

Exploring at nanoscale from first principles

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Systems at the nanoscale can exhibit distinctive and unexpected properties in electrical, magnetic, mechanical, and chemical aspects. Understanding these properties not only is of importance from the fundamental scientific view but also offers great opportunities for future applications. Theoretical calculations can provide important information to interpret, modify, and predict the novel properties of objects at the nanoscale and therefore play a significant role in the process of exploring the nano world. In this review, six different areas are briefly presented, namely, prediction of new stable structures, modification of properties (especially the electronic structures), design of novel devices for applications, the structures and catalytic effects of clusters, the mechanical and transport properties of gold nanowires, and improvement of materials for hydrogen storage. Based on these examples, we show what can be done and what can be found in the investigations of nanoscale systems with participation of theoretical calculations.

Keywords first-principles calculations, nanostructures, electronic structures, design of novel devices, catalytic effects of clusters, gold nanowires, hydrogen storage

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1 Introduction

“There’s Plenty of Room at the Bottom.” In 1959, Feynman gave his classic talk on nanotechnology at the annual meeting of American Physical Society [1]. Now, it is widely accepted that when materials are below 100 nanometers in size, distinctive and unexpected properties can be exhibited. Two principal reasons are responsible for this [2]. First, the properties of a nanoscale system must be described with quantum mechanics, and

the quantum effects lead to new properties, especially when the dimension of the object is comparable with the characteristic wavelength of its fundamental excitations such as electron, photon, phonon, and magnon [2]. Second, as the system becomes smaller and smaller, more and more percentages of atoms are located on its surface, and the large surface-to-volume ratio results in novel features [2]. The properties of nanoscale objects depend significantly on their sizes, shapes, and compositions. Such dependences lead to versatile properties in electrical, magnetic, mechanical, and chemical aspects. These special properties associated with nano systems provide great opportunities in applications.

Experimentally, nanoscale systems can be investigated in many ways. Mass spectroscopy, with which the fullerenes were discovered [3], can be used to explore stable clusters. Transmission electron microscopy (TEM) can be used to observe the structures of nanoscale materials. For example, using TEM, Iijima discovered the carbon nanotubes [4]. The invention of scanning tunnelling microscopy (STM) is a revolutionary advance in that it enables scientists to image, manipulate, charac-

terize, and control the geometries and electronic structures at atomic scale. Atomic force microscope (AFM), photoelectron spectroscopy, and even X-ray structure determination method [103] can also be used to study nano materials. However, most results of these experimental methods cannot be directly understood without collaboration of theoretical calculations. Therefore, the role of theoretical calculations is vital in understanding phenomena at the nanoscale and in designing new nanomaterials.

At present, first-principles calculations within density functional theory (DFT) are widely used in studying the properties at the nanoscale. Despite of some drawbacks such as self-interaction error, in general DFT calculations can give accurate and reasonable descriptions of nano systems. Some examples of popular software packages are Gaussian [5], VASP [6, 7], DMol^{3†}, SIESTA [8], and ADF [9]. The recently developed linear scaling methods make it possible to investigate properties of systems with tens of thousands atoms with first-principles calculations. For larger systems, semiempirical and force field methods may become more suitable. Along with the development of computational methods and programs, the capabilities of computing facilities are continuing to expand. These advances make theoretical calculations a powerful and increasingly important tool in the investigations of nano systems.

In this review, we briefly present what can be done and what can be found by theoretical calculations in the study of nanoscale systems. The examples are taken from six areas of research, including prediction of new stable structures, modification of properties (especially the electronic structures), design of novel devices for applications, the structures and catalytic effects of clusters, the mechanical and transport properties of gold nanowires, and the improvement of materials for hydrogen storage. Instead of going into details, we hope that by providing some representative examples, the readers will see how theoretical calculations work and how they play an important and useful role in the investigations at the nanoscale. Interested readers can refer to the original literature for further information.

2 Prediction of new stable structures

Fullerenes, carbon nanotubes (CNT), and graphene all belong to the family of carbon allotropes, along with graphite and diamond. Dramatic developments in the chemistry and physics of these materials have triggered enormous investigations toward their structures and similar configurations theoretically.

Since the first report on the spherical cage of C₆₀, extensive research has been devoted to investigating the structures of the fullerene family. For example, using

a tight-binding molecular dynamics (MD) method, the ground-state structures of carbon fullerenes from C₂₀ to C₇₀ and from C₇₁ to C₁₀₂ were determined by Zhang *et al.* [10, 11].

Endohedral metallofullerene is also an important subject studied through first-principles calculations [12–17]. For example, the ground state structure, electronic, and transport properties of Gd@C₈₂ were investigated by Senapati *et al.* with DFT and the Landauer–Buttiker formalism [12], while the geometry and magnetic properties of Gd₃N@C₈₀ were studied by Lu *et al.* using relativistic and on-site correlation-corrected DFT [13].

CNT is another kind of allotrope and can be regarded as graphene rolled up into a seamless cylinder. According to the way of rolling, CNT can be classified into three categories with different structures and electronic properties: zigzag, armchair, and chiral. In reality, it is inevitable for CNTs to have defects, such as vacancy, adatom, substitution, and Stone–Wales defects. These defects have significant influence on the nanotubes' chemical and physical properties. For a deep understanding of defects in CNTs, much theoretical effort has been devoted to this area [18–21]. As boron-nitrogen nanotubes (BNNTs) have similar structure as CNTs, defects on BNNTs were also studied [22].

Recently, a new type of buckyball composed of boron atoms instead of carbon was predicted through first-principles calculations by Szwacki *et al.* [23]. The proposed B₈₀ cluster has a structure similar to C₆₀, with additional 20 B atoms in the centers of all the hexagons. The B₈₀ cage preserves the *I_h* symmetry of C₆₀ and has a large HOMO–LUMO gap. Its stability was further confirmed by comparing its cohesive energy with that of boron double rings, whose existence has been verified experimentally. Further calculations found that the *I_h* B₈₀ cage has seven imaginary frequencies and exhibits a spontaneous symmetry breaking to achieve even lower energy [24, 25]. In another work, Prasad and Jemmis studied a B₈₄ cluster that is a basic unit of bulk β -boron and found that it is deficient by 50 electrons according to the Wade–Mingos rule. To make up the 50 electrons, they tried to stuff 14 to 18 B atoms into the B₈₄ cluster (each B atom contributes three electrons), making a series of boron clusters B_{*N*} (98 ≤ *N* ≤ 102). Interestingly, these clusters are even more stable than the B₈₀ cluster [26].

Except the above cages, planar structures also attract much attention. Koskinen *et al.* studied the planar reconstruction patterns of the zigzag and armchair edges of graphene through DFT calculations [27]. It was found that at a hydrogen-lacking atmosphere, zz(57), a reconstruction of zigzag edge wherein two hexagons transform into a pentagon and a heptagon, is more stable than

[†] DMol³ is a density functional theory quantum mechanical package available from Accelrys. Delley Software, Inc.

zigzag and armchair edges, showing self-passivating property [27]. In the case of element boron, a new boron α -sheet composed of both triangular (electron donor) and hexagonal (electron acceptor) motifs was put forward and found to be energetically more favorable than structures considered before. This boron α -sheet may also be rolled up into boron tube, and its structural, electronic, and mechanical properties were studied by Singh *et al.* [28].

So far, all the nanotubes we have discussed are seamless. Actually, there is another kind of nanotubes constructed through self-binding of nanofilms. Using theoretical analysis and molecular dynamics simulation, Zang *et al.* demonstrated that a freestanding nanofilm can bend itself into a nanotube without external stress load, due to the intrinsic surface-stress imbalance from surface reconstruction [29]. Pure Si and Ge self-rolled-up nanotubes, as well as SiGe nanotubes with Ge in both the inner and outer layer, were constructed with this method (Fig. 1).

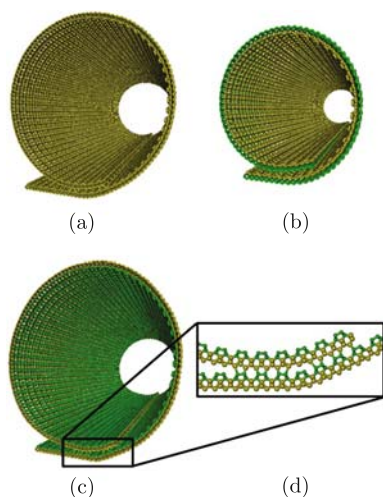


Fig. 1 Structures of the self-bending nanotubes from MD simulations. (a) A Si nanotube. (b) A SiGe nanotube with Si as the inner layer. (c) A SiGe nanotube with Ge as the inner layer. (d) Enlarged view of selected part in (c). Reprinted with permission from Ref. [29]. Copyright © 2007 American Physical Society.

The study of novel stable structures is being continued and is expected to provide a great chance to find new systems with unusual electronic, optical, mechanical properties and to offer novel device opportunities based on nanostructures.

3 Modification of electronic properties

As a matter of fact, some properties of nanostructures are not convenient for potential applications. For example, CNTs can be either metallic or semiconducting depending on the way by which a graphene layer is rolled up. However, the difficulty of separation limits their usefulness.

Fortunately, electric field, adsorption, doping, and some other methods are all feasible ways to generate novel electronic properties that pristine structures do not have. As first-principles calculations are well accepted in the study of electronic properties, they can also be used to investigate possible ways for modification of electronic properties.

It is well-known that zigzag edge graphene nanoribbon (ZGNR) is a semiconductor with two electronic edge states [30, 31], which are ferromagnetically ordered but antiferromagnetically coupled to each other. Therefore, it is expected that the external transverse electric fields will have significant effect on such magnetic states. Based on their calculations, Son *et al.* demonstrated that ZGNR turns to be half-metallic, i.e., metallic for one spin while insulating for the other, under an electric field with appreciable field strengths (Fig. 2) [32]. Furthermore, it was shown that the half-metallicity is robust even in the presence of different kinds of defects [32]. On the other hand, Rudberg *et al.* studied ZGNR with finite lengths using hybrid density functional B3LYP and found that ZGNR behaves as a half-semiconductor instead of half-metal as a result of the nonlocal exchange interaction [33]. Later, Kan *et al.* proposed that the half-metallicity of ZGNR with infinite length can be realized under an external electric field according to their B3LYP results [34]. However, if the strength of applied electric field is too strong, both spin polarization and half-metallic property will be removed. Therefore, there is an electric field range under which ZGNR is a half-metal [34].

Electric field can also be used to modify the band gap and transport properties of nanostructures [35–38]. Zhang *et al.* investigated the modifications of energy gap in BN nanoribbons (BNNR) by transverse electric fields [35]. It was shown that electric field is an effective way to modulate the band gap, and an insulator-metal transition can be realized at critical field strength, which is much more practical and effective than varying the width of BNNR. He *et al.* studied the effects of transverse electric field on the electronic structures of BNNT with organic molecule encapsulated and found that a better P-type doping can be achieved as the lowest unoccupied bands of electrophilic molecules become very close to the BNNT's valence band edge under electric field [36]. Son *et al.* investigated the spin transport properties of defective CNTs under transverse electric field and found that the spin orientation of the majority channel can be switched to the opposite one under the electric field, which offers promise to potential applications [38].

Chemical decoration is another way to modify the electronic properties of nanostructures [39–50]. Kan *et al.* investigated the effects of edge decorations on the electronic properties of ZGNR [39]. Different terminal groups such as $-H$, $-NH_2$, $-NO_2$, and $-CH_3$ were

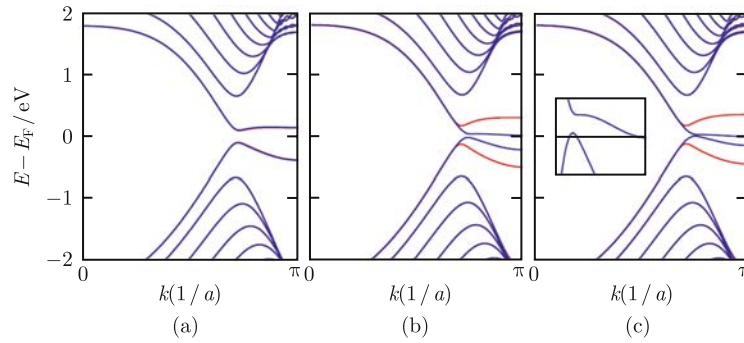


Fig. 2 The spin-resolved band structures of zigzag 16-GNR under external electric field with $E_{ext} = 0.0$ (a), 0.05 (b), and 0.1 (c) $\text{V}\cdot\text{\AA}^{-1}$. Red and blue lines are denoted as bands of α and β spin state, respectively. Reprinted with permission from Ref. [32]. Copyright © 2006 Nature Publishing Group.

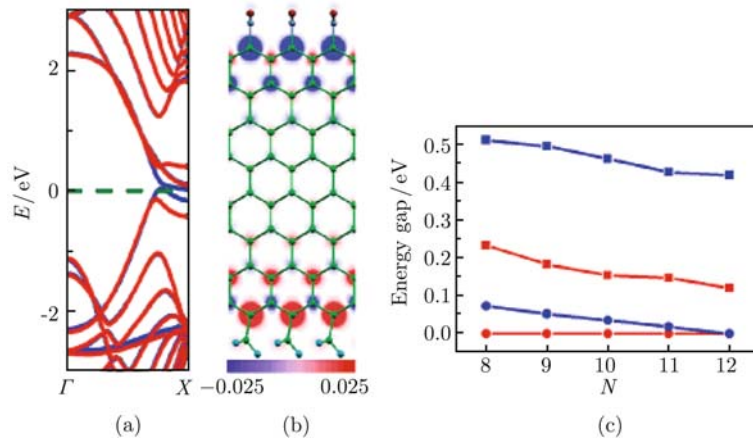


Fig. 3 (a) Band structure and (b) spin density of ZGNRs modified by $\text{NO}_2\text{-CH}_3$ pair. Red and blue are represented as spin-up and spin-down state, respectively. (c) The band gaps of ZGNR-full (red) and ZGNR-half (blue) with spin-up (square) and spin-down (circle) channels. Reprinted with permission from Ref. [39]. Copyright © 2008 American Chemical Society.

considered, and it was found that ZGNR decorated by $-\text{NO}_2$ at one edge and $-\text{CH}_3$ at the other behaves as a half-metal (Fig. 3). The electronic structures of atomic Ti chains adsorbed on armchair GNR (a-GNR) were also studied by Kan *et al.* [40]. According to their results, the adsorbed system shows ferromagnetism and metallicity. Besides, when the width of a-GNR is less than 2.1 nm, half-metallic ferromagnetism is predicted. Durgun *et al.* investigated the electronic property of Si nanowire with transition metal (TM) atom adsorption and found that hydrogen-passivated SiNWs can show half-metallic property when decorated with specific TM atoms [41]. Another kind of GNR structure, edge-oxidized zigzag GNRs, was studied by Hod *et al.* [42]. They have a spin-polarized ground state with antiferromagnetic coupling at the edges and can be turned to half-metal under electric field with a lower threshold and a wider range. Noting that it is difficult to separate carbon nanotubes with different electronic properties, Chang *et al.* studied the silanization of carbon nanotube. Their conclusion was that the silyl radicals can form strong covalent bonds and transform all carbon nanotubes into semiconductors [43]. In order to modify the band structure of

BN nanotube to obtain P-type/N-type semiconductor, He *et al.* studied the electronic structure of BNNT encapsulated by organic molecule and found that BNNT with an electrophilic molecule inside behaves as a P-type semiconductor [44].

Changing the symmetry of nanostructure can also be used to modify its transport properties. Li *et al.* studied the transport properties of zigzag GNR [51]. It was found that although all zigzag GNRs have similar band structures, transport behaviors of zigzag GNR with mirror symmetry differ significantly from those of zigzag GNR without mirror symmetry [51]. Their different transport behaviours originate from their differences in hopping integral due to parity symmetry matching of the frontier orbitals [51]. Therefore, it is expected that breaking the symmetry of an electronic structure can effectively increase the conductance through zigzag GNRs [51].

Strain can be used as a feasible method to modify the electronic structures too [52–54]. Gulseren *et al.* studied the effects of a radial strain on the band gap of semiconducting CNTs [52]. The band gap is closed with an insulator–metal transition under the radial strain. He *et al.* investigated the effects of strain on conductance of

metallic CNTs and found that the conductance monotonically decreases with increasing strain for both compression and elongation [53]. Sun *et al.* studied the electronic structures of GNR with strain and showed that the gap of armchair GNR can be modified significantly by strain in a nonmonotonic manner, while the gap of zigzag GNR is not sensitive to strain [54].

Owing to the novel properties of graphene, two-dimensional layers with similar structures are also investigated through first-principles calculations [55, 56]. Kan *et al.* constructed a kind of hybrid BCN nanoribbons and studied their electronic properties [55]. It was found that half-metallicity can be obtained in these structures as a result of a competition between charge and spin polarizations. Sun *et al.* studied the electronic structures of SiC nanoribbons [56]. It was found that zigzag SiC nanoribbons have the ground state with the two edges ferrimagnetically coupled. Half metallic behavior can be obtained in zigzag SiC nanoribbons when the width is less than 4 nm.

4 Design of novel devices

Nanostructures hold great promise for future applications due to the conceptual breakthroughs arising from their special properties. As DFT has been quite reliable for calculating different properties of nanostructures, first-principles calculations are indispensable for the purpose of using nanostructures as building blocks of novel nanodevice. In the following, some examples are given.

Electron conduction. The electron-conduction properties of fullerene-based nanostructures were investigated by Ono *et al.* [57]. The C_{60} -dimer bridge has low electron conductivity. However, when Li atoms are inserted into the cage of fullerenes, the conductivity is increased significantly. These results demonstrate that doping fullerenes with metal atoms may play a prominent role in electronic properties improvement and has potential applications in electronic device [57].

Molecular rectifier. Single azafullerene $C_{59}N$ molecule in a double-barrier tunnel was reported to show evident rectifying effect by Zhao *et al.* [58]. Through theoretical analysis, they proved that the half-occupied molecular orbital and the asymmetric shift of Fermi level of $C_{59}N$ are responsible for the rectifier effect. Xie *et al.* proposed a kind of nanostructures composed of boron doped fullerene as electron acceptor and nitrogen doped fullerene as electron donor and found that the engineered acceptor-donor pair can show rectifier characteristic [59].

Spintronics device. Spintronics utilizes not only the charge of electrons but also their spin. The ability to manipulate electron spin offers a big chance for the new generation of device. Theoretical calculations were per-

formed to search materials with special properties, such as transport with high polarization and stable half metallicity.

Based on non-equilibrium transport methods and density functional theory, Rocha *et al.* demonstrated that a large bias-dependent magnetoresistance can be obtained in an organic spin valve, which is constructed by sandwiching alkane-dithiolate and phenyl-dithiolate molecules between nickel contacts [60]. By encapsulating metallocene molecules inside carbon nanotube, Garcia-Suarez *et al.* put forward a new family of molecular wires and suggested that parallel $CoCp_2@3(7, 7)$ and $CoCp_2@3(8, 8)$ are the best candidates for spintronics applications not only because they are stable, but also because they have a spin-polarized transport channel at the Fermi level [61]. Koleini *et al.* constructed another class of structures with an organometallic benzene-vanadium cluster sandwiched between CNT or graphene contacts and found a high degree of spin polarization for electron transmission, which is not significantly dependent on the bonding strength [62].

Half metal is ideal for applications such as spin-polarized tunnelling. The search for materials with half-metallic property attracts great interests. Xiang *et al.* studied one-dimensional (1-D) transition metal-benzene sandwich polymers and found that $[V(Bz)]_\infty$ is a quasi-half-metallic ferromagnet, while $[Mn(Bz)]_\infty$ holds half-metallic ferromagnetism (Fig. 4) [63]. Besides, inter-chain coupling within hexagonal bundles can be used to stabilize long-range ferromagnetic order in the quasi-1-D system. Later, Zhou *et al.* proposed a similar structure constructed with alternating iron atoms and cyclopentadienyl rings. They found that this structure shows half-metallic properties, nearly perfect spin filter effect, and negative differential resistance at the same time, which holds promise for application in molecular electronics [64].

Memory element. Meunier *et al.* proposed a structure where a F_4TCNQ molecule is encapsulated inside a metallic carbon nanotube [65]. The system has good conductive property with F_4TCNQ perpendicular to the axis, while the conductance is suppressed significantly with F_4TCNQ in the parallel configuration. The structure can be used as a memory element with the advantages of being robust, fatigue-free, and working at room temperature [65].

Switch. Huang *et al.* investigated the transport properties of $[PhCrCrPh]$ molecule and found that the conductance of the two configurations of the molecule was remarkably distinctive from each other, which implies that this structure has potential to be used as molecular switch (Fig. 5) [66].

Gas sensor. Rocha *et al.* applied DFT and recursive Green's function method to investigate the adsorption

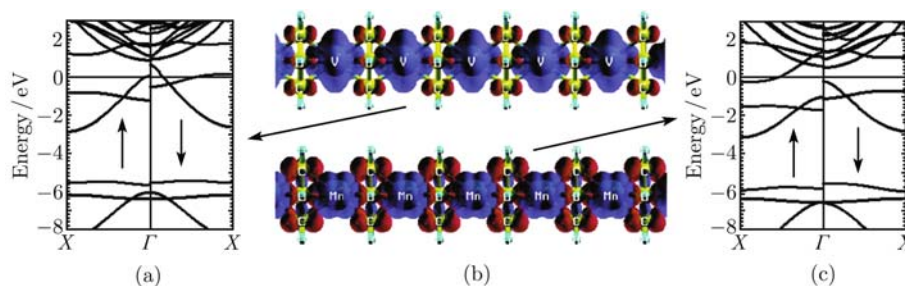


Fig. 4 Electronic band structures for $[V(Bz)]_{\infty}$ (a) and $[Mn(Bz)]_{\infty}$ (c), respectively. (b) Spin density for $[V(Bz)]_{\infty}$ (top) and $[Mn(Bz)]_{\infty}$ (bottom). Red and blue are denoted as the isovalues with -0.014 and 0.014 $e/\text{\AA}^3$. Reprinted with permission from Ref. [63]. Copyright © 2006 American Chemical Society.

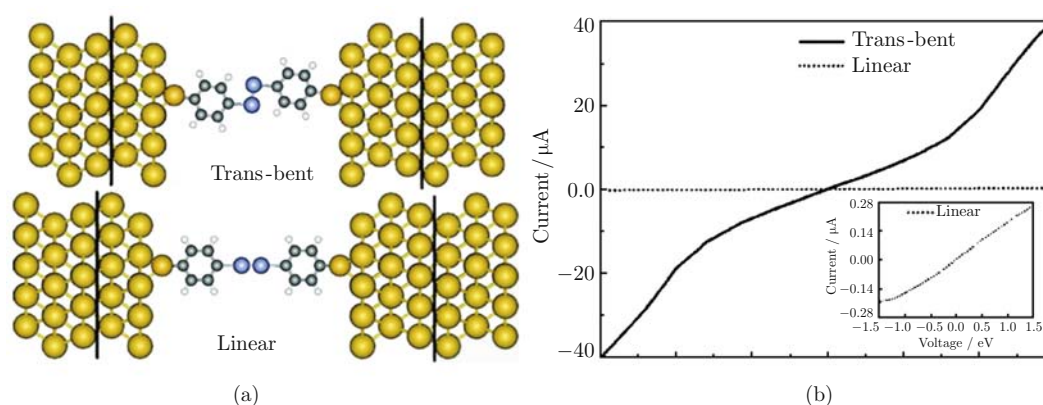


Fig. 5 The computational model (a) and the calculated current-voltage characteristic (b) of the proposed molecular switch. The trans-bent structure is regarded as the ON state and the linear structure as the OFF state. Reprinted with permission from Ref. [66]. Copyright © 2006 American Institute of Physics.

and transport properties of nitrogen-rich CNT. It was found that the conduction of CNT decreases gradually with ammonia adsorption. Thus, this structure can be used as an ammonia sensor [67]. This kind of sensor has the advantages of easy reversion and high sensitivity.

High energetic material. Through theoretical calculations, Abou-Rachid *et al.* proposed to encapsulate a polymeric nitrogen chain inside a CNT [68]. The structure is stable even at ambient pressure and room temperature. This stability originates from a charge transfer induced by hybridization between the CNT and the N-chain conduction bands. Considering the big difference of bonding energy between N–N or N=N and that of N_2 , this material has the potential to be used as explosive or propellant [68].

Field emission source. Khazaei *et al.* introduced a general approach to calculate the field emission properties of nanostructures. Pristine capped carbon nanotubes were studied, and the results agree well with experiments [69]. Furthermore, the authors demonstrated that the structures can be modified to have better field emission properties through doping Cs atoms to nanotubes [69].

Nano generator. It is found by Kaun *et al.* that resonance inelastic conduction in Au– C_{60} –Au junctions can be used to transfer energy to a given mode of C_{60}

molecule, showing current-driven molecular oscillation phenomenon. It is expected that under electromagnetic field, this system can be used as nanoscale generator of alternating current [70].

Nano motor. Bailey *et al.* designed a system composed of a double-wall CNT with an achiral outer tube encompassing a chiral inner tube [71]. As current flows through the CNT, flux of electrons passing through the inner tube generates a torque due to conservation of angular momentum. The torque is sufficient to overcome the frictional force between the outer and the inner tube and makes the inner tube rotate as a motor. Wang *et al.* proposed another system composed of a CNT shaft connecting molecular stalks with “conducting” blades [72]. Periodic charging and discharging of the blades generate an electric dipole, which can be driven by an external electric field, making the system a nano motor.

5 Structures and catalytic effects of clusters

Nanoclusters with their dimension between single atom and bulk matter have peculiar properties that are qualitatively different from those of both the extremes and cannot be deduced simply by extrapolation. The emergence of special properties originates from the particu-

larity at nanoscale such as quantum confinement effect and large surface to volume ratio. Besides, properties of nanoclusters vary dramatically with size. For example, bulk gold shows inertness for chemical reaction, but gold nanoclusters can be used to catalyze many reactions like oxidation of carbon monoxide. It was concluded experimentally that cluster with diameter of about 3 nm has the best performance [73]. In the following, we will take Au clusters as examples, focusing on construction of stable clusters and modifications of properties.

It was confirmed by joint theoretical-experimental investigations that for gold cluster with a few atoms (up to 7 for cation and 13 for anion), planar structures are energetically favorable due to the effect of relativistic effect and strong hybridization of the 5d and 6s orbital [74–76]. Bulusu *et al.* studied the structure evolution of gold clusters in the range of more than ten atoms (Fig. 6). They found formation of hollow cage structures for clusters with 16–18 atoms and a tendency to form 3-D compact structures for larger size [77]. Structures of gold clusters with particular number of atoms were also explored [78–82]. Li *et al.* found a tetrahedral Au_{20} cluster with T_d symmetry [78]. The cluster has a large HOMO–LUMO gap as a symbol of stability and chemical inertness. The structure of Au_{20} with high symmetry was further confirmed by Gruene *et al.* [79]. Johansson *et al.* proposed the existence of an icosahedral Au_{32} cluster, which is stable and energetically competitive with respect to compact isomers [80]. Lechtken *et al.* found an Au_{34}^- cluster with C_3 symmetry chirality [81]. Besides, Gao *et al.* proposed a stable icosahedral gold cage Au_{42} , which can hold up to 13 gold atoms inside [82].

The empty space inside the hollow cages of gold cluster makes it possible to dope foreign atoms, which is a feasible way not only to stabilize the cage structure but also to tune the chemical and physical properties of the clusters. Wang *et al.* observed Cu-doped gold

buckyballs and found that the endohedral structure is energetically favorable over other isomers, while the outer cage of Au_{16}^- and Au_{17}^- are not significantly distorted [83]. Good agreement between theoretical results with experiments further confirms the existence of the doped cage geometry. Nonmetal atoms can also be doped inside the cage. Wang *et al.* investigated the structures of Au_{16}^- cage with group IV atoms inserted and found that the global minimum is not an endohedral structure, but an exohedral one [84], which is quite different from the case of Cu. Magnetic atoms can also be doped inside the cage and novel magnetic properties is expected to occur. Wang *et al.* studied Mn_{13}^- and Co_{13}^- inserted Au_{20} cages and found that $[\text{Mn}_{13}@\text{Au}_{20}]^-$ possesses a magnetic moment 20-fold higher than that of bare M_{13}^- , resulting in a doped cluster with ultrahigh magnetic moment [85].

Clusters with remarkable stability are regarded as potential building blocks for further applications in nanotechnology. Closed electronic shells and close atomic packing are considered as two important factors determining the stability of clusters. As Khanna and Jena side, “It will be ideal if the close atomic packing as well as the electronic shell closure can be simultaneously achieved to give cluster enhanced stability” [86]. Following the general principles, some clusters with great stability can be constructed and anticipated theoretically [87–89]. Pyykkö *et al.* predicted that WAu_{12} , an icosahedral cluster with I_h symmetry, holds an exceeding stability and a quite large HOMO–LUMO gap, due to the closure of electronic shell with 18 electrons [87]. Later, this cluster was observed experimentally by Li *et al.* [88]. Dognon *et al.* further put forward PuPb_{12} , a 32-electron systems, with great stability [89]. Chen *et al.* proposed a general principle to design stable clusters with high symmetry [90]. In their scheme, a highly symmetrical hollow cage should be selected with appropriate choice of doped atoms to gain electronic shell closure as well as aromatic

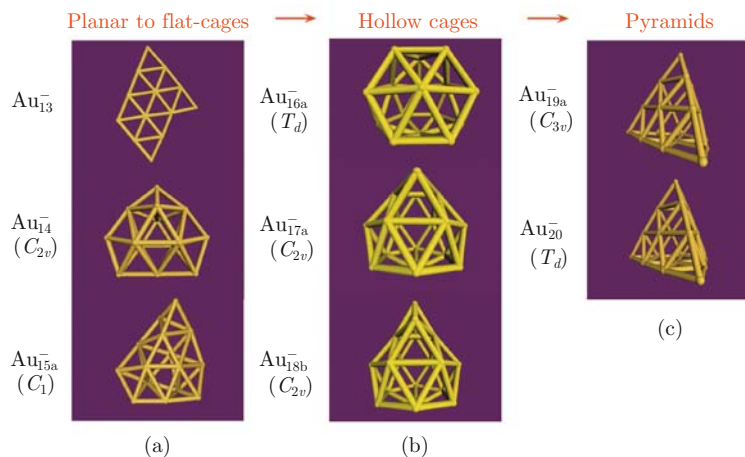


Fig. 6 Structural evolution of gold anion clusters from Au_{13}^- to Au_{20}^- . (a) Structure transition from 2-D planar to 3-D flat cages. (b) Gold clusters with hollow cages. (c) Gold clusters with pyramids structures which resemble the bulk. Reprinted with permission from Ref. [77]. Copyright © 2006 National Academy of Sciences (USA).

character [90]. The principles were widely confirmed by experimental observations as well as other calculations.

Much attention has been paid to the catalytic properties of gold cluster since Haruta *et al.* found that gold nanostructures supported by Fe_2O_3 surface can catalyze carbon monoxide oxidation in 1987 [91]. Now, it is widely accepted that gold nanostructures can be used to catalyze many reactions. Enormous effort has been devoted to understanding the catalysis mechanisms and studying factors that influence the catalysis capability. Ding *et al.* performed calculations on the adsorption of reactant on gold clusters [92, 93] and found that the charge transfer from gold clusters to adsorbed O_2 results in weakening and elongation of $\text{O}=\text{O}$ bond, as an essential factor of the following reactions. Yoon *et al.* studied the adsorption of CO on Au_8 cluster adsorbed on reduced $\text{MgO}(100)$ surface and found that charging of the supported clusters plays a key role in promoting its chemical activity [94]. Socaciu *et al.* investigated the catalytic CO oxidation by free Au_2^- cluster [95]. The whole process along the reaction pathway was elucidated by a formulation of the catalytic cycle. An *et al.* studied the catalytic performance of single-walled helical gold nanotubes $\text{Au}(5, 3)$ on oxidation of CO molecule and found that $\text{Au}(5, 3)$ holds high catalytic activity to promote CO oxidation at room temperature [96]. Different factors that influence the catalytic capacity of gold clusters, such as the charging effect, the electronic size effect, the impurity-doping effect, the role of substrate, and the structural dynamical fluxionality were well discussed and summarized [97, 98]. It should be noted that the structures of supported gold clusters can also be tuned by changing the thickness of thin film or applying external electric field, which is another way to improve the catalytic performance of gold clusters [99–101].

Thiol-protected gold nanoparticles have attracted great interest in nanoscience due to their importance in both fundamental research and technological applications. However, there still remains significant challenge on determining their structures and the reason of their extraordinary stability is still unclear. Recently, the structure of gold nanoparticle with 102 gold atoms coated by 44 p-MBAs was determined [102, 103]. The “divide and protect” scheme and the closure of electronic shell are suggested to be responsible for its stability [102]. These works not only mark a breakthrough in experiments but also provide a new way of theoretical thinking. For example, Akola *et al.* studied the structure of $\text{Au}_{25}(\text{RS})_{18}$ and put forward a similar bonding mode as that of the Au_{102} particle [104].

scanning probe microscopy (SPM) or mechanically controllable break-junction technique (MCBJ), has attracted great interest due to their novel properties, such as inherent quantum effect, enhanced mechanical strength, and quantum conductance. Understanding the formation, structure, and transport properties of gold single-atom chain is of great importance not only in scientific research but also in technological applications such as molecular electronics devices [105, 106]. A great deal of effort has been devoted into theoretical calculations about the formation process, mechanical strength, involvement of contaminations, and effects on the transport properties [107–118, 121–124].

Molecular dynamics (MD) simulations were performed to investigate the structural evolutions of the atomic-scale nanowires under tensile strains until single-atom chains are generated [107–115]. For example, Sørensen *et al.* simulated mechanical deformation of the gold nanowire under tensile strain and found a variety of atomic rearrangement mechanisms that depend on the size, shape, crystal orientation, and structural order degree of the nanowires [109]. Rubio-Bolliger *et al.* investigated the structural changes and force variations during the fabrication of single atomic chain [110]. The sawtooth shape of the force curve during the stretching is well shown in the calculations, and it was found that the sudden change of the force corresponds to the abrupt atomic rearrangements [110]. Calculations also showed an enhanced mechanical strength of the atomic wire comparing with that of bulk. Recently, Pu *et al.* performed comprehensive MD simulations to investigate the mechanism of the formation of different junction structures of gold nanowires under stretching. They put forward a “rate-dependent energy release” mechanism for the pulling process, which takes the effect of system size, temperature, and elongation rate into account [115]. They found that the stretching of nanowires can be regarded as a competition between pulling a long monoatomic chain and generating some low energy defects such as short monoatomic chain, thick helical chain, surface dislocations, and reconstructions [115]. More atoms, higher temperature and lower elongation rate are conducive to the formation of such low energy defects. Therefore, it was predicted that the formation of long monoatomic chains is favored at low temperatures with high elongation rate [115].

The rupture of monoatomic gold chain was also studied theoretically [116–118]. From the MD simulations by Silva *et al.* [116], it was found that a five-atom long monoatomic chain can be generated before the rupture of the chain and the longest distance between adjacent atoms is about 3.1 Å at the stage of fracture. Kruger *et al.* studied the rupture of gold wire when connected by a thiolate molecule and found that the sulfur-gold bond

6 Gold nanowires

Gold single-atom chains, which can be generated with

is stronger than gold–gold bond, resulting in the rupture of Au–Au rather than Au–S bond [117]. The thiolate molecule studied here can be used as an anchor to manipulate the gold wire or modify the transport properties of the system. Velez *et al.* studied another case, where 4,4'-bipyridine molecule is attached to gold nanowires [118]. It was found that the comparison of force needed to rupture chemical bond between Au–N and Au–Au depends on the configuration of connection. The force for Au–N bond is close to that of Au–Au when 4,4'-bipyridine is attached to monoatomic gold chain, while lower when connected to gold cluster. Thus, it is not easy to distinguish the rupture bond in some experiments.

Large Au–Au bond length (3.6 Å) was observed within the monoatomic chain experimentally [119, 120], although calculation showed that the maximum length is only 3.1 Å [116]. Theoretical effort was devoted into explanation of this disagreement [121, 122]. Now, it is widely accepted that impurities are the origin of such large distance, as suggested by Novaes *et al.* [121]. The authors studied H, B, C, N, O, and S impurities and found that H is responsible for the distance in the range of 3.6 Å while S for 4.8 Å. The effect of H was further supported by Jelinek *et al.* who showed that the dissociation of H₂ molecule over stretched Au nanowires is feasible due to the catalytic effect of such low-dimensional structures [122].

Impurity atoms can be used to modify the mechanical and transport properties of monoatomic chains [114, 122–124]. Novaes *et al.* investigated the effect of inserting an oxygen atom into monoatomic gold chain and found that strong chemical bond is formed, resulting in a longer single-atom chain [123]. Zhang *et al.* found that insertion of molecular and atomic oxygen can both enhance the strength of chemical bond [124]. Jelínek *et al.*

studied the transport properties of gold nanowire with hydrogen adsorption [122]. It was found that adsorption of hydrogen molecule does not affect the conduction, while hydrogen atom results in appearance of fractional conductance. Similar results were also reported by Zhang *et al.* that inserted oxygen atom can induce fractional conductance of gold chain, while oxygen molecule leads to conductance of about 1 G₀ [124]. Recently, Jelínek *et al.* performed systematic calculations to study the evolution of the mechanical and transport properties of clean and contaminated Au nanowires during the rupture (Fig. 7) [114].

7 Hydrogen storage materials

Hydrogen has attracted enormous attention as a future energy resource, which can dramatically decrease pollution while conserving fossil fuel. However, a serious bottleneck for its full usage is lack of safe and economical way of storage and transportation. Thanks to the large surface area and potentially high binding energy, materials at nanoscale may show advantage for hydrogen storage. A lot of effort is devoted to searching for such materials, which should meet some stringent requirements: high gravimetric or volumetric density, fast hydrogen adsorption and desorption, and recycling reversibly under near ambient conditions.

Carbon-based nanomaterials for hydrogen storage are widely studied by first-principles calculations [125–134]. Pristine carbon nanostructures cannot be used for practical hydrogen storage since they are chemically inert. Dodziuk and Dolgonos performed molecular mechanics calculations and molecular dynamics simulations for a single nanotube as well as a nanotube bundle and found that high hydrogen content cannot be achieved

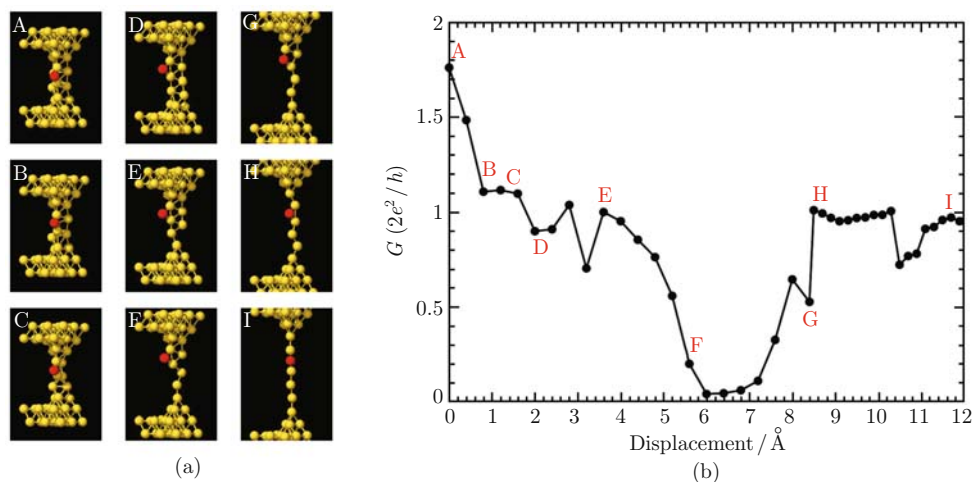


Fig. 7 Structural and conductance evolution in the process of stretching of a gold nanocontact under the presence of atomic oxygen impurity. (a) Snapshots from MD simulations to show the oxygen incorporation and the monoatomic chain formation. (b) Conductance variance along the stretching process. Reprinted with permission from Ref. [114]. Copyright © 2008 American Physical Society.

through physisorption [125]. Fortunately, decoration is an effective way to increase the storage capacity of materials, and some modified structures were suggested theoretically. On the basis of orbital interactions in organometallic chemistry, Zhao *et al.* proposed a novel type of organometallic buckyballs, in which transition metal atoms are adsorbed on fullerenes. The available storage densities for the $C_{60}[ScH_2(H_2)_4]_{12}$ and $C_{48}B_{12}[ScH(H_2)_5]_{12}$ structures are 7.0 wt% and 8.77 wt%, respectively [126]. Almost at the same time, Yildirim *et al.* demonstrated that Ti-decorated CNTs can be used as potential high-capacity hydrogen storage. They found that a single Ti atom in SWCNT can bind up to four hydrogen molecules, and the storage density can reach 8 wt% at a high Ti coverage [127]. Lee *et al.* proposed the concept of “thermodynamically usable hydrogen capacity,” which takes into account the zero-point vibration as well as the pressure- and temperature-dependent adsorption-desorption probability of hydrogen molecules [128]. Based on their new concept, they found that Ti-decorated *cis*-polyacetylene is an optimal material with **usable** gravimetric density 7.6 wt%, much higher than the corresponding value for $C_{48}B_{12}Sc_{12}$ and Ti-decorated carbon nanotube (<5wt%) mentioned above [128]. Durgun *et al.* later predicted that transition-metal-ethylene complexes can be used as another high-capacity hydrogen-storage media [129].

The high-storage capacity rests heavily on stability of the nanostructures. However, it was found that clustering of transition atoms is energetic favorable. Thus, the capacity is dramatically limited, which is a serious obstacle for hydrogen storage [130, 131]. Some proposals were raised in order to deal with the problem of clustering. Sun *et al.* proposed a $Li_{12}@C_{60}$ structure in which the adsorbed Li atoms do not aggregate because Li atoms bind more strongly to C than to themselves [132]. However, to $Li_{12}@C_{60}$, the binding energy of H_2 is somewhat too small. Durgun *et al.* suggested to incorporate TM-ethylene complexes with nanostructures such as graphene layer. However, the maximum gravimetric density decreases correspondingly [129]. Park *et al.* proposed a structure in which transition atoms are adsorbed on covalently bonded graphenes [133]; nevertheless, it is not easy to be synthesized in experiments. Recently, Yoon *et al.* put forward a structure in which light alkaline-earth metals are adsorbed on fullerenes. It was found that $Ca_{32}C_{60}$ achieves a hydrogen uptake more than 8.4 wt% (Fig. 8), with a binding energy and structure stability appropriate for practical use, which means that Ca is the most promising coating element considered so far [134].

The ideal system for hydrogen storage is the one where H_2 binds molecularly with an intermediate binding energy between physisorption and chemisorption. There-

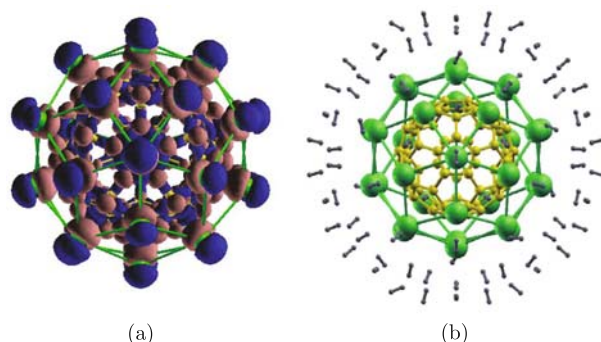


Fig. 8 $Ca_{32}C_{60}$ as a potential hydrogen storage material. (a) The isosurface of charge density difference as 32 Ca atoms adsorbed on C_{60} cage. (b) Optimized structures of 92 H_2 adsorbed on $Ca_{32}C_{60}$ with a storage uptake of 8.4 wt%. Reprinted with permission from Ref. [134]. Copyright © 2008 American Physical Society.

fore, it is important to discuss the interaction mechanism between hydrogen molecule and storage systems in order to achieve optimal capacity effect. So far, there are two mechanisms revealed in the literatures. One is Kubas interaction [135] between H_2 and transition atoms, for example, in Refs. [126, 129], in which the hydrogen σ^* -antibonding orbitals are hybridized with the *d* orbitals of transitional atom, resulting in elongation of H-H bond. The other is polarization mechanism, in which H_2 molecule is polarized by the electric field associated with the charge redistribution, as the cases in Refs. [134, 136].

It should be noted that the decoration method as mentioned above can also be applied into BNNT, which has also been reported [137–141].

8 Summary

In this review, six different aspects were discussed to present the participation of theoretical calculations in investigations of nano systems. We show that theoretical calculations can be used to understand their properties and to design novel structures with desirable functions. Theoretical calculations can provide not only important but also necessary knowledge. Moreover, they play a significant role in the process of the exploration within the world of nano.

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