

# Formation of quantum structures on a single nanotube by modulating hydrogen adsorption

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Using first-principles density functional calculations we showed that quantum structures can be generated on a single carbon nanotube by modulating adsorption of hydrogen atoms. While the hydrogen free part of the tube remains semiconducting or metallic, a wide band gap opens in the part covered by hydrogen. The type of the nanotube, the extent and sequence of hydrogen-free and hydrogen-covered regions can provide several options to design a desired optoelectronic device.

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Novel properties and fundamental effects of electrons have been revealed in lower dimensional quantum structures, such as multiple quantum wells, quantum dots, *etc.* During last two decades several new electronic devices have been developed from these quantum structures.<sup>1</sup> Fabricating even smaller and more efficient devices is now the prime drive towards nanotechnology and molecular electronics. One of the grand challenges of research on carbon nanotubes has been the realization of nanometer optoelectronic devices.<sup>2,3</sup> In this letter we present a new nanodevice model, which is based on a quantum well structure generated by the modulating adsorption of hydrogen atom on a semiconducting single-wall carbon nanotube (SWNT). It is known that a SWNT can be either a metal or a semiconductor depending on its chiral vector and radius, but becomes always a semiconductor even with a larger band gap, when it is exohydrogenated.<sup>4</sup> Hence, our idea of forming quantum structures on a SWNT exploits this important effect of hydrogenation. Electrons or holes can be confined in a hydrogen free region of SWNT sandwiched between two regions, which are uniformly hydrogenated.

These findings are obtained from extensive state of the art, first-principle density functional calculations<sup>5</sup> within the generalized gradient approximation for fully optimized atomic positions as well as the lattice constant. The predictive power of the density functional theory was proven in the earlier studies related to atomic structure, energetics and electronic structure of various carbon nanotubes.<sup>4,6</sup> Using a periodically repeating supercell geometry we expressed wave functions in terms of plane waves up to an energy cutoff of 500 eV. Other details of the calculations can be found in Ref.6

First we demonstrate how the electronic structure is modulated periodically in direct space so that multiple quantum well structure (MQWS) is generated on a prototype zigzag (8, 0) SWNT. The bare (8, 0) SWNT is a semiconductor with a direct band gap of 0.64 eV. Unsaturated  $\pi^*$ -states of carbons are active sites for the adsorption of hydrogen atoms. Single hydrogen atom

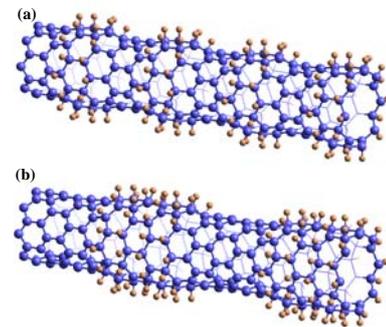


FIG. 1: Superlattice structures,  $[(C_{32})_l(C_{32}H_{32})_q]$  formed on a single (8, 0) SWNT by modulating adsorption of hydrogen atoms. (a)  $l = q = 1$ ; (b)  $l = q = 2$ . The positions of 64 H and 128 C atoms, as well as superlattice parameter are calculated from full structure optimization by using conjugate gradient method.

is adsorbed on top of each carbon and completes the fourth covalent bond. The adsorption changes the planar  $sp^2$ -bonding on the cylindrical surface to a local  $sp^3$ -like bonding. The resulting structure is stable by an energy gain of 2.5 eV. This binding energy is relatively higher than the binding energy of H on the graphene due to the curvature effects.<sup>6,7</sup> Owing to the coupling between nearest neighbor H atoms, saturation of all carbon atoms with hydrogens appears to be even more stable with an average binding energy,  $E_b \sim 2.7$  eV/atom. Exohydrogenation gives rise to remarkable effects on the atomic and electronic structure. For example the C-C bonds are lengthen, bond angles change, and the radius of the tube expands by 16 %. More importantly, the band gap of the bare (8, 0) tube increases from 0.64 eV to  $\sim 2$  eV. Moreover, the conductance is extremely sensitive to hydrogen adsorption.<sup>8</sup> Let us now consider a single (8, 0) SWNT, on which a part (or region) of  $l$  unit cells [specified by  $(C_{32})_l$ ] is kept clean, while the adjacent part of  $q$  unit cells [specified by  $(C_{32}H_{32})_q$ ] is fully hydrogenated. We also assume that the supercell,  $[(C_{32})_l(C_{32}H_{32})_q]$  is

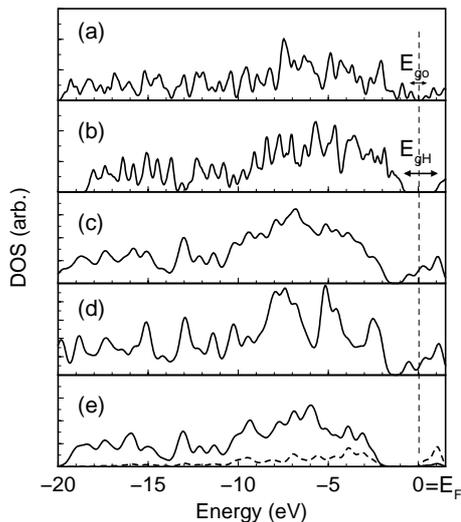


FIG. 2: Total density of states of a bare (8,0) SWNT, *i.e.*  $l \rightarrow \infty$  (a); exohydrogenated (8,0) SWNT *i.e.*  $q \rightarrow \infty$  (b);  $[(C_{32})_2(C_{32}H_{32})_2]$  superlattice (c). Local density of states of superlattice at  $(C_{32})_2$  (d); at  $(C_{32}H_{32})_2$  region with dashed curve indicating states derived from H. Band gaps  $E_{g0}$  (bare SWNT) and  $E_{gH}$  (exohydrogenated SWNT) are also indicated.

repeated periodically to form a superlattice. Such a superlattice structures generated on a (8,0) tube are illustrated in Fig. 1. Here the region which is kept clean and the region which is hydrogenated, are expected to have different band structure. This is the most crucial aspect that we have to explore. Normally, states in  $(C_{32})_l$  can be continued to the states in the adjacent  $(C_{32}H_{32})_q$  region, if they can be matched. Otherwise, states which cannot be matched have to confine to the region they belong to. These confined states have played an important role in the optoelectronic device applications of MQWSs in the past.<sup>1</sup> At this point, following three questions have to be addressed, before we conclude whether MQWSs can be realized from the above superlattice structure: (i) Does the hydrogenated region persist, or else adsorbed hydrogens can diffuse away to degrade the superlattice structure? (ii) What should be the extent of the regions,  $(C_{32})_l$  and  $(C_{32}H_{32})_q$ , in order their electronic structure and hence their band gaps to be distinguishable from each other? (iii) How are the bands aligned, and hence how is the energy band diagram modulated along the nanotube?

Starting from the first question, we found the fully hydrogenated region  $(C_{32}H_{32})_q$  is stable, since H atoms remained bound to the carbon atoms at the end of full structure optimization. Our static calculation at  $T = 0^\circ$  K did not yield diffusion of H towards the neighboring  $(C_{32})_l$  regions. The analysis of charge density for various states suggests that indeed two different electronic structure can be realized in the part of a SWNT which is as short as two unit cell. When the extent of zones,  $(C_{32})_l$

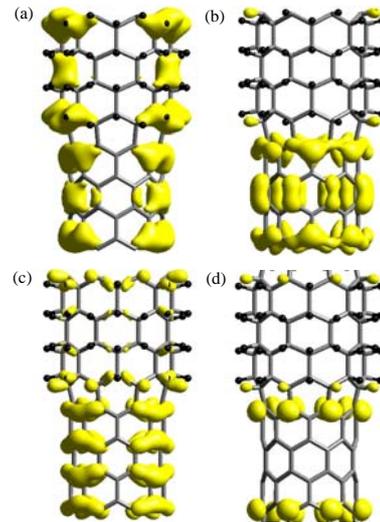


FIG. 3: Calculated self-consistent charge densities of propagating and confined states of the superlattice,  $[(C_{32})_2(C_{32}H_{32})_2]$ . See text.

and  $(C_{32}H_{32})_q$ , gets longer, for example for  $l = q = 2$ , differences become even more pronounced. It is, therefore, concluded that an (8,0) SWNT as short as a few nanometer is enough to make an electronic device. These arguments are better clarified by the calculated total and local density of states in Fig 2. Comparison of Fig. 2(a) and (b) shows how the band gap of a bare (8,0) SWNT becomes wider as a result of exohydrogenation. The width of the valence band decreases by  $\sim 2.5$  eV, because the radius of the underlying hydrogenated tube increased by 16%. Even if the total density of states of the superlattice  $[(C_{32})_2(C_{32}H_{32})_2]$  in Fig 2(c) reflects the combination of state densities in Fig. 2(a) and (b), different regions display markedly different electronic structure. This can be revealed by calculating the local density of states,  $\mathcal{L}(X, E) = \sum_{n,k} \int_X \Psi_{n,k}^*(\mathbf{r}) \Psi_{n,k}(\mathbf{r}) \delta(E_{n,k} - E) d\mathbf{r}$ . Here  $X$  indicates either one of the regions.  $\mathcal{L}[(C_{32})_2, E]$  presented in Fig. 2(d) is similar to state density of the bare (8,0) in Fig. 2(a), except some modifications in the gap region. On the other hand, we see from the local density of states of the hydrogenated region,  $\mathcal{L}[(C_{32}H_{32})_2, E]$  in Fig. 2(e) that the edge of the valence band is lowered and band gap becomes even larger than  $E_{gH}$ . A significant contribution of states originating from hydrogen is found near the top of valence band. We also note that  $\mathcal{L}[(C_{32}H_{32})_2, E]$  is well compared with the total density of states of uniformly hydrogenated (8,0) tube ( $q \rightarrow \infty$ ) in Fig. 2(b).

Further understanding of the electronic structure leading to the formation of MQWS can be obtained by examining energy bands and corresponding state charge densities. The population analysis indicate that approximately one electron is transferred to  $(C_{32})_2$ . Propagating and confined states are easily distinguishable in Fig. 3. The charge density of a propagating state down in the

valence band is shown in Fig. 3(a). Charge densities of highest valence ( $E = -0.52$  eV) and lowest conduction band ( $E = -0.03$  eV) states confined in  $(C_{32})_2$  are shown in Fig. 3(b) and (c), respectively. These states displays almost no dispersion in the superlattice Brillouin zone. Charge density of a state confined to the interface between two regions is in Fig. 3(d). We found also states confined to either  $(C_{32})$  or  $(C_{32}H_{32})_2$  in the valence and conduction band. More confined states are formed, because the present superlattice is a one-dimensional system with small extension of  $l$  and  $q$ , and hence offers relatively small number of states in order to match two adjacent regions. By increasing extension of two different regions confinements and energy band diagram in direct space becomes pronounced. Nevertheless, the above analysis clearly indicates that a MQWS with markedly different band gaps is generated. Then the estimation of the band offsets to determine the energy band diagram with quantum wells and barriers is our next task.

Band-lineup of regions,  $(C_{32})_l$  and  $(C_{32}H_{32})_q$ , is a complex process involving the deformation of the structure and charge transfer at the interface, and also resulting modification of the electronic potential. Experimental and theoretical methods have been proposed in the past to determine the band offsets, and hence to obtain band diagram perpetuating along the semiconductor heterostructures. A direct solution of this problem<sup>9</sup> involves the calculation of the average electronic potentials for finite and infinite  $l$  and  $q$ , and also alignment of the energy of valence band edges of infinite (hydrogen-free and hydrogenated (8,0) tube) systems with respect to the average potentials of finite systems. The superlattice system here does not allow us an accurate averaging of potential owing to short periodicity of  $l + q = 4$ . Since our objective is only to show whether MQWS can form, we take a more practical approach and estimate the band offsets and resulting energy band diagram from the calculated electronic structure of superlattice. In the present system the actual atomic positions, especially at the interface, and the charge transfer between regions are of crucial importance for the band offsets and are

incorporated self-consistently in the calculated electronic structure. The band diagram we estimated from the calculated electronic structure is shown in Fig. 4. The part of the superlattice which was free of H atoms behaves as quantum well and gives rise to a normal band-line up. Band-offset values for valence ( $\Delta E_v$ ) and conduction ( $\Delta E_c$ ) bands are given in Fig. 4.

The present discussion for the periodically repeating quantum wells can be extended to finite systems, for example to resonant tunneling double barriers, made by a region  $(C_{32})_l$  placed between two regions of  $(C_{32}H_{32})_q$ , i.e.  $(C_{32}H_{32})_q(C_{32})_l(C_{32}H_{32})_q$ . The metallic connects of barriers from both sides can be achieved by metal coating<sup>10</sup> or by oxygenation<sup>11</sup> of the same tube. Also a metal-semiconductor heterostructure can be formed by modulating hydrogenation of a  $(n, n)$  armchair SWNT. This way metallic connects are provided by the hydrogen

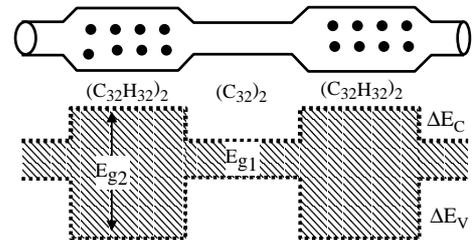


FIG. 4: Schematic illustration of the energy band diagram estimated from the self-consistent electronic structure.  $E_{g1} \sim 0.5$  eV,  $E_{g2} \sim 2.6$  eV,  $\Delta E_v \sim 1.4$  eV, and  $\Delta E_c \sim 0.7$  eV.

free ends of the tube.

In conclusion, one can generate a variety of device characteristics by changing the sequence and  $l$  and  $q$  extension, and also by applying different patterns of hydrogenation on different kinds of SWNTs.

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