

Multiscale modeling of carbon nanotube growth on a supercapacitor electrode

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ABSTRACT

Vertically Aligned Carbon Nanotube (VACNT) – based electrochemical double layer capacitors, called “supercapacitors” are intermediate systems that can potentially bridge the power/energy gap between traditional dielectric capacitors (high power) and batteries (high power density). However, their future is uncertain because of technical stumbling block in their fabrication related to the post-growth manipulations of VACNTs. This problem was addressed in the current work through design of synthesis process capable of depositing VACNTs on conducting metal oxide surface at reduced growth temperature by controlling the graphene layer formation and the catalyst deactivation via catalytic oxidation.

1 SUPERCAPACITOR

Electrochemical double layer capacitors utilizing Vertically Aligned Carbon Nanotubes (VACNTs) as an electrode active material, often referred to as supercapacitors, are innovative power sources that can potentially bridge the power and energy gap existing between traditional dielectric capacitors (high power) and chemical batteries (high power density). Such a supercapacitor is characterized by a power density greater than 100 kW/kg, three orders of magnitude higher than batteries, a lifetime longer than 300,000 cycles, and an energy density higher than 60 Wh/kg [1]. VACNT supercapacitors have the potential to revolutionize our transportation technology (electric and hybrid electric vehicles), consumer electronics (laptops, cell phones, pagers, camcorders, and hand-held tools), medical electronics (defibrillators, drug delivery units, and neurological stimulators), and military/defense devices (communication devices, unmanned aerial vehicles, spacecraft probes, and missile systems) [2]. For example, portable power sources for laptops, cell phones, pagers, camcorders, and hand-held tools will be fully rechargeable within a few minutes.

2 VACNT-BASED ELECTRODE

A critical element of the VACNT-based supercapacitor is an electrode schematically shown in Figure 1. The current collector is typically made from aluminum because

of its low cost, high conductivity, and low weight [1]. The drawback of aluminum is that it easily reacts with oxygen, forming a dielectric layer that negates the low resistivity of pure aluminum. To address this issue, a layer of conductive metal oxides such as indium tin oxide, tin oxide, zinc oxide, or ruthenium oxide is often introduced between VACNTs and the aluminum collector. These metal oxides typically have very low resistivity. For example, the resistivity of zinc oxide thin layer can be as low as $1.4 \times 10^{-4} \Omega \text{ cm}$ [3].

A critical technological challenge in the fabrication of supercapacitor electrode is in developing a direct process for the deposition of VACNTs on a conductive layer at a temperature below the melting temperature of aluminum current collector. The current absence of such a process makes the fabrication of VACNT electrode difficult and expensive because it requires the post-growth manipulations of VACNTs. To address this critical deficiency, we design of VACNT growth on conducting surface at reduced temperature.

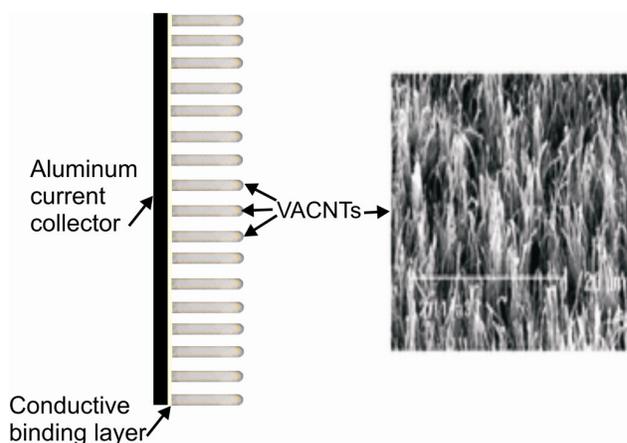


Figure 1: A critical element of a supercapacitor is a VACNT based electrode.

3 LOW-TEMPERATURE SYNTHESIS OF VACNT VIA CATALYTIC OXIDATION

Recently, we experimentally demonstrated that the addition of gaseous oxygen to the processing gases enables the reduction of VACNT growth temperature down to 600°C without deteriorating VACNT internal structure [4]. To provide insight to the role of oxygen during VACNT

growth, we developed surface reaction mechanism and implemented it into continuum kinetic-growth model. This reaction mechanism accounts for the absorption, catalytic thermal decomposition of carbon-containing gas species, hydrogen abstraction reactions, exothermic and endothermic reactions with oxygen-containing species, carbon diffusion through the catalyst and carbon incorporation into VACNT. The reactions were classified into three different types: Type I reactions that occur on the surface of catalyst, Type II reactions in the surface underlayer of catalyst, and Type III reactions that include carbon diffusion through catalyst and its incorporation into VACNT. Below is a detailed description of each type of reaction.

We defined type I reactions as those which involve a gas species and a site on the surface of catalyst. The first example of Type I reaction is the absorption of gaseous C_2H_2 species, whose surface sticking coefficient is close to 1 [5]. We recently showed that C_2H_2 absorption on the iron surface (Fe_n) is accompanied by dissociation involving the formation of a C_2H-Fe_n complex [6]. The second example of Type I reaction is the decomposition of molecular oxygen resulting into formation of two oxidized surface sites [$O(Fe_n)$]. These sites can further react with gaseous hydrogen species to produce $OH(Fe_n)$, $OH(g)$ and $H_2O(g)$ species [7].

We defined type II reactions as those which affect catalyst underlayer rather than the surface of catalyst. In our model, these reactions occur if a surface site, located on the top of catalyst underlayer, was occupied by oxygen. The existence of such a reaction was previously established via multi-scale modeling of C_2H_2 interaction with oxidized iron surface. Particularly, we found that C_2H_2 diffuses between two oxygen surface atoms and then decomposes in the underlayer of catalytic material.

The type III reactions include diffusion of carbon through the catalyst and its incorporation into VACNT. These processes were represented by a single-step reaction [8].

To validate the developed mechanism, we performed the simulation of VACNT growth at experimental conditions reported in [4]. In brief, our reactor was a tube of 182.9 cm long, and 9.82 cm in diameter. The tests were performed at 2.5-3 Torr with the following flow rates: 100

sccm of C_2H_2 , 80 sccm of NH_3 , and 20 sccm of O_2 . The growth time was 60 min. The rate constants for C_2H_2 dissociation on the clean and oxidized surface of iron, and oxygen dissociation rate on iron surface were determined from our multi-scale simulations. Rate constants for reactions with oxygen-contained species were taken from Ref. [7]. The iron surface site density was estimated to be 10^{-7} kmol/m² [9].

Table I compares computed and measured weights of VACNT material grown at different temperatures with and without oxygen. At 700°C, typical temperature for growing VACNTs without oxygen, there is a very good agreement between experimental and theoretical results. At 600°C, the computational results slightly underestimate the weight of VACNTs grown with oxygen, but about five times smaller than the experimental data without oxygen. Such a large discrepancy in the theoretical and experimental data without oxygen indicates on the existence of additional reaction path for the formation of carbon-based material with an activation barrier lower than that for VACNT growth. Indeed, scanning transmission electron microscopy images of material grown without oxygen at 600°C showed the absence of structure typical for VACNTs [4]. Computed and measured weights at 500°C are very low indicating on the absence of VACNT growth at this temperature.

4 MODELING CONTACT BETWEEN VACNT AND METAL OXIDE LAYER

A necessary step in showing the feasibility for the assembly of VACNT-based electrode is to show that Ohmic contact can be formed between VACNT and a conducting layer. Often, the Schottky barrier is formed at the nanotube/metal junction which severely limits VACNT-based electrode performance. In our feasibility study, we analyzed contact between metallic VACNT and ZnO layer which is often deposited on the top of aluminum current collector to prevent its oxidation.

Temperature (C)	Measured CNT weight (g)	Computed CNT weight (g)
700	4.0 g (without O2)	4.03 g (without O2)
	3.3 g (with O2)	3.39 g (with O2)
600	3.1 g (without O2)	0.71 g (without O2)
	1.2 g (with O2)	0.74 g (with O2)
500	0.005 g (without O2)	0.08 g (without O2)
	0.02 g (with O2)	0.09 g (with O2)

Table 1: Computed and measured weights of VACNT material grown at different temperature with and without oxygen. The details of experiments are given in [4]

In this work we theoretically analyzed the type of contact between (6,6) metallic (armchair) VACNT and ZnO layer using the Molecular Dynamics with Quantum Semiempirical Hamiltonian (MD-QSH) method [6]. The MD-QSH method is very efficient in determining minimum energy configuration via dynamic quenching procedure that is considerably faster than the traditional static quenching algorithms based on complete removal of kinetic energy. In our approach, velocities of individual atoms were monitored during the simulation and were set to zero when reach the maximum value. The high efficiency of this procedure is due to inverse relationship between kinetic and potential energy. When the velocity of an atom is large, its potential energy must be small.

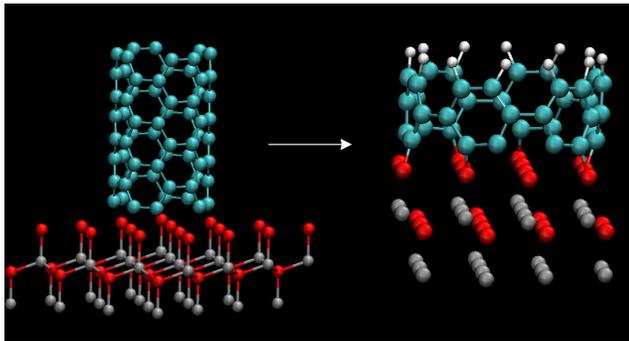


Figure 2: Example of surface model for modeling contact between ZnO layer and armchair CNT. Initial configuration (left panel) was truncated to computationally tractable atomic model (right panel).

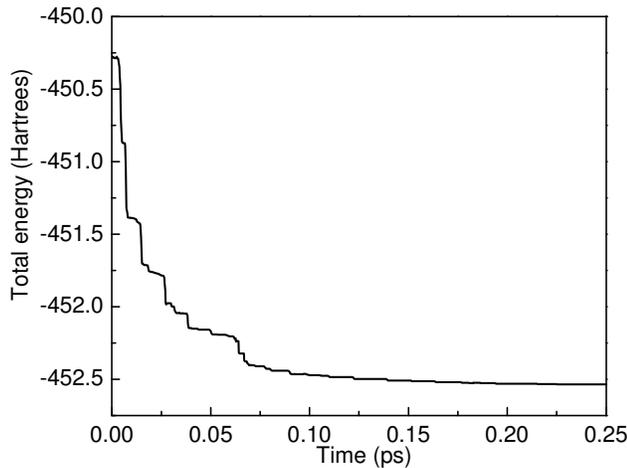


Figure 3: Total energy of VACNT-ZnO system versus time during energy minimization.

Prior to running simulations, we have prepared a simulation domain by truncating the surface of ZnO layer and single-wall VACNT to a size that is a computationally tractable by the MD-QSH simulator as schematically shown

in Figure 2. During the simulations, the truncated atoms were treated as empirical atoms whose interaction was given by analytical (empirical) Morse potential. At the same time, C, Zn, and O atoms shown in the right panel of Figure 2 constitute the quantum cluster. At the end of each dynamic step in the MD module, coordinates of atoms constituting the quantum cluster were saturated with hydrogen atoms as shown in Figure 2 and transferred to the QSH module. The distance between the hydrogen atoms and the quantum cluster was determined by scaling distances between boundary atoms from the quantum and empirical regions. Instantaneous potential energy and interatomic forces were computed and fed back to the MD module. The contributions from the ghost hydrogen atoms were zeroed and forces acting on quantum atoms were combined with the Morse-type forces computed for empirical atoms.

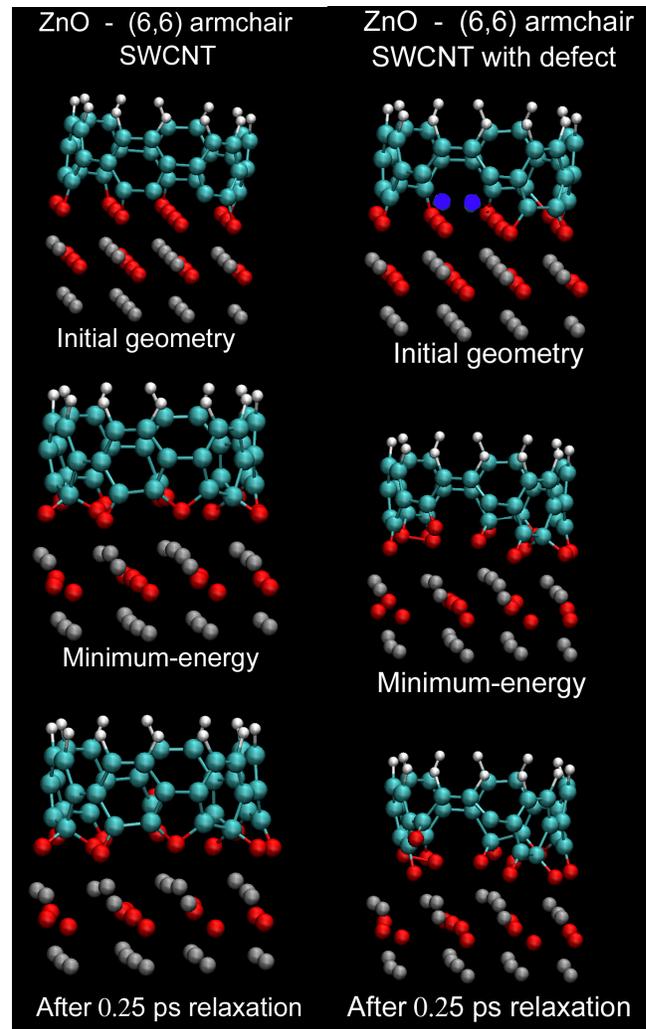


Figure 4: Top view for ZnO - (6,6) armchair VACNT configurations (from top to bottom): after minimum-energy simulation, and after 0.25 ps relaxation at 300K. The left and right panels are for VACNT without and with defect (shown by blue atoms), respectively.

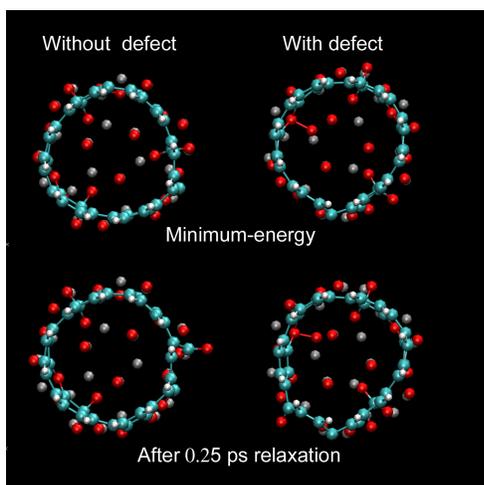


Figure 5: Side view for ZnO - (6,6) armchair VACNT configurations (from top to bottom): after minimum-energy simulation, and after 0.25 ps relaxation at 300K. The left and right panels are for VACNT without and with defect, respectively.

Each multi-scale simulation includes energy minimization and then the relaxation of the system to room temperature. By monitoring the total energy of ZnO - (6,6) armchair VACNT system we found that 500 time steps (typical time step of 0.5 fs was used) were sufficient to achieve a minimum energy configuration as shown in Figure 3. We analyzed ZnO - (6,6) armchair VACNT systems without and with defect. Side view of their initial spatial configurations is given in two top panels of Figure 4. Side and top views of the spatial configurations after energy minimization and relaxation to room temperature are given in Figure 4 and Figure 5, respectively. The inspection of these systems showed: (1) the absence of any significant distortion in the single-wall VACNT structure (even for VACNT with defect), and (2) the absence of clusterization of ZnO atoms. Consequently, we concluded that the Ohmic contact can be formed between VACNT and ZnO layer.

5 MODELING CONTACT BETWEEN VACNT AND METAL OXIDE LAYER

In this work, we provided insight to the mechanism for reducing growth temperature of VACNTs to a temperature suitable for the direct assembly of VACNT-based electrode of supercapacitor. The developed mechanism controls the graphene formation and catalyst deactivation via catalytic oxidation. Also, we theoretically demonstrated the feasibility for forming Ohmic contact between metallic VACNT and ZnO layer deposited on the top of supercapacitor's aluminum current collector.

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