometric experiments. There is a large energy penalty for the formation of clusters with Zn-Zn bonds, although it is energetically feasible to produce clusters with S-S bonds⁹³. The removal of an electron affects the cluster geometries, causing, in some cases, rather large atomic rearrangements. This ability to form S-S bonds might also be a reason why small ZnS clusters in water solution tend to be sulphur rich⁷⁵.

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Controversy over $(\text{ZnS})_{13}$ magic clusters.

The first study of $(\text{ZnS})_n$ clusters with $n > 9$ was carried out in 2002 by Burnin and Belbruno⁹⁴. They employed a laser beam to ablate ZnS and ZnO surfaces. The positive ions produced were analysed with a time-of-flight (TOF) mass spectrometer. The most remarkable finding is the existence of a prominent peak with a mass of 1280 a.m.u. (in the case of ZnS), suggesting that $(\text{ZnS})_{13}^+$ is a magic cluster. Another prominent peak is found at approximately 3315 a.m.u., which corresponds to a $(\text{ZnS})_{34}^+$ cluster. For ZnO, there were no “magic” clusters. In order to understand the formation of the $(\text{ZnS})_{13}^+$ magic cluster, they employed semi-empirical MNDO calculations to scan a number of different structures of $(\text{ZnS})_{13}^+$ clusters. The MNDO structures were then optimised at the HF/CEP-31G level, and the energies were calculated with single point calculations at the B3LYP/CEP-31G level. They studied 4 different $(\text{ZnS})_{13}^+$ cluster structures: I (basket-like), II (open cage), III (zinc-blende) and IV (wurtzite) structures. Structures I and II were formed by the arrangement of 4-, 6- and 8-member rings, where all atoms are three-coordinated, as predicted previously for some MgO clusters⁹⁵ using Genetic Algorithms. Structures III and IV initially had some four-coordinated atoms, although upon minimisation they became open structures with only three-coordinated atoms. The most stable configurations were clusters I and II. These results suggest that ZnS clusters might be more stable in spheroidal structures, in accordance with the results of Matxain et al.⁸⁵ for smaller clusters.

Kasuya et al.⁹⁶ carried out a study similar to that of Burnin and Belbruno⁹⁴ (laser ablation followed by TOF mass spectrometry and a subsequent computational study), although in addition to ZnS they also studied CdSe, CdS and ZnSe. $(\text{CdSe})_{13}^+$, $(\text{CdSe})_{33}^+$ and $(\text{CdSe})_{34}^+$ were found to

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be magic clusters, as in the case of ZnS ⁹⁴. The main difference between the two studies is that Kasuya et al.⁹⁶ suggested a different structure to account for the high stability of the $(\text{CdSe})_{13}^+$ cluster, the so-called core-cage cluster, in which 12 Se and 13 Cd atoms form a cage with 3 four-member and 10 six-member rings, which encloses a Se atom in the centre of the cluster, as shown in Figure 5. Employing DFT calculations they showed that the binding energy of the $(\text{CdSe})_{34}$ cluster is higher than that of $(\text{CdSe})_{33}$ and $(\text{CdSe})_{35}$ clusters (by 0.005 eV and 0.04 eV per CdSe unit respectively), but unfortunately they did not provide similar data for $(\text{CdSe})_{13}$. More recently, Woodley et al.⁹⁷ carried out an extensive study of the stability of $(\text{MX})_{13}$ clusters for a range of II-VI compounds (ZnO , CdO , ZnS , CdS , ZnSe , CdSe , ZnTe and CdTe) using a DFT (PBE/DNP) approach and structures found by means of Genetic Algorithm search of the interatomic potential based energy landscape for ZnS . They advanced the hypothesis that magic numbers may be related to the number of different configurations accessible within thermal range from the global minimum. The $(\text{ZnS})_{13}$ core-cage cluster, where one Zn atom is contained within the pore of a bubble, was among the less stable of a series of different structures, while the most stable structure investigated was a spheroidal cluster with only three-coordinated atoms and no atoms inside – thus corroborating and extending the initial findings of Burnin and Belbruno⁹⁴. Both groups have performed further studies in order to shed some light onto this controversy. The balance of interatomic interactions in the series of 1-1 compounds is in the focus of current work by Woodley and co-workers. In turn, Burnin et al.⁹⁸ has carried out a further study on the structure and stability of $(\text{ZnS})_n$ and $(\text{ZnS})_n^+$ clusters for $n=1-16$. They employed algorithms that generate a large number of possible structures having predefined constraints. These clusters were then optimised at the B3LYP/6-311+G* level of theory. The smaller clusters ($n < 6$) have planar structures for neutral and positive clusters. Large neutral clusters have the geometries of close-cage polyhedra (with only three-coordinated atoms) formed by 4- and 6-member rings. The structures of large positive

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clusters are similar to that of the neutral clusters, but with an important difference: there are two 2-coordinated atoms (one S and one Zn atom) in each cluster. Only for $n=12, 15$ and 16 , do the structures of the neutral and positive clusters coincide⁹⁸ being the close-cage polyhedra with only 3-coordinated atoms. The core-cage structure of the $(\text{ZnS})_{13}$ cluster suggested by Kasuya et al.⁹⁶ was not considered in that study. That structure was studied in another experimental and computational study of ZnSe, CdSe, ZnS and CdS clusters⁹⁹. It was found that the core-cage structure was the global minimum energy structure for $(\text{CdS})_{13}$ and $(\text{CdSe})_{13}$ clusters, but it was only a local minimum for $(\text{ZnS})_{13}$ and $(\text{ZnSe})_{13}$ clusters. Therefore they suggest that Cd has a higher tendency than Zn to stabilise structures with 4-coordinated atoms. Although a partial understanding of the TOF spectra was obtained⁹⁹ with the analysis of the cluster energies calculated with DFT, the controversy over the reasons why magic clusters appear in II-VI materials is far from over, and our investigations show that different basis sets and exchange and correlation functionals can lead to differing results, which will be reported in the near future.

Larger ZnS clusters

The structures of small $(\text{ZnS})_n$ clusters ($n < 10$) can be obtained with reasonable confidence using chemical intuition to create small sets of possible structures. But the number of possible configurations increases exponentially as the number of atoms increases, making essential the use of global optimisation techniques that generate low energy structures. A recent review of the use of different global minimisation techniques (Genetic Algorithms, Monte Carlo Basin Hopping, Simulated Annealing, etc) to study a wide range of systems can be found in reference¹⁰⁰. Spanó et al.¹⁰¹ employed Simulated Annealing (SA) simulations based on suitable interatomic potentials¹⁰² to obtain the most stable structures of $(\text{ZnS})_n$ clusters with $n=1-47$. The clusters with global energy

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1 minimum were hollow, cage-like structures, formed by the polyhedral arrangement of 4-, 6- and 8-
 2 member rings, in which all the atoms are three coordinated. They denoted these as bubble
 3 clusters¹⁰¹. They have also been called spheroids⁸⁵ or Euler clusters⁹⁹ by other authors. Some
 4 representative bubble clusters are shown in Figure 6. One of their main features is that they follow
 5 Euler's Theorem of closed polyhedra, which means that the number of 4-, 6- and 8-member rings
 6 in a $(\text{ZnS})_n$ cluster are related by these two formulae:

$$N_{6\text{-ring}} = n - 4 - 2N_{8\text{-ring}},$$

$$N_{4\text{-ring}} = 6 + N_{8\text{-ring}}.$$

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19 For perfect bubbles (all atoms at the surface and three coordinated) there is a minimum of
20 "n - 4" 6-member rings and six 4-member rings, when there are no 8- or larger member rings. For
21 every 8-member ring created there is a loss of two 6-member rings and an increase in one four-
22 member ring. It can be argued that bubble ZnS clusters prefer to be composed of 6-member rings
23 (hexagonal faces): either an increase in 4 or 8-member rings tend to destabilise the structures, and
24 typically the most stable structures do not have any 8-member rings (or additional four member
25 rings by increasing the average coordination number). Moreover, the 4-member rings (tetragons)
26 tend to be separated from each other (an additional hexagonal ring can be formed from two
27 adjacent tetragons by breaking just one bond). An analogous observation can be made with 5-
28 member rings in fullerenes, which is another system in which Euler's Theorem applies. In
29 fullerenes, the isolated pentagon rule¹⁰³ favours structures in which pentagons (the analogous of
30 our squares) are isolated. In bubble clusters the building units are squares, hexagons and octagons,
31 and the rule could be named as the isolated tetragon rule⁹⁸. For small clusters the existence of non-
32 bulk-like clusters was generally accepted, but for clusters as large as $(\text{ZnS})_{47}$ it was thought that
33 the system was large enough to create at least a small bulk-like region in the centre, so the hollow
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1 bubble clusters provided by the Simulated Annealing process were unexpected. In order to test
 2 whether the bubble clusters appeared as a result of inaccuracies in the interatomic potentials
 3 employed¹⁰², a series of DFT calculations (PW91 functional with effective core potential and
 4 double numerical plus polarisation basis sets) were carried out, which yielded more accurate
 5 energies of bubble clusters and other bulk-like clusters¹⁰¹. The DFT calculations showed that the
 6 higher stability of bubble clusters with respect to the bulk-like clusters was not due to a failure of
 7 the interatomic potentials, since the average difference in energy between the two structural
 8 families was ~200 kJ/mol.

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9 TDDFT calculations show¹⁰⁴ that the clusters with higher oscillator strengths are (ZnS)₁₈,
 10 (ZnS)₂₀ and (ZnS)₂₆. Their excitation energies are of the order of 4.9eV. There are several
 11 experimental measures of the band gaps of ZnS nanoparticles. Calandra et al.¹⁰⁵ measured the
 12 band gap of ZnS nanoparticles between 2nm and 6nm, which was in the range 5.25-6.0 eV. The
 13 band gap of 2nm ZnS sphalerite nanoparticles has also been measured¹⁰⁶ as 4.5eV. For hollow
 14 2.8nm ZnS nanoparticles, the band gap was 4.3eV. The band gaps (calculated as the HOMO-
 15 LUMO energy difference) of (ZnS)_n clusters⁴⁴ with n=10-47 lie within the range 4.4-4.8eV. For
 16 clusters⁴⁴ with bulk-like structures, the band gaps were in the range 3.65-3.95eV. The wide range
 17 of structures that the nanoparticles adopt and the experimental difficulties in elucidating them can
 18 explain the disparity in the reported values for the band gap.

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19 It is observed experimentally that for sufficiently large sizes (> 3nm) ZnS nanoparticles
 20 adopt bulk-like (sphalerite or wurtzite) structures, in which most of the atoms are four-
 21 coordinated, so there is a size in which bubble clusters start being less stable than other cluster
 22 geometries. In order to study the sizes at which this transition in stability takes place, another set of
 23 Simulated Annealing simulations were carried out^{44,107} for (ZnS)_n clusters with sizes n=50, 60, 70
 24 and 80. The results were again surprising, as the most stable structures turned out to be core-shell

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1 structures in which one bubble cluster was enclosed inside a larger cluster. These new clusters
 2 were denoted double bubbles. Figure 7 shows the double bubbles ($n=50, 60, 70$ and 80) as well as
 3 the component single bubble clusters. The core bubble in the case of $n=50$ is the $(ZnS)_6$ cluster.
 4 $(ZnS)_{12}$ is the core bubble in the two intermediate sizes ($n=50,60$), while in the largest ($n=80$)
 5 double bubble, the cluster enclosed is the $(ZnS)_{17}$ bubble. In order to test the validity of the
 6 predictions based on interatomic potentials, the difference in energy between a double bubble
 7 $(ZnS)_{60}$ cluster and two $(ZnS)_{60}$ bulk-like clusters was calculated¹⁰⁸ with both interatomic
 8 potentials and DFT calculations (PW91/ecp-dnp). The energy differences were around 12eV for
 9 both methods. For the $(ZnS)_{70}$ cluster, the energy difference was 6.65eV and 3.85eV when
 10 calculated with DFT and interatomic potential methods respectively. The two methods therefore
 11 agree in the prediction of double bubbles as the most stable structures for $(ZnS)_n$ clusters with
 12 $n=50, 60, 70$ and 80 .

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 26 Sarkar and co-workers have carried out a series of theoretical studies regarding the stability
 27 of the different $(ZnS)_n$ cluster structures. In their earlier work they reported¹⁰⁹ that DFT-Tight
 28 Binding calculations predict small ($n<17$) bubble clusters to be more stable than bulk-like (zinc-
 29 blende) clusters, which agrees with the PW91/ecp-dnp results obtained by Hamad et al.^{44,107}
 30 mentioned above. But they also reported that for larger clusters, especially $(ZnS)_{58}$ and $(ZnS)_{68}$,
 31 bulk-like clusters are more stable than bubble clusters. However, in a more recent investigation¹¹⁰
 32 where they compared a different set of stable hollow, bubble clusters with zinc-blende and
 33 wurtzite $(ZnS)_n$ clusters for $n=10, 16, 37, 57, 68, 86$ and 116 , their reported DFT-Tight Binding
 34 results showed that hollow clusters are more stable than bulk-like clusters¹¹⁰. An interesting result
 35 of that study is the existence of a minimum in the plot of the band gap versus number of atoms in
 36 the cluster, for both single and double bubble clusters. The minimum is located between $n=80$ and
 37 $n=110$, and it is attributed to the balance between two competing effects: quantum size effects

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(which cause a decrease of band gap as the cluster size increases) and curvature-induced σ - π hybridisation (which causes an increase of band gap as the cluster size increases).

As mentioned above, energetic considerations are obviously very important, but kinetic effects may also have great influence in the outcome of ZnS crystallisation. Very few studies have considered the growth dynamics of large bubble and bulk-like clusters. The discovery of hollow, multi-shelled Co_xS_y nanoparticles¹¹¹ lead Pal et al.¹¹² to carry out a theoretical study of the influence of diffusion rates on the dynamics of ZnS cluster growth, starting from different building units (namely ZnS, Zn_2S_2 , Zn_5S_5 and Zn_8S_8). Although hollow clusters are more stable, under certain conditions, the energy barriers to their formation are larger than for bulk-like clusters¹¹² which can be used experimentally to exert some kinetic control and favour one particular structure over the other.

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Transition from 3-coordinated to 4-coordinated clusters: BCT structure

Global Minimisation techniques predict structures of $(\text{ZnS})_n$ clusters (for $n=10-80$) which are predominantly made up of arrangements of 3-coordinated atoms. Even in double bubbles, where a network of 4-coordinated atoms connect the two bubbles¹⁰⁷, most of the atoms are still 3-coordinated. In order to obtain the structure of larger clusters, in which 4-coordinated atoms are predominant, Hamad and Catlow¹⁰⁸ performed a Simulated Annealing study of two large $(\text{ZnS})_n$ clusters: $n=256$ and $n=512$. The clusters (which initially had zinc-blende structures) were simulated with Molecular Dynamics at 3000K. The high temperature caused the clusters to melt, losing all crystalline order. The temperature was slowly decreased, until in one part of the melted nanoparticles a crystalline nucleus appeared, which expanded throughout the whole nanoparticle. Nucleation events are very rare, and very long simulations on HPC terascale computers were

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needed. Figure 8 shows the structure of the two nanoparticles after crystallisation has taken place. The interior of the nanoparticles is crystalline, while there is some degree of disorder in the outer shell. This is also observed in other MD studies of nanoparticles⁶², as shown in Figure 1. But the unexpected feature of the two (ZnS)₂₅₆ and (ZnS)₅₁₂ nanoparticles is the structure of the crystalline interior. At first sight they resemble the hexagonal phase of ZnS (wurtzite), but closer examination shows that the unit cell contains 4-member and 6-member rings (see Figure 9), as in the case of bubble clusters. The structure is topologically equivalent to that of the BCT zeolite, so this new ZnS phase was denoted the BCT phase. The two nanoparticles with the BCT structure were obtained just by decreasing the temperature in MD simulations; no template or capping agents were needed. This is an indication of the absence of large energy barriers, which suggests that there might be a simple kinetic route for the experimental synthesis of these clusters. The existence of BCT structures is not limited to ZnS. Morgan and Madden¹¹³⁻¹¹⁶ have found domains with the BCT structure in nanocrystals modelling systems such as ZnO and CdSe. Doll et al.^{117,118} observed the formation of metastable crystalline BCT structures in BN¹¹⁷ and LiF¹¹⁸ from ab initio simulated annealing simulations. BCT structures have also been observed experimentally in PbSe nanoparticles¹¹⁹. Sayle et al.¹²⁰ observed the formation of BCT structures in MgO and CaO nanoparticles. And in a MD study of the formation of mesoporous materials via self-assembly of amorphous ZnO and ZnS nanoparticles, Sayle et al.^{120,121} also observed the formation of extended regions with both wurtzite and BCT structures. The emergence of these two structures and the transformation from one to another during the process of crystallisation of the mesoporous material is shown in Figure 10. As shown in Figure 10e, there is a very smooth transition from the two structures, and therefore there is no need to create defects to release structural strain.

In order to check whether the nanoparticles crystallised with the BCT structure just for kinetic reasons rather than for energetic reasons, the energies of large sets of clusters with different

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structures were calculated¹⁰⁸ using DFT and interatomic potentials. a shows the energies, calculated with interatomic potentials of (ZnS)_n clusters (n=18-80) with 4 different structures: a) cubic, b) hexagonal, c) BCT and d) the bubble clusters obtained from Simulated Annealing simulations. Clusters with cubic, hexagonal and BCT structures are generated without dangling bonds and with the lowest dipoles possible, in order to minimise the distortions after optimisation. It is clear that that bubble clusters are the most stable in all cases, followed by the BCT clusters. The energies of 6 hexagonal and BCT clusters (in the range n=18-70) were also calculated with the PW91/ecp-dnp level of theory, obtaining very good agreement with the results derived from interatomic potentials¹⁰⁸ which enhances our confidence to the validity of the results. b shows the same data as a, extending the range of the clusters from n=18 to n=560, which correspond to sizes between 1 and 4nm. For clusters larger than (ZnS)₈₀ the most stable clusters have the BCT structure. It is worth noting that two interatomic potentials for ZnS were employed in that study, those obtained by Hamad et al.¹⁰⁸ and those obtained by Wright and Gale¹²². The latter did not perform as well as the former in predicting the structure and energies of clusters, since it was fitted in order to model accurately the two phases of ZnS¹²², while the comparison with some data from DFT calculations of ZnS clusters was taken into account during the fitting of the former potential¹⁰⁸.

DFT calculations (PW91/ecp-dnp) show that a ZnS solid with BCT structure is 69.1kJ/mol less stable than the cubic (sphalerite) phase, suggesting that there is a strong energetic gain for small nanoparticles to adopt that crystallise phase, rather than the cubic or hexagonal phases which are the most stable crystalline phases for larger nanoparticles and bulk solids. The greater stability of the BCT based cluster structures probably arises from the ability to accommodate distortions within these structures more easily than in the bulk-like structures. Cubic and hexagonal clusters undergo considerable rearrangements upon minimisation, because their crystallinity makes it very

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1 difficult to achieve a structure with low dipole and no dangling bonds. On the other hand, bubble
 2 clusters do not have any dipoles, and their surface strain is very low. Since BCT clusters present 4-
 3 and 6-member rings naturally in their bulk interior, there is a smooth transition between the bulk
 4 and 6-member rings naturally in their bulk interior, there is a smooth transition between the bulk
 5 and the surface of the nanoparticles, which makes them very stable.
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 10 ZnS nanoparticles with BCT structure have not yet been observed experimentally, which
 11 might be due to three main reasons: a) this structural motif is not as stable as simulations would
 12 predict or the most stable clusters are not BCT structures. However, we note that the BCT
 13 structures have been predicted independently using either Molecular Dynamics or global
 14 minimisation techniques for several systems and using a range of measures of stability, b) they
 15 have not been synthesised for kinetic reasons, or c) they could have been synthesised, but
 16 characterised as either wurtzite or sphalerite because it has features similar to both of them¹⁰⁸
 17 while the diffraction techniques become less reliable in the range of the particle size of interest. If
 18 kinetic issues were the cause, then the use of several crystallisation methods employing different
 19 solvents (similar to the polymorph screenings performed in pharmaceutical sciences) could help
 20 their synthesis, since the solvent has a strong influence on the nanoparticle crystallinity^{62-64,123}
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35 ZnS nanotubes and nanowires.

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 37 If hollow, polyhedral ZnS clusters, in which all the atoms are three-coordinated, can be
 38 considered as the ZnS-based structures analogous to C-based fullerenes, the analogy can be
 39 extended to another important type of C structures: nanotubes. This subject has attracted much
 40 experimental^{26,124-128} and theoretical^{129, 130, 131, 132} attention recently. Pal et al.¹²⁹ carried out the first
 41 computational study of ZnS nanotubes, employing Tight-Binding DFT calculations. They found a
 42 certain degree of buckling in the structure, i.e. Zn atoms tend to be displaced towards the nanotube
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axis, while S atoms tend to be displaced in the opposite direction. This is similar to what happens in surfaces¹⁰² and hollow clusters¹⁰⁹. The buckling decreased from $\sim 0.4\text{\AA}$ to $\sim 0.19\text{\AA}$ as the nanotube radius increased from 4\AA to 9\AA . The band gap behaves differently depending on the way the graphite-like ZnS structure is folded to create the nanotubes. For zigzag nanotubes, (n,0), the band gap decreases as the radius of the nanotube increases, whereas for armchair nanotubes (n,n), there is a broad maximum in the band gap¹²⁹ between 6\AA and 8\AA . Pal et al.¹³³ have employed Tight-Binding DFT calculations in conjunction with Genetic Algorithms to study systems with 10, 16, 37, 57 and 68 ZnS units. Contrary to other studies, they found that the most stable structures are ring-like configurations, with large radii and band widths of just two atoms. Most of the atoms in these structures are two-coordinated. Since these low-coordinated, low-density structures are totally unexpected, they compared their energies with those of hollow clusters, using DFT calculations with ecp-dnp, as implemented in the SIESTA code. Their results suggest that rings are more stable than hollow clusters by 0.4-0.8 eV/atom.

Li et al.¹³⁰ made use of interatomic potential-based¹⁰² and PBE/DZP calculations to study ZnS nanotubes, nanowires and nanosheets. Figure 12 shows an example of a nanowire (NW, with wurtzite structure), single-walled nanotube (SWNT) and double-walled nanotube (DWNT). Both NWs and MWNTs are hexagonally faceted in order to minimize the energy. The formation energies of all the structures are shown in Figure 12d. The most stable structures are NWs, followed by MWNTs, and the least stable structures are SWNTs, which do not undergo significant stabilization as the size increases. All NWs and NTs are found to be wide band gap semiconductors, with a direct band gap at the Γ point.

PBE/DNP calculations¹³² show that the formation energy of DWNTs is lower than that of the $(\text{ZnS})_{60}$ double bubble, which in turn is lower than those of SWNTs, $(\text{ZnS})_{12}$ and $(\text{ZnS})_{48}$ single bubbles. The fact that NTs or NWs are more stable than single or double bubbles cannot be

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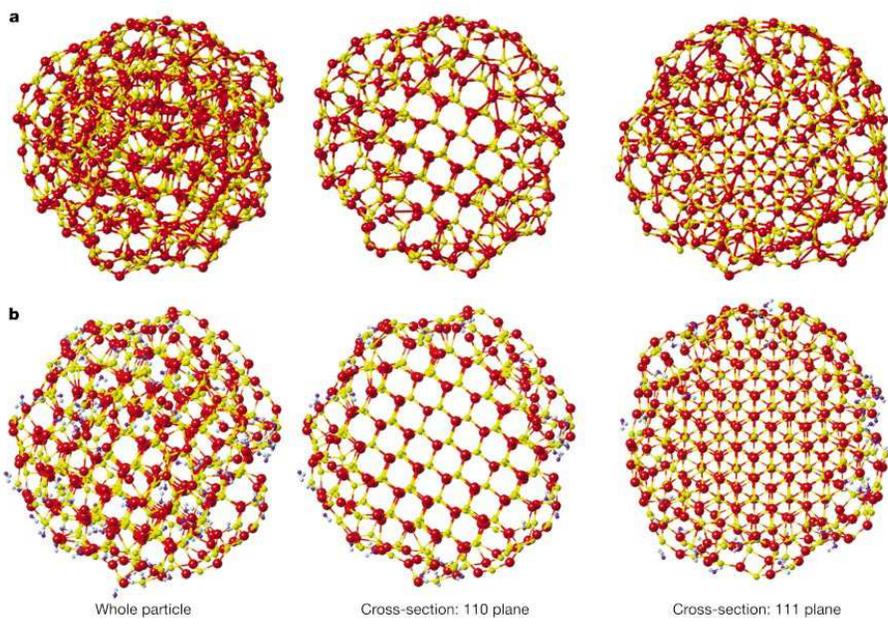
seen as a factor precluding the formation of bubbles, since NTs and NWs are also less stable than bulk structures, but they can be produced under the right conditions. As happens in the case of carbon fullerenes and nanotubes, ultimately the kinetic effects are the ones that determine the formation of the particular structures, and these structures can be stabilized by large energy barriers which stop the aggregation and transformation processes that would lead to the formation of the most stable diamond structure.

3. Summary

Nanoparticulate ZnS shows a fascinating range of structures, which contrast with those observed for the bulk material. Computer simulation methods have proved particularly effective in modeling and predicting possible structures. Further experimental work to test predictions would be of great interest.

4. Acknowledgement

We are grateful to the EU (funding through the NUCLEUS project) and EPSRC (Portfolio Grant EP/D504872). We also thank Eleonora Spanó and Alexey A Sokol for useful discussions and contributions. S. H. would like to thank the Spanish Ministry of Science and Innovation for funding through a “Juan de la Cierva” Fellowship.



24 **Figure 1**

25 Molecular dynamics predictions of the structure of a 3 nm ZnS nanoparticle. a) Without surface-
26 bound water, and b) with surface-bound water. S atoms yellow, Zn red, O blue, H light blue.

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28 Central cross-sections through the particles give a clearer picture of internal structure. Regular
29 interior (110) and (111) planes are evident in both structures, but in the absence of water ligands
30 the outer shell is severely distorted.
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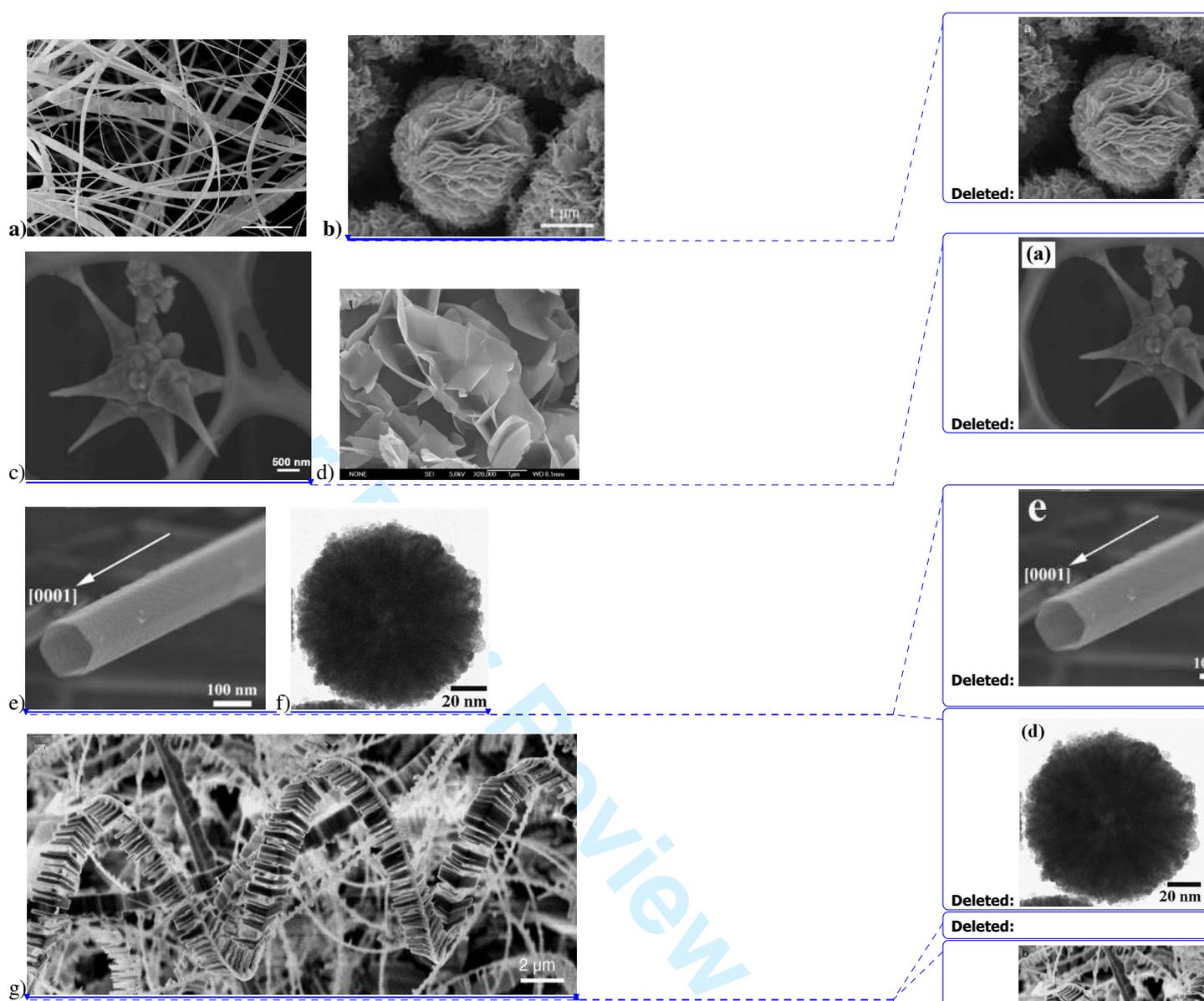


Figure 2

SEM and TEM images of various ZnS nanostructures. a) ZnS nanobelts with wurtzite-structure. b) Wurtzite ZnS flowers composed of nanosheets. c) Multiangular branched ZnS nanostructure with needle-shaped tips. d) Aggregate of ZnS nanosheets, formed by treating ZnS nanoparticles at 230 °C in 17 M NaOH. e) Single ZnS nanotubes, clearly showing hexagonal cross-sections. f) A single nanosphere, indicating self-assembly of ZnS nanoparticles. g) Branched ZnS nanohelix. The Y-shaped branches always point towards the inside of the coil, regardless of the handedness of the nanohelix.

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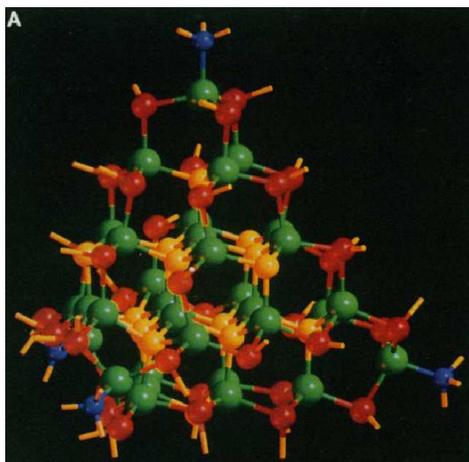


Figure 3

Crystal structure of $\text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_3\text{-DMF}_4$ core. All phenyl groups have been omitted for clarity, but their orientations with respect to the cluster are implied by the non-terminated stick bonds that protrude from the thiophenolate S atoms. The spheres represent Cd (green), sulphide S (yellow), thiophenolate S (red), and N (blue) atoms.

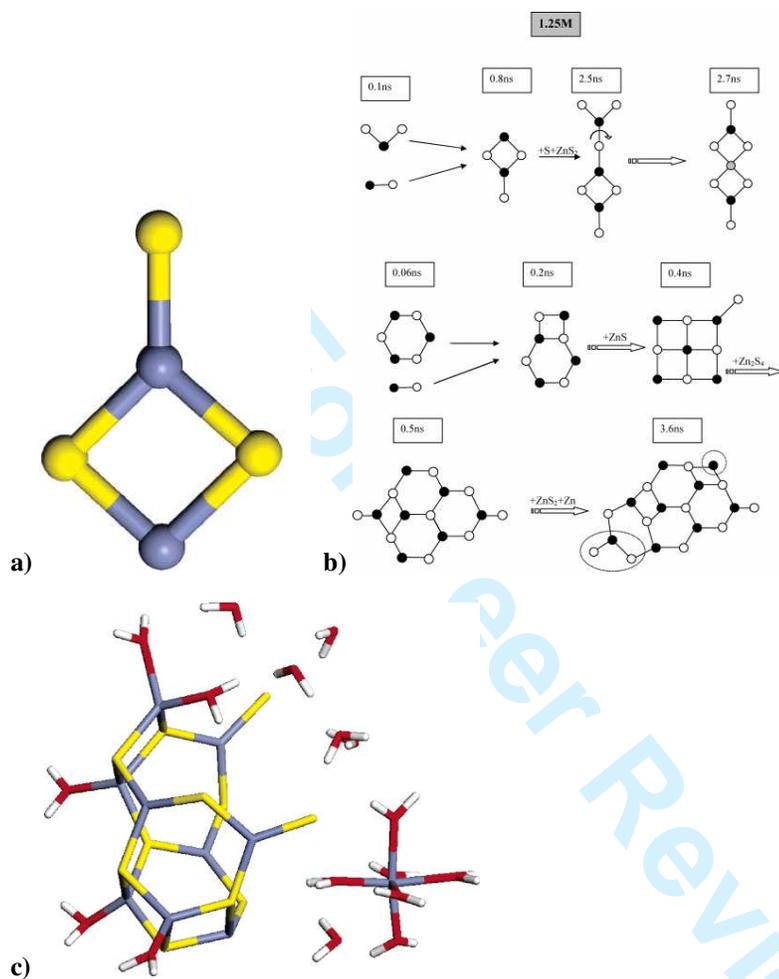


Figure 4

a) Structure of the $(Zn_2S_3)^{2-}$ cluster formed in classical MD simulations of ZnS cluster growth. b) Schematic view of the growth sequence of a 1.25M ZnS solution at room temperature. c) $(Zn_9S_{11})^{4-}$ cluster formed after 6 ns simulation in the system with 1.25 M concentration. The structure is nonplanar, due to the presence of three squares. There are no water molecules bound to the internal side of the developing cluster, suggesting that the addition of more atoms would easily form a closed cluster without water inside.

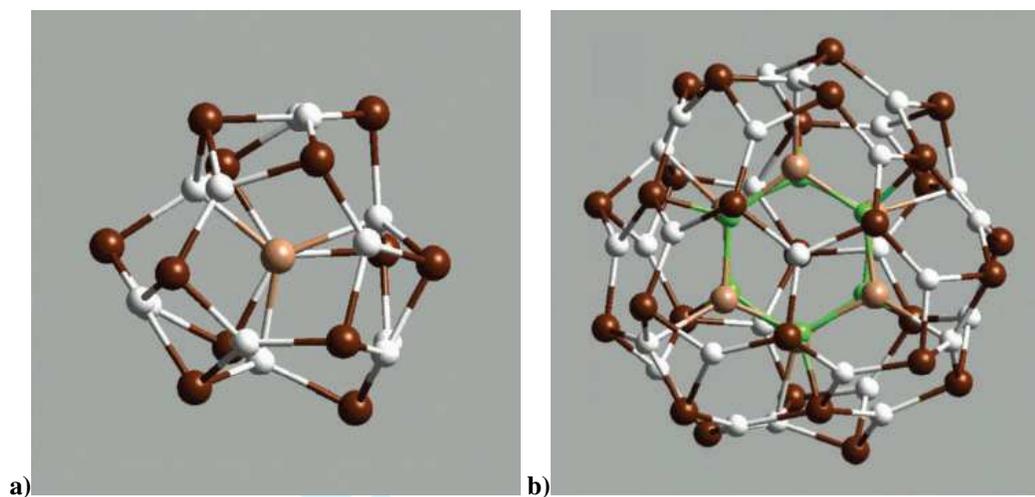


Figure 5

Structures of the $(\text{CdSe})_n$ core-cage nanoparticles calculated to be most stable, viewed down a threefold symmetry axis. a) $(\text{CdSe})_{13}$ has 3 four-membered and 10 six-membered rings on the cage of 12 Se (dark brown) and 13 Cd (white) ions with a Se (light brown) ion inside. b) $(\text{CdSe})_{34}$ has a truncated-octahedral morphology formed by a $(\text{CdSe})_{28}$ -cage (Se, dark brown; Cd, white) with 6 four-membered and 8×3 six-membered rings. A $(\text{CdSe})_6$ cluster (Se, light brown; Cd, green) encapsulated inside this cage provides additional network and stability.

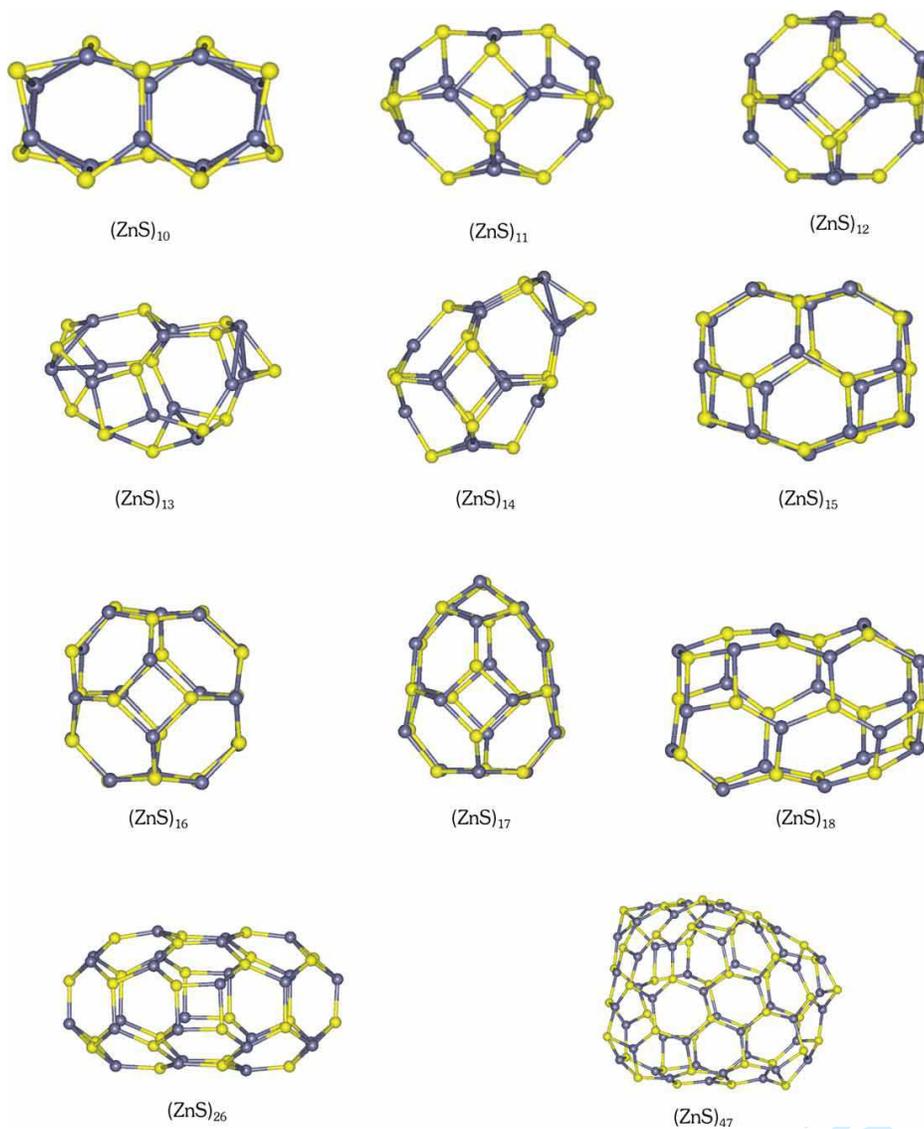


Figure 6

Predicted structures of selected bubble clusters. Blue sticks refer to sulfur and yellow to zinc.

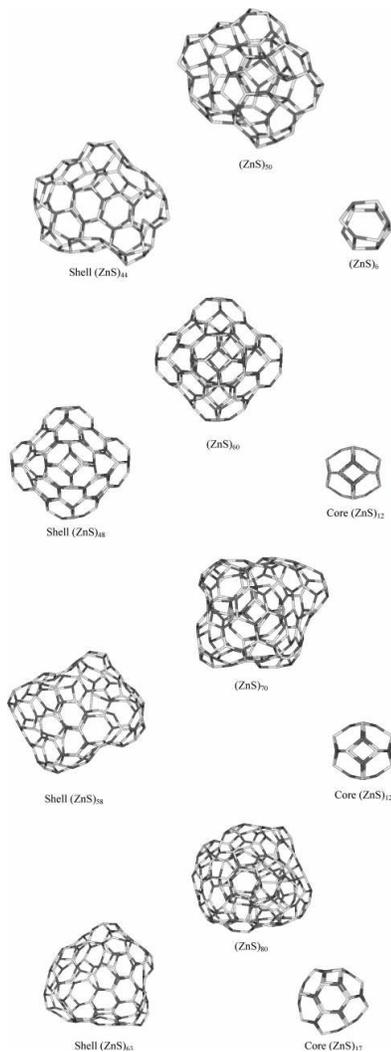
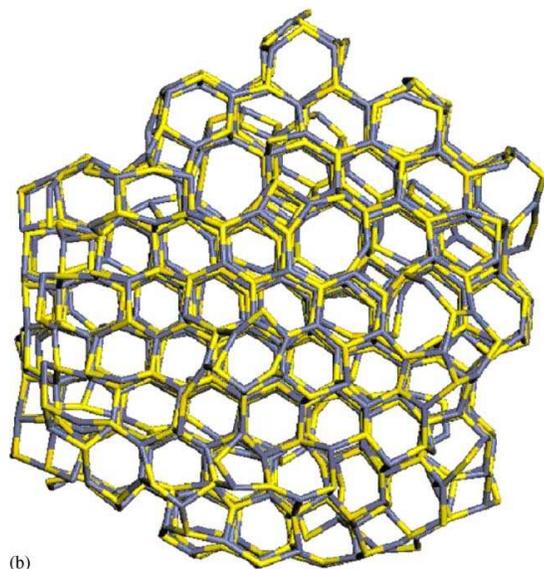
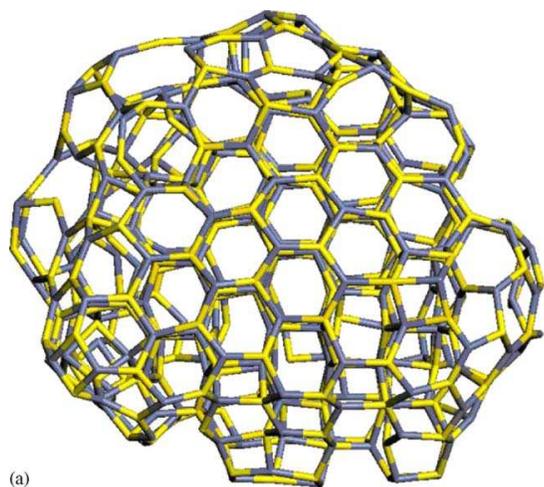


Figure 7

Structures of the four bubble clusters studied. The complete structures are shown in the center of each panel, while the innermost and outermost clusters are shown below them. Light gray sticks refer to sulfur and dark gray to zinc.



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Figure 8

39 Structures of two clusters, obtained with simulated annealing. (a) $(\text{ZnS})_{256}$, (b) $(\text{ZnS})_{512}$. Light gray
40 sticks refer to sulfur and dark gray to zinc.
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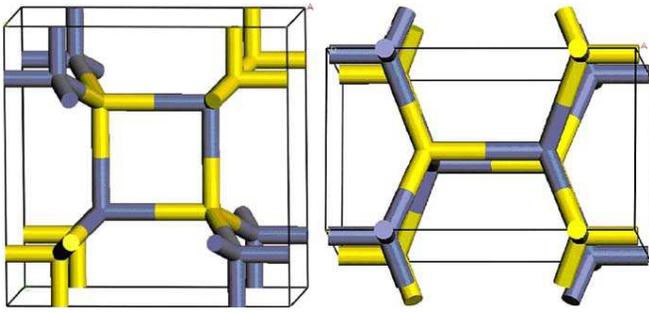


Figure 9

Front and top views of the unit cell which generates the $(\text{ZnS})_{256}$ and $(\text{ZnS})_{512}$ clusters. This is the same structure of the BCT zeolite, although in zeolites each Zn and S sites are occupied by Si atoms, with O atoms connecting them, creating a more open structure.

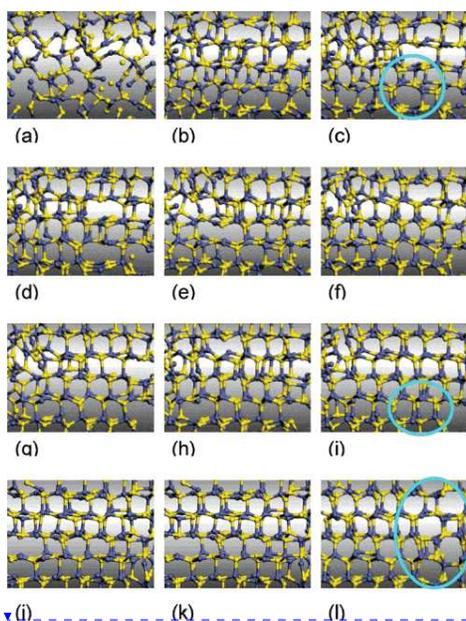


Figure 10

Snapshots taken during the MD simulation of the 2D system showing the crystallization of the ZnS; ball-and-stick model representations of the Zn (blue) and S (yellow) atom positions. (a) After 5 ps showing the amorphous/molten ZnS; (b) after 500 ps revealing the (partial) crystallization of the ZnS; (c) after 700 ps, the area circled accommodates a 4-8-membered ring structure; (d) 750 ps; (e) 800 ps; (f) 850 ps; (g) 900 ps; (h) 950 ps; (i) 1000 ps the region highlighted by the blue circle has now rearranged into a wurtzite structure; (j) 1250 ps; (k) 1500 ps; (l) 1895 ps the region highlighted has returned to a 4-8-membered ring conformation.

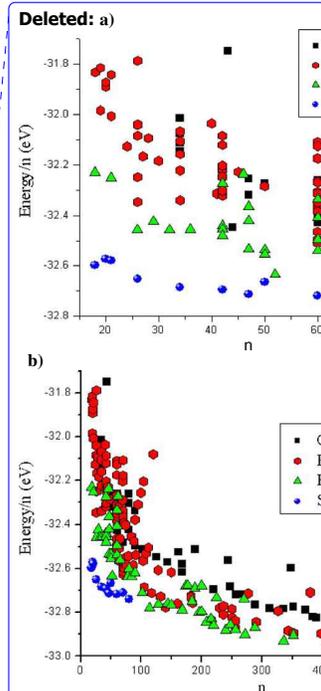


Figure 10
 a) Energies of $(\text{ZnS})_n$ clusters for $n=18-80$, after the geometry optimization has been performed using interatomic potential energy minimisation techniques. The structure of the clusters is indicated in the legend. The SA clusters are bubble and double bubbles, which were obtained from simulated annealing methods. b) Energies of all the geometry optimized $(\text{ZnS})_n$ clusters for $n=18-560$, using IPED techniques. The structure of the clusters is indicated in the legend.

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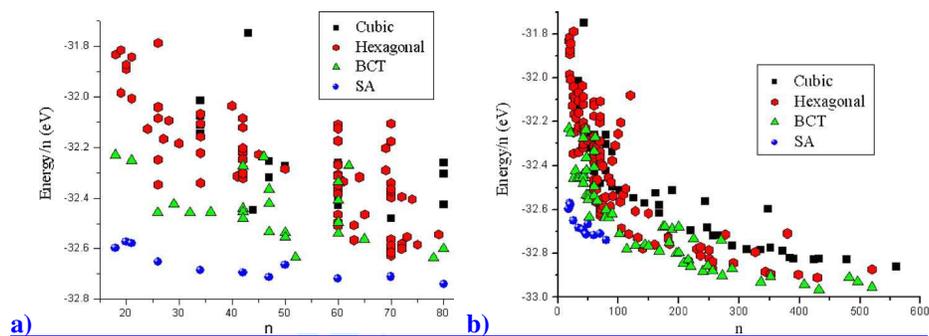


Figure 11

a) Energies of $(\text{ZnS})_n$ clusters for $n=18-80$, after the geometry optimization has been performed using interatomic potential energy minimisation techniques. The structure of the clusters is indicated in the legend. The SA clusters are bubble and double bubbles, which were obtained from simulated annealing methods. b) Energies of all the geometry optimized $(\text{ZnS})_n$ clusters for $n=18-560$, using IPEM techniques. The structure of the clusters is indicated in the legend.

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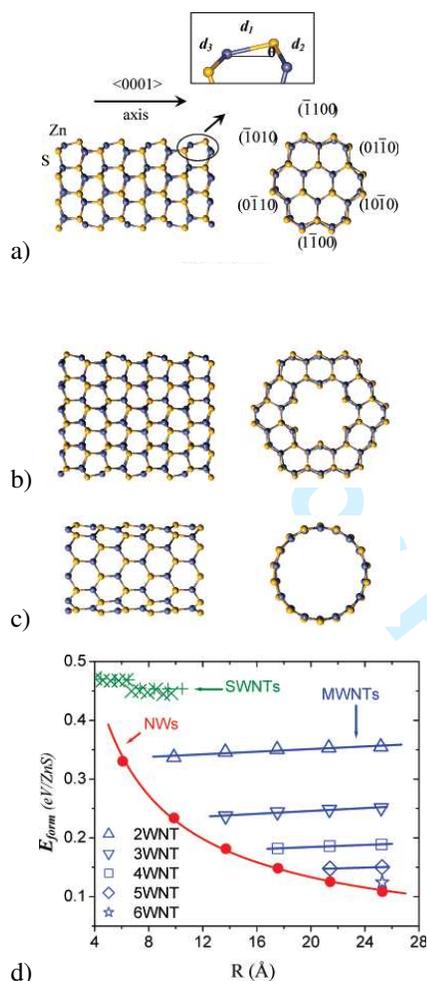


Figure 12

Side (left column) and top views (right column) of (a) ZnS nanowire; (b) faceted double-walled ZnS nanotube; (c) (9,0) singlewalled ZnS nanotube. The structural parameters (d_1 , d_2 , d_3 , θ) representing the surface relaxations are indicated in the inset of figure a. (d) Evolution of the formation energy (E_{form}) of ZnS-NWs (red solid circles), multiwalled ZnS-NTs (open up triangles, down triangles, squares, and diamonds), and ZnS-SWNTs (crosses) as a function of radius. The red solid line represents the fitting data of ZnS-NWs given by the expression $E_{form}=0.689/R^{0.78}$. The radii of the multiwalled ZnS-NTs are the outer radii.

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