Controllable growth of ZnO nanorod-carbon nanotube heterojunction arrays by low-temperature wet chemical bath deposition method for using in dye solar cell

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ABSTRACT

In this paper, we describe a cost-effective and efficient approach for the large-scale synthesis of heterojunctions between ZnO NRs and MWCNTs. Our work represents a new type of heterostructure with many benefits. The effects of precursor concentration, growth temperature and time on nanorods morphology on MWCNT were investigated systematically. It is demonstrated that the controllable growth of ZnO nanorods on MWCNT can be realized by readily adjusting the preparation parameters.

Keywords: ZnO NR- MWCNT arrays, Chemical bath deposition, nanothorns

1 INTRODUCTION

The fabrication of well-defined structures with nanoscale materials is important to both an understanding of scientific fundamentals in nanoscience and potential applications in nanoscale systems, and building nanoscales materials into the ordered macroscopic structures are especially useful to be incorporated into devices [1]. Although recent work has demonstrated the growth of ZnO nanostructures (coating, nanowires and nanoparticles) on aligned MWCNT arrays [2], the formation of large area ordered MWCNT-ZnO heterojunction with micro- and nanoscale hierarchy still remains a big challenge. Various 1D heterostructures have been reported; examples include aligned ZnO heterojunction arrays on GaN, Al0.5Ga0.5N, carbon nanotube (CNT)-Si nanowire heterojunctions by a VLS process, a-CNT-Ag nanowire heterojunctions by a combination of electrochemical deposition and chemical vapor deposition (CVD), and single-walled carbon nanotube (SWCNT)-Au nanorod 1D heterojunctions through the selective solution growth of Au nanorods on SWCNT.[3] Among them, CNT-based heterostructures are of particular interest because of their unique geometric morphologies (high aspect ratios and surface areas), as well as the remarkable electronic, thermal, and the mechanical properties intrinsically associated with CNTs.[4] ZnO is an optically transparent semiconductor with a large exciton banding energy of 60 meV and has shown many potential applications in sensors, solar energy conversion and optoelectronic devices [5]. Charge recombination in ZnO nanostructures plays a quite important role for the performance of a highly efficient photoelectric device. The charge transport in ZnO nanostructures is limited due to the lack of driving force. Therefore, a strategy of using SWNT–ZnO heterostructures is likely to overcome the problems associated with charge recombination at the junction interface because the SWNTs can help in collecting and transporting photogenerated charge carriers to the electrodes. Recently, many research groups have focused on these types of heterogeneous nanosensors. In particular, the direct growth of single crystalline ZnONRs- MWCNT heterojunctions remains a big challenge. There are many methods for growing nanosized ZnO but wet chemical base deposition (CBD) method have many advantages such as scalability, low-cost, environmental friendliness and easy of handling. Additionally, wet chemical base deposition methods allow for a greater choice of substrates, including both inorganic and organic substrates, since solution phase reactions occur at relatively low temperatures and larg scales on each layer compared to those in other method.

2 EXPERIMENT

1.1 Preparation of CNT arrays on Si substrates

Si (0 0 1) wafers were used as the substrates for growth of CNTs by direct current plasma enhanced chemical vapor deposition (DC–PECVD). Initially <100>- oriented silicon wafers were cleaned in a standard RCA#1 solution (NH4OH:H2O2:H2O; 1:1:5), rinsed in deionized water and blow-dried by air [40]. Then, a 8 nm Ni thin film was deposited on the Si by using e-beam evaporation. The Ni/Si samples were heat treated at 650 ℃ in H2 environment with flow rate of 35 standard cubic centimeters per minute (sccm) for 10–15 min. Then, the samples were hydrogenated by using a hydrogen plasma treatment with a power density of 5.5 W/cm2 for about 5 min in order to produce Ni nanoparticles with a size of 50–100 nm as the seeds of CNT growth as the catalyst for the growth of CNTs on the surface. Subsequently, CNTs were grown in an environment containing a mixture of H2 and C2H2 gases with flow rates of 35 and 25 sccm at temperature and pressure of 650 ℃ and $2.8 \cdot 10^2$ Pa, respectively. The synthesized MWNTs were not purified, because some

attempts for their oxygen purification resulted in disintegration of the CNT arrays.

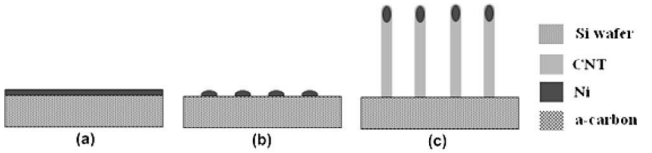


Fig. 1 – The fabrication process of branched nanostructures. (a) Ni deposition, and (b) nano-size island formation. (c) The growth of vertical CNTs

1.2 Growth of ZnO nanorod on CNT /Si substrates

CBD technique was utilized to deposit ZnO nanorod on the grown MWNTs. Firstly, 20 nm of RF sputtered ZnO seed layer on MW-CNT was used as catalyst. The substrates were placed inside the chamber and then were evacuated to a base pressure of 8.6×10^{-6} Torr. ZnO deposition was performed using an RF sputtering unit in argon ambient at a frequency of 13.56 MHz with RF power of 300W and Ar gas flow of 30 sccm. A 100 ml aqueous solution composed of zinc nitrate (Zn(NO3)2-6H2O, 98%) and hexamethylenetetramine (HMT) (C6H12N4, 99%) was used as a precursor source for the growth of ZnO nanowires. All of the employed chemicals were reagent grade. The concentration of (Zn(NO3)2-6H2O was varied in the range of 6–36 mM while keeping the molar ratio of (Zn(NO3)2-6H2O and HMT to be 1:1. The solution was then transferred into a ٢٥٠ mL capped Pyrex vessel in which the substrates were fastened to the top directly from the edge cap. After time of growth, the substrates are rinsed several times with de-ionized water and dried under dry air flow.

The crystal structure and morphology of the as-grown ZnO nanowires were investigated by X-ray diffraction (XRD) on (Philips Xpert pro) using Cu-kα radiation (λ=1.54), The morphology of the resulting samples was characterized by field emission scanning electron microscopy (FE-SEM) on HITACHI S- 4160. To investigate the optical properties, PL measurements were performed at room temperature with an excitation wavelength of 380 nm.

3 RESULT AND DISCUSSION

The phase composition and phase structure of the as synthesized products were examined by X-ray diffraction (XRD) on (Philips Xpert pro) using Cu-kα radiation (λ=1.54) on different crystal planes. Figure 2 shows a typical XRD pattern of the as-synthesized ZnO products on different crystal planes. It can be seen that the dominant diffraction peaks, as assigned in the spectrum, originated from wurtzite structure ZnO, which can be readily assigned to hexagonal cells of ZnO with the lattice constants a = 3.25 A ° and c =5.01A ° (Joint Committee on Powder Diffraction Standard Card No. 79-0206). The strong (h, k, l) reflection peaks usually indicate that the ZnO nanocrystal has a preferential orientation of [0 0 2]. Otherwise, it is obvious that a weak diffraction peak at 26.48° can be readily assigned to carbon (0 0 2) [12].

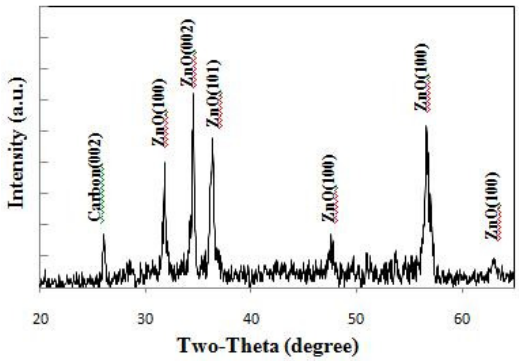
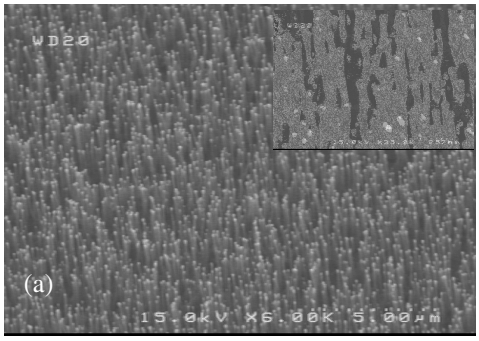
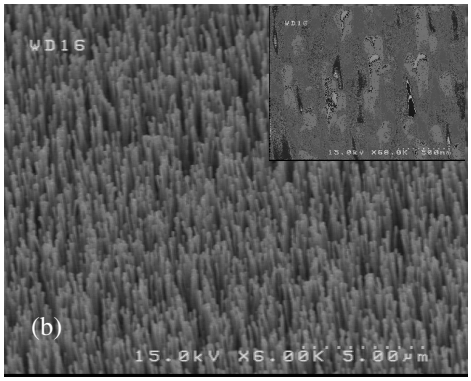


Figure2: The XRD patterns of the CNT-ZnO NR heterojunction arrays.

Figure 2 displays the SEM images of MWCNT arrays before

The MWCNT and the ZnO coating with about 20 nm thickness are clearly seen in Fig. 2b When MWNTs are coated by ZnO, the nanotube diameters are significantly larger than those of pristine MWNTs. The resulting high density of ZnO NRs on MWCNT is shown in Figure2c. We can see that entire surfaces of CNTs are covered with a high density of ZnO NRs.





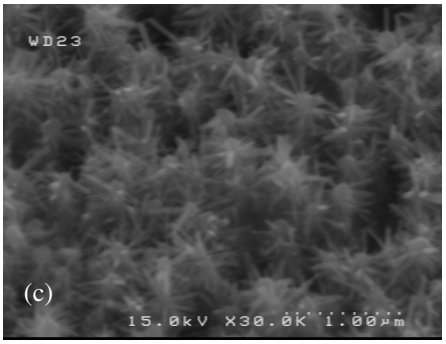
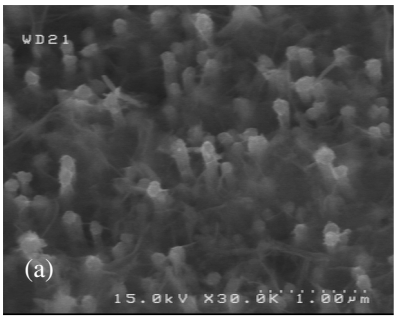
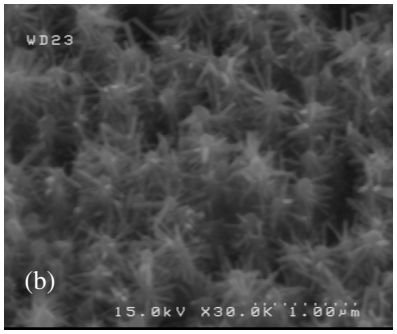


Fig.1**:** SEM image of process growth ZnO NR –MWCNT heteronanostructure (a) MWCNT (b) ZnO seed layer on carbon nanotube and (c)growth nanorod ZnO on MWCNT

Figure (1a) and Figure (1b) coating with ZnO nanoparticles and then growth ZnO nanorod. SEM images of the vertically aligned CNT arrays grown on the Ni/Si thin film have been shown in Fig. 2a. It is seen that the CNTs were uniformly grown on the Ni catalyst layer. The diameter of the CNTs was measured in the range of 90– 250 nm and their length was evaluated in the range of 2– 4 lm. In addition, SEM analyses showed that the CNT arrays coated about 30% of the film surface.

Fig.2 shows the SEM images of ZnO NR-MWCNT array with precursor concentration vary from 6 mM to 24 mM. The growth temperature and time were 85˚C and 4h, respectively , Fig.2a shows that nanowires on carbon nanotube are small with poorly dense preferred orientations**.** The average diameter and lenght of ZnO NR increased 20 nm to 70 nm and 150nm to 800nm respectively when the precursor concentration increased.





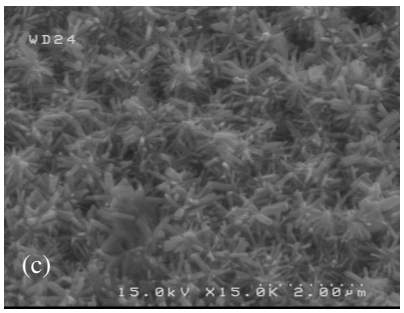
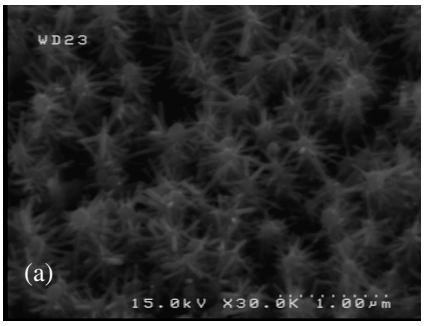
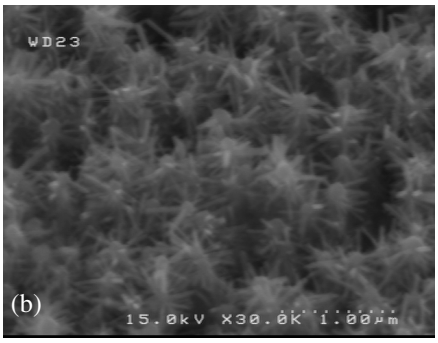


Fig. 2: SEM images of the growth ZnO NR –MWCNT heteronanostructure under different precursor concentrations: (a) 6 mM, (b) 12 mM, (c24 mMand The growth temperature and time were 80˚C and 4 h, respectively.





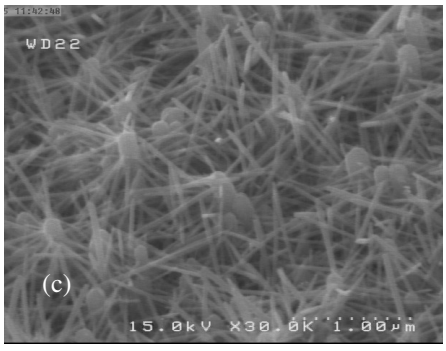


Fig. 3: SEM images of the growth ZnO NR –MWCNT heteronanostructure with different reaction times: (a) 4h, (b) 5 h, (c) 6 h and (d) 8 h. The precursor concentration and growth temperature were 12 mM and 80˚C, respectively.

Fig.3 shows the SEM images of ZnO NR-MWCNT as a function of growth time from 4 h to 8 h. The precursor

concentration and growth temperature were 12 mM and 80˚C, respectively. All the ZnO NR show hexagonal prism shape independent of the growth time. The average diameter and length of ZnO nanorods increased from ~20 nm to ~70 nm and from 150 nm to 800 nm, respectively. The growth temperature has a strong impact on the diameter.

Figure 4 shows the SEM images of ZnO nanowire grown on MWCNT substrate as a function of growth temperature ranging from 60˚C to 95˚C with the optimized precursor concentration of 12 mM for 3 h. The corresponding SEM images of the nanowire grown at each temperature are shown in Fig. 4. It shows that all of the ZnO nanowires are at random orientations. The top-view SEM images suggest that the nanowires are in hexagonal prism shape. However, the diameter, length and aspect ratio of the nanowire are strongly affected by the growth temperature. As shown in Fig. 4a–c, the average diameter and length increased dramatically with the increase of the growth temperature. The average diameter increased from 70 nm to 160 nm and the length increased dramatically from 400 nm to 1800 nm. Figure 5 depicts the image of ZnO nanowire growth on AZO seed layer of ITO-coated glass. It shows that ZnO nanowires are perpendicularly oriented to the substrate regardless of the growth temperature. The growth temperature has a strong impact on the diameter. The length increased with the increase of growth temperature.

In summary, ZnO NR arrays were self-assembled onto the surfaces of MWCNTs by a facile solution method at low temperature, forming ZnO NR -MWCNT heterojunction nanostructures. The ZnO NR surface density on CNTs could be easily controlled by manipulating time and temperature an precursor concentration solution.

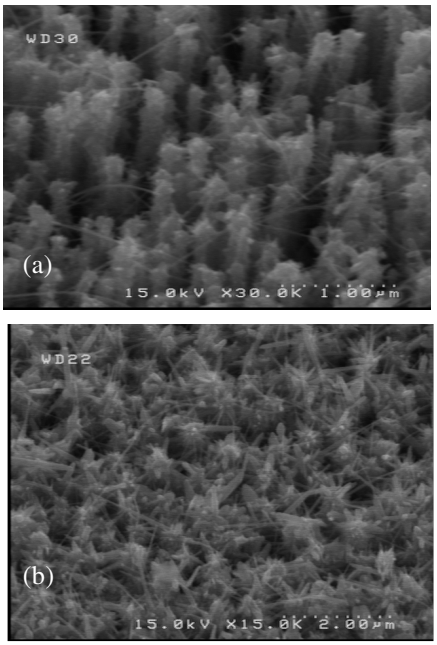


Fig. 4: SEM images of the growth ZnO NR –MWCNT heteronanostructure under different growth temperature: (a) 60℃, (b) 80℃, (c) 95℃ and The precursor concentration and and time were 12mM and 4 h, respectively.

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