Chapter 1

Introduction

1.1 Preface

Technology in the twenty first century requires the miniaturization of devices into micrometer, even nanometer sizes while their ultimate performance is significantly improved. This raises many issues regarding new materials for achieving specific demand. Nanostructured materials, a new branch of material research, has been attracted much attention because of their potential applications such as electronics [1], optics [2], catalysis [3], ceramics [4], magnetic data storage [5-6] and nanocomposites. Their sizes, surface structures and inter-particle interaction determine the unique properties and the improved performances of nanomaterials.

A specific parameter introduced by nanomaterials is the surface/interface to volume ratio. A high percentage of surface atoms induces many size-dependent phenomena. The finite size of the particle confines the spatial distribution of the electrons, leading to the quantized energy levels due to the size effect. Nanomaterials provide an ideal system for understanding effects in a nanostructured system, which could lead to major discoveries in solid state physics.

Since the discovery of fullerenes and carbon nanotubes and the recent progress in the synthesis of diamond-like nanostructures, carbon occupies a strategic position in materials science and engineering as one of the most versatile and far-reaching materials. An arsenal of advanced growth methods has now the potential to provide a large variety of novel carbon materials with tailored properties and functions. Nanostructured carbon-based materials, in particular, offer a growing number of applications which apparently depend on its nanoscale constitution. In order to establish a link between nanostructure and materials performances, characterization and manipulation techniques have to be developed and fully mastered on the nanometric scale.

1.2 Why carbon-based materials?

Carbon is a remarkable element showing a variety of stable forms ranging from 3D semiconducting diamond to 2D semi-metallic graphite to 1D conducting and semiconducting carbon nanotubes to 0D fullerenes [7]. One distinction between these forms of carbon relates to the many possible configurations of the electronic states of a carbon atom, which is known as the hybridization of atomic orbitals and relates to the bonding of carbon atom to its nearest neighbors. In particular, the structural and functional properties of carbon critically depend on the ratio between the number of sp^2 (graphite-like) and sp^3 (diamond-like) bonds. The control of such ratio, which has become possible through the most recent techniques such as, the one based on supersonic cluster beam assembling, enables one to synthesize a variety of carbon thin films of great interest in tribology (self-lubrication, wear-resistant, super-hard coatings), electronics (field emission for flat panel displays) or electrochemistry (molecular sievies, ionic and molecular insertion for various applications, including supercapacitors).

Carbon nanostructures assume a large variety of forms because of the unique position of carbon on periodic table, thereby allowing the formation of many structures with nearly the same energy per carbon atom. Here, some representative carbon-based nanomaterials are listed as follows:

(1) Fullerenes (C_{60}, C_{70},….)

A joint collaborative research between Kroto, Smalley, Curl and coworkers to identify unusual infrared emission from large carbon clusters in red giant carbon stars resulted in the birth of the C_{60} molecule shown in Fig. 1.1 (a) [8].

(2) Carbon onions

Hollow concentric caarbon spheres are also formed upon intense electron beam irradiation of carbon nanoparticles with faced shapes, as shown in Fig. 1.1 (b) [9]. Of particular interest is the observation of an innermost sphere with an inner diameter of 7.1 Å, corresponding to the diameter of the C_{60} molecule.

(3) Carbon nanofibers

Carbon fibers represent an import class of graphite-related materials which are closely connected to carbon nanotubes, with regard to structure properties. Despite the many precursors that can be used to synthesize carbon fibers, each having a different cross-sectional morphology, the preferred orientation of the graphene planes is parallel to the fiber axis for all carbon fibers which is necessary to obtain the high mechanical strength in carbon fibers shown in Fig. 1.2 (a) [10].

(4) Carbon nanotubes

Since the first observation of carbon nanotubes shown in Fig. 1.2 (b)~(c) [11] by Iijima [12], carbon nanotubes have attracted a great deal of attention owing to their advantageous properties, such as effective field emission characteristic [13-14]. capability for the storage of a large amount of hydrogen [15-17], high Young's modulus [18-19] and structural diversities that make them possible for band gap engineering [20-21].

The possibility of connecting nanotubes of different diameter and chirality has generated considerable interest since these nanotube junctions can serve as potential building blocks for nanoscale electronic devices. Recently, For the T or Y even multijunction nanotubes networks have been synthesized. These unusual nanotubes are shown in Fig. 1.3 ~ Fig. 1.4 [22-23].

(5) Carbon nano-parallelepipeds

Saito and Matsumoto produced graphitic nanocages as rectangular parallelepipeds shown in Fig. 1.5 or cubes from arc evaporation of carbon with alkaline earth metals- calcium or strontium catalytic particles [24]. The cubes contain 5 to 20 layers of multiwalled graphitic carbon (c spacing of 0.34 nm) and have edges ranging in length from 20 to 100 nm.

(6) Carbon nanoring

Martel and coworkers have reported the production of rings of single walled carbon nanotubes in high yields (up to 50 %) [25]. They found that SWNTs can be induced to organize themselves into rings or coils and are stabilized by Van der Walls force shown in Fig. 1.6.

(7) Carbon nanocones

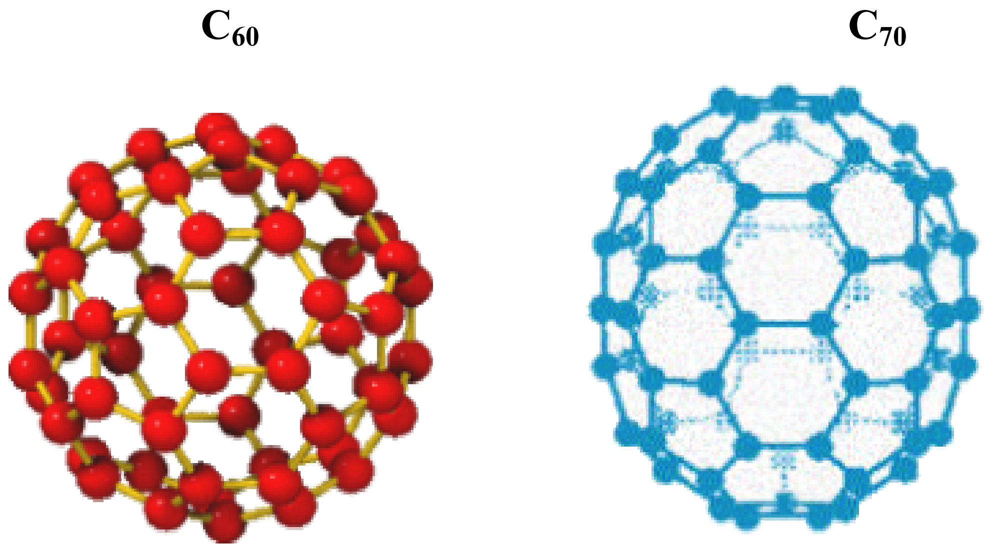
Ebbesen and coworkers produced disks (no pentagons), five types of cones (one to five pentagons) and open tubes (six pentagons) shown in Fig. 1.7 by pyrolyzing a continuous flow (50-150 kg/h) of heavy oil inside an industrial grade carbon arc plasma generator [26].

(8) Carbon nanohorns

Iijima and coworkers found that the morphology of the carbons generated using a CO_2 laser on a rotating graphite target at room temperature and 760 torr of Ar pressure in the ablation chamber is quite different from that of tubes [27]. TEM images shown in Fig. 1.8 of the products showed nearly spherical particles that were ~80 nm in diameter with tubule-like structures arranged in a pattern that bears a resemblance to the *dahlia* flower.

It should be stated that beyond the examples enumerated, which focus primarily on sp^2 bonding structure, are other known carbon forms featuring sp^3 tetrahedral bonding and *sp* linear bonding. Extrapolating from the rapid discovery of new carbon forms that has occurred recently, we can expect that new forms of carbon are still awaiting discovery. We can expect that some of the newly discovered carbon nanostructures will have unusual properties with potential for interesting scientific studies and usual applications.

(a)



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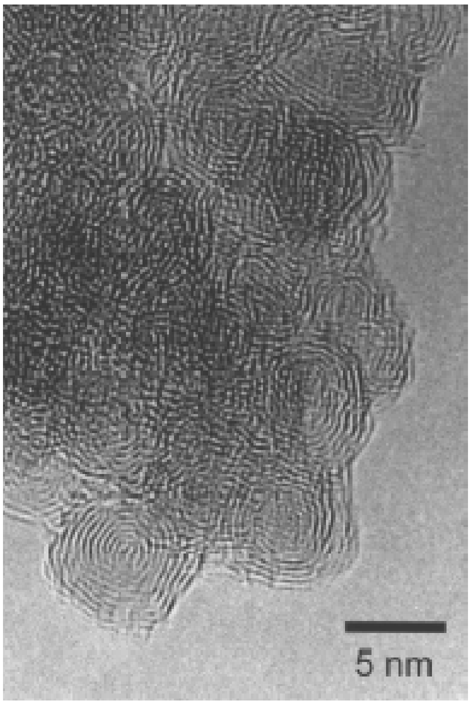


Fig. 1.1 (a) orientational correlations and intermolecular interactions of C_{60} and C_{70}.
(b) spherical-like carbon onions [9].

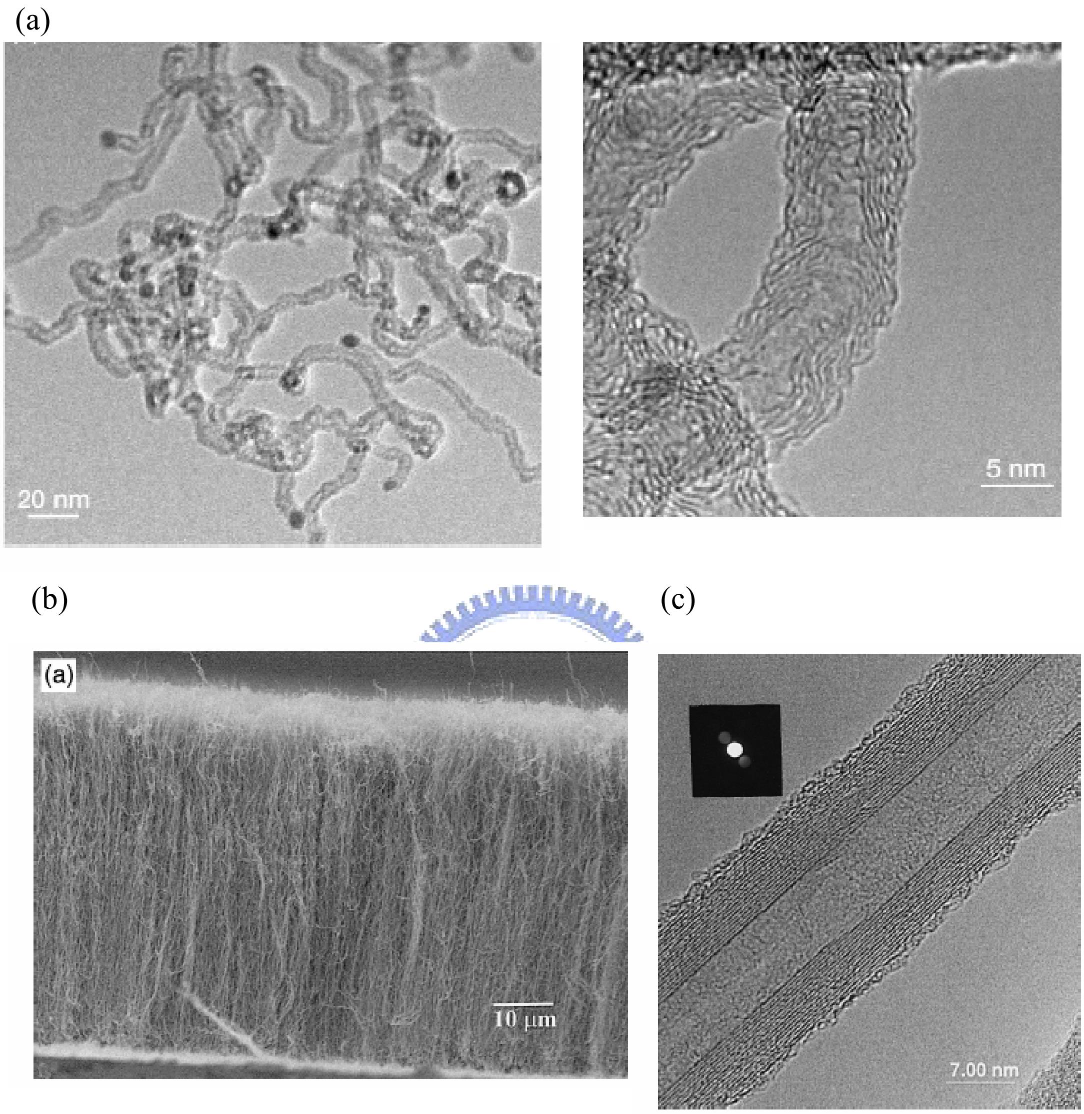


Fig. 1.2 (a) TEM images as the indicated magnification of Ni catalyzed nanofibers [10]; (b) SEM image of as-grown MWNT and (c) HRTEM image of individual MWNT. Inset-figure shows the (002) diffraction spots [11].

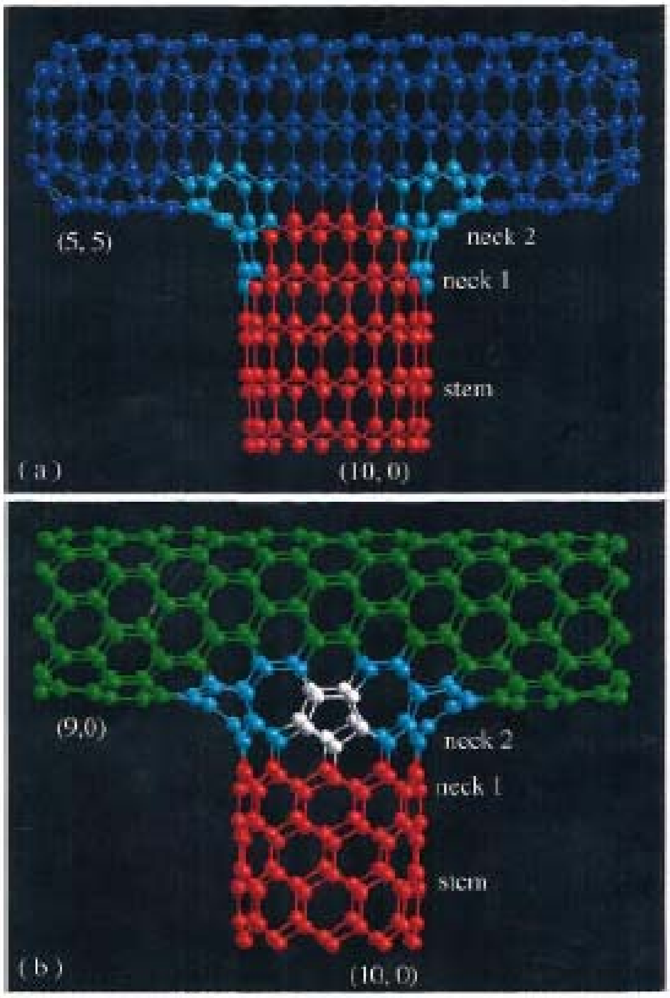
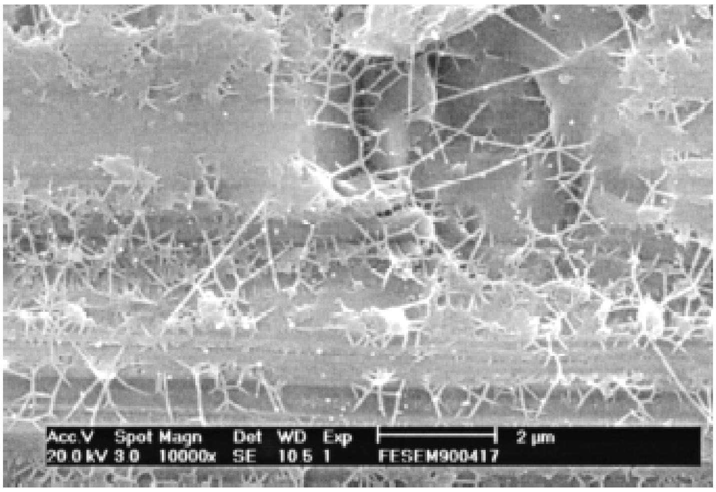


Fig. 1.3 Optimized structures for a T carbon nanotube junction obtained using a GTBMD simulation [22].

(a)



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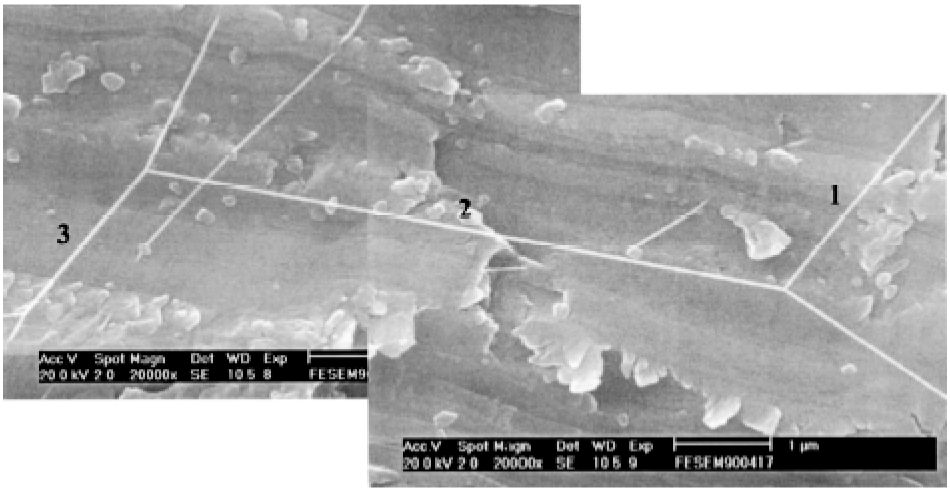


Fig. 1.4 (a) CNTs grown on Si substrate., there are Y and H-junction CNTs and 3D CNT webs. (b) *H*-junction or multiple *Y*-junction CNTs on the substrate [23].

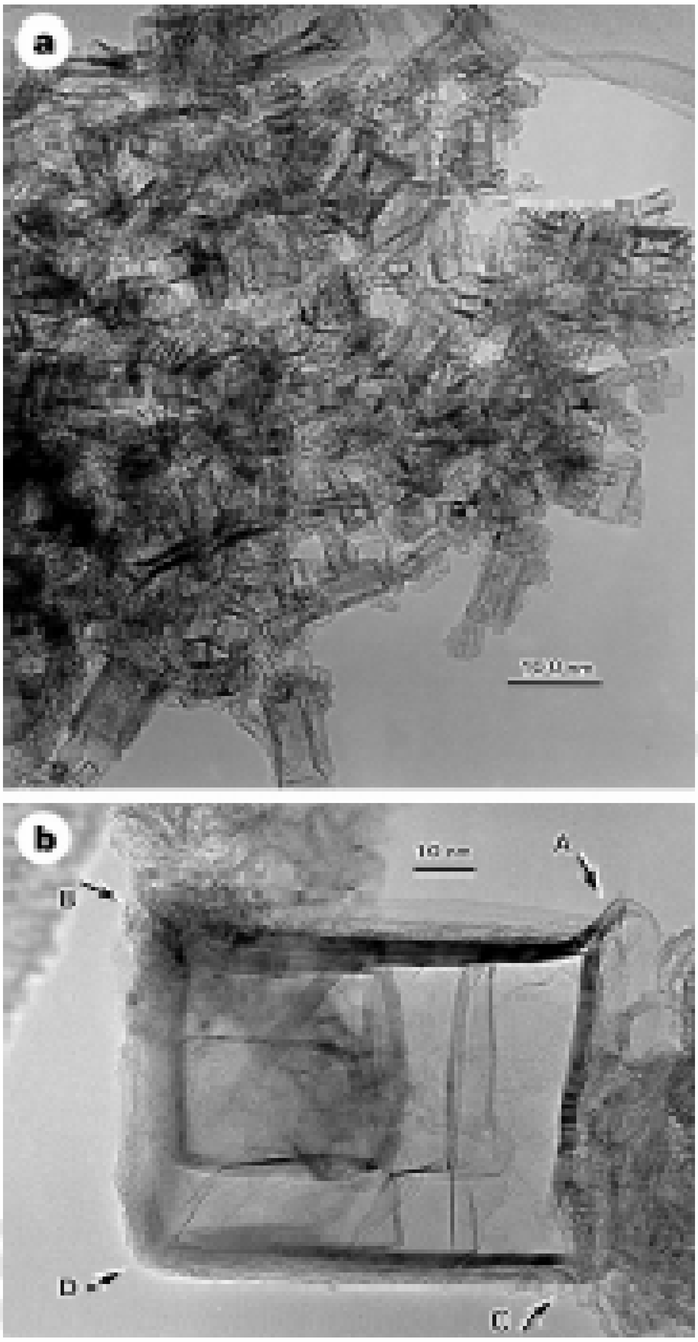


Fig. 1.5 (a) TEM images of hollow rectangular parallelepiped graphitic cages and (b) breakage of graphitic layers can be seen at corners A-D [24].

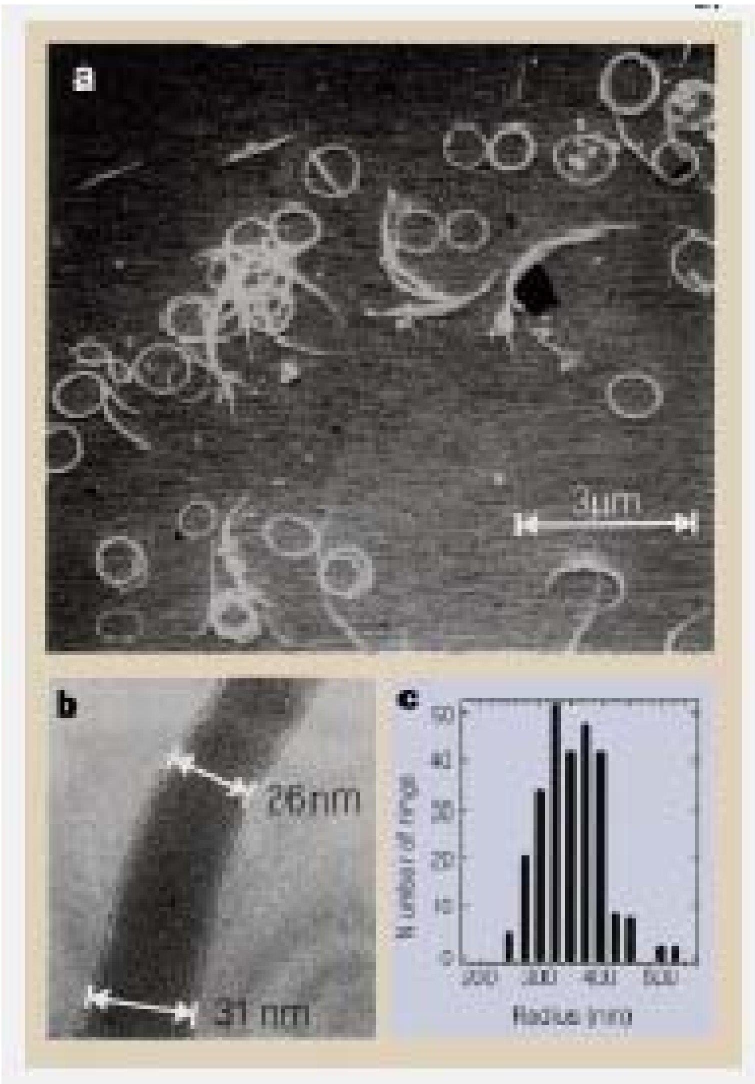
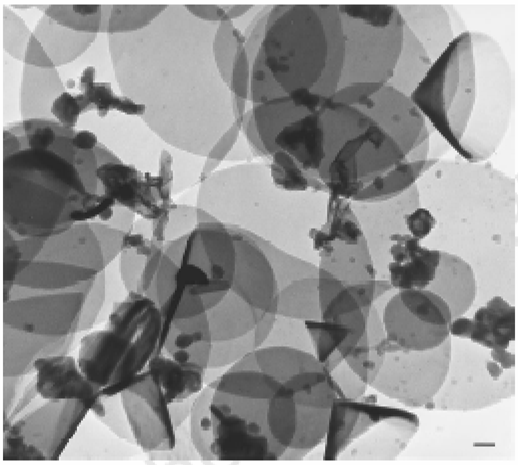


Fig. 1.6 (a) SEM image of SWNT rings and (b) TEM image of a section of the ring and (c) Histogram showing distribution of ring radii [25].

(a)



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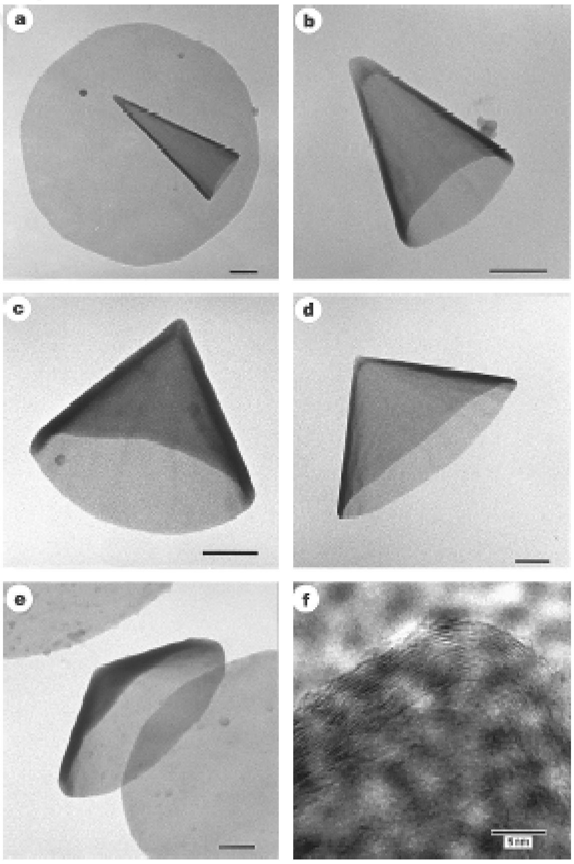


Fig. 1.7 (a) TEM images (with scale bar=200 nm) of the carbon nanocones and (b) Five different types of cones in a-e (with scale bar=200 nm). Magnified image of a cone tip is shown in f (with scale bar=5 nm) [26].

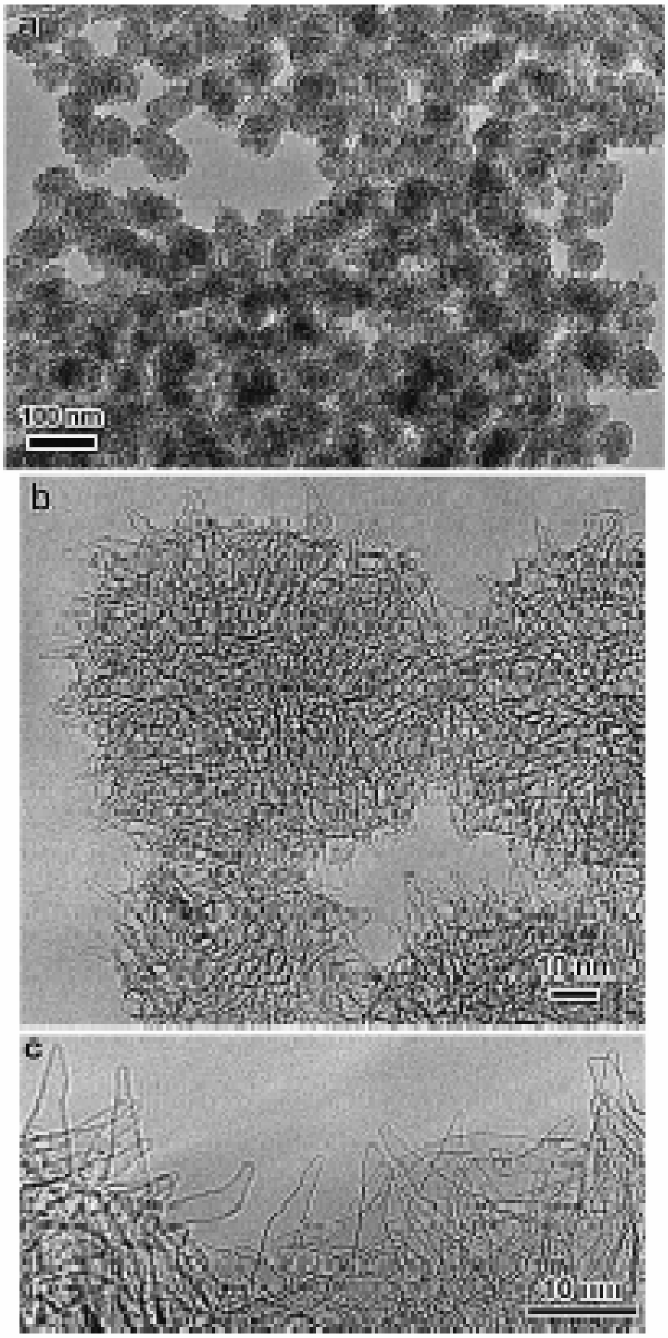


Fig. 1.8 (a) TEM images of uniformly shaped spherical particles (b) image of a particle, showing aggregation of tube-like structures; and (c) Conical horn-like tips can be seen at the end of the tube-like structure [27].

1.3 Why nanosize requirement?

Nanosystem, system which is defined as having features or characterisyic lengths betwee 1 ~ 100 nm, exhibit particularly peculiar and interesting properties. The new revolution compared to the previous micro and meso-scale systems shows two significant advantages.

(I) Miniaturization

In microelectronics, “smaller” has always meant better more components per system, faster response, lower cost, lower power consumption and higher performance. To achieve above-mentioned requirements, it is thought to be efficient to use nanostructured materials instead of the microsize ones.

(II) Fascinating unpredictable property

Nanoscale materials possess many special physical and chemical properties, such as quantized excitation [28-29], Coulomb blockade [30] and metal-insulator transition [31]. For the application on field emission, nanoscale materials are expected to provide desirable improvement.

1.4 Advantages of field emission display

Field emission display (FED) is evolving as a promising technique of flat panel display in the future. In FED, electrons coming from millions of tiny emitters pass through gates and excite phosphor to light up pixels on the screen. This principle is similar to that of cathode-ray tube in television sets. Instead of just one gun spraying electrons against inside of the screen face, there are as many as millions electrons of emitters in FED. Fig. 1.9 illustrates the fundamental structure of FED by PixTech company. Because of the simpler assembly, custom performance and special sizes are less costly to produce. The performance characteristics of FEDs are well suited to highly-brightness required imaging. If an instrument is not facing the viewer, or if the viewer moves about, displays with narrow viewing angles are difficult or impossible to read. At 60° off-axis, text is 10 times more difficult to read than at 0° off-axis if the text remains at the same brightness. If brightness or contrast drops with increased viewing angle, a display may become significantly more difficult to read at only modest off-axis angles. Because FEDs are emissive, they allow equal brightness at all angles. FED technology also offers many advantages as following [32]:

Brightness

Outdoor instruments such as emergency medical technicians and panels on aircraft require high brightness to compete with direct sunlight. Most displays are adequate in normal (50–100 fc) room lighting. However, in dimly lit situations, such as a patient bedside at night, dim (reflective) displays are difficult to read. Most alarming, a dim display may be deceptively easy to misread. Because a FED is an emissive display that produces its own light, it can be dimmed continuously from full brightness to less than 0.05 fL.

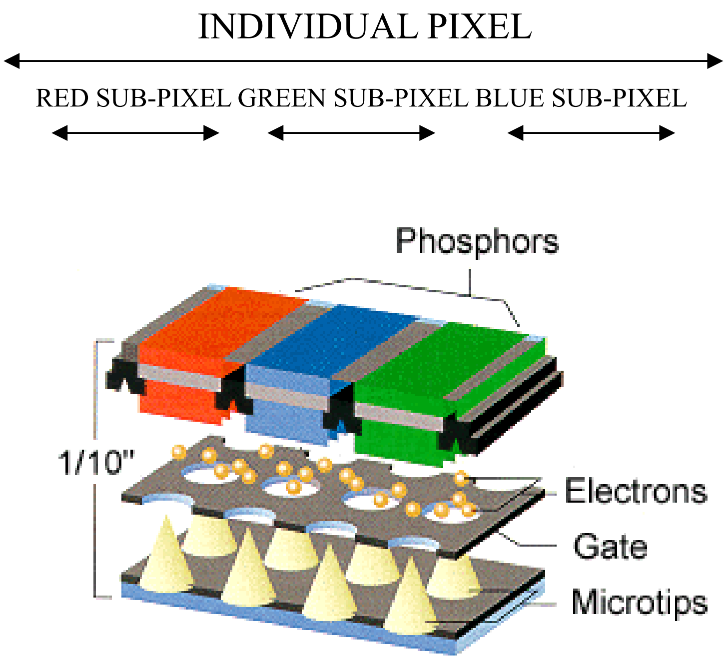
Lightness

Field emission displays are thin flat solid state displays that provide image quality similar to television or CRT. Typical thickness of a screen is less than one half centimeter making it low in weight and highly portable with low power consumption capabilities.

Speed

Display speed is the rate at which the image can be changed while maintaining image detail. Displays with inadequate response times will create image "smear" that can be confused with defective blood flow, or will hide jitter that can indicate instability or electrical interference. With a response time of 20 nanoseconds, FED technology produces smear-free video images.

FED Technology



In field emission displays, electron coming from millions of tiny microtips pass through gates and light up pixels on a screen.This principle is similar to that of cathode-ray tubes in television sets. The difference: Instead of just one "gun" spraying electrons against inside of the screens face, there are as many as 500 million of them (microtips).

Fig 1.9 Schematic cross section of a Field Emission Display

1.5 Motivation

The goal of this dissertation is to fabricate various carbon-based nanomaterials and modify their properties for the application of field emission. Development and modification of nanomaterials involve several key steps. First, synthesis of size and even shape controlled nanomaterials is the key for developing new emitters. Second, characterization of naomaterilas is indispensable to understand the behavior and properties of nanomaterials. Third, theoretical and experimental results are vitally important to understand and predict the difference of material's performance. Finally, the ultimate aim is to modify the nanomaterials for the improvement on field emission performance. Further modification process includes the intrinsic and extrinsic fields of materials. These reformations are focus on the diamond-clad enhancement; doping effect; morphology alteration and synthesis of various nanomaterials. Many factors affect the performance of field emitters, such as the shape, work function and aspect ratio of emission materials. How to search an ideal field emitter is one of the tough courses of the development of field emission displays.

Owing to the negative electron affinity (NEA) and robust mechanical and chemical properties of diamond, considerable interest has been focused on the electron field from diamond and related materials. However, experimental results show that non diamond phases such as diamond-like carbon (DLC), and other carbon-based materials exhibit better characteristics than that of diamond. Recently, with the advent of mature nano-technology, nano-sized materials are regarded as new cathode candidate of FED because of their unique properties and potentials. Thus, the dissertation is mainly concentrated on the carbon nano-sized materials.

Different kinds of carbon-based nanomaterials are synthesized and modified for improving the diode-structured characteristic of field emission. By using IC technology, new novel scheme gated structure is fabricated. Thus, suitable materials are applied in triode gated metal-insulator-semiconductor (MIS) structured. This triode-type diode with 4 μm gate aperture is expected to efficiently enhance the current density and reduces the turn-on filed.

1.6 Reference

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