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Effective way to control the size of well-aligned ZnO nanorod arrays with two-step chemical bath deposition

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Abstract

The diameter of well-aligned ZnO nanorod arrays (ZNAs) grown on Si substrates has been well controlled from 150nm to 40nm by two-step chemical bath deposition method (CBD), i.e. substrate pretreatment with spin coating to form ZnO nanoparticles seed layer and CBD growth. The effects of ZnO nanoparticles density and diameter on size and alignment of ZNAs were investigated in detail by atomic force microscope (AFM), X-ray diffraction (XRD), scan electronic microscope (SEM), transmission electron microscope (TEM) and photoluminescence (PL). The results indicate that both diameter and density of ZnO nanoparticles which were pre-coated on the substrates will influence the size and alignment of ZNAs, but the density will play a key role to determine the diameter of ZNAs when the density is higher than the value of $2.3 \times 10^8 \text{ cm}^{-2}$. Moreover, only a strong UV peak at 385 nm appears in room temperature PL spectrum for these samples, which indicates that as-synthesized ZnO nanorods have a perfect crystallization and low density of deep level defects.

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Keywords: B1.ZnO nanorods arrays; A3.CBD; A3. Size-controlled growth

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1. Introduction

In recent years, one-dimensional (1D) nanostructures such as nanotubes [1], nanowires [2], nanorods [3], nanobelts [4], nanocables [5], and nanoribbons [6] have stimulated a considerable interest for scientific research due to their importance in fundamental physics studies and their potential applications in nanoelectronics, nanomechanics and flat panel displays. Among various 1D nanostructural materials, Zinc oxide (ZnO) has generated great interests due to its direct wide band gap of 3.37eV at room temperature, large exciton binding energy of 60meV, and stable physical and chemical properties. Until now, different fabrication methods, such as vapor-phase transport [7-9], pulsed laser deposition [10], chemical vapor deposition [11, 12] and electrochemical deposition [13], have been widely reported for the preparation of 1-D ZnO nanorods. According to these methods, the complex processes, sophisticated equipment and high temperatures are usually required. On the contrary, chemical bath deposition (CBD) method can be operated easily, and do not need sophisticated equipments [14, 15]. The most important thing is that the experiments can be carried out under low temperature. However, the nanorods grown on Si substrate by this method show a poor reproducibility, difficulty to control size and bad orientation. Until now, the most successful approach for CBD is growing ZnO nanorods on pretreated substrates, i.e. two-step CBD method [16-19]. Among those pretreated methods, thermal deposition [17], radio frequency magnetron-sputtering [18] and spin coating [19] techniques were usually applied to prepare ZnO seed layer on substrates. Clearly, the latter is much more easily carried out and the process is more economical. However, as well as we known, the previous researches with two-step CBD mainly focused on the effects of seed layer on

the density of the ZNAs [20]. No studies on size-controlled ZNAs by this method have been reported so far. Therefore, it is necessary to explore an effective way to control the size of ZNAs by the two-step CBD method.

In this paper, we present an optimized procedure to grow well-aligned ZNAs with different diameters by means of the two-step CBD method. The effects of ZnO nanoparticles density and diameter on size and alignment of ZNAs were investigated in detail, which successfully revealed the size-controlled mechanism of well-aligned ZNAs.

2. Experimental procedure

In our experiments, the synthesis process of ZnO nanorods contains two steps, i.e the substrate pre-treatment and CBD growth. All chemicals were analytical reagent grade and used without further purification. All the aqueous solutions were prepared using distilled water. For the substrate pre-treatment process, first Si (100) substrates were ultrasonically cleaned for 15min in ethanol before spin coating. Then zinc acetate dihydrate ($\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$) was dissolved in the pure ethanol with concentration of 5mM. This solution was coated for several times onto Si (100) substrates by a spin coater (Laurell WS-400-8TFW-Full) at the rate of 2000 rpm for 30s. The coated substrates were dried in room temperature and then annealed in air at 250°C for 30min. The annealed temperature of 250°C is a little above the decomposition temperature of zinc acetate particles in order to form ZnO nanoparticles seed layer. In the following, all substrates were pretreated twice for the above processes before final growth of ZnO nanorods. The density of ZnO nanoparticles on the substrate can be controlled by the number of spin times, which shows a high reproducibility in this process. For CBD growth process, the

aqueous solutions of zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.9% purity] and hexamethyltetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, 99.9% purity) were first prepared respectively and then were mixed together. The concentrations of both were fixed at 0.1M. The pretreated Si substrates were immersed into the aqueous solution and tilted against the wall of beaker. The angle between substrate and beaker bottom is $\sim 70^\circ$. Then the beaker was put into the oven and kept in it for 2h at a constant temperature of 93°C . After growth, the substrate was removed from the solution, rinsed with deionized water and then dried at room temperature.

Scanning electron microscopy (SEM) images were recorded by using a JEOL JSM-6301F. An atomic force microscope (AFM, Dimension 3100) was used to detect the morphology of pretreated substrates. The powder diffraction curves were measured by using Philips PW1729 x-ray generator. Transmission electron microscope (TEM) (200keV, JEM-2100HR, Japan) was used to get the high resolution TEM image and the selected-area electron diffraction pattern of samples. Photoluminescence (PL) measurements were carried out at room temperature. A CCD detector (Spectrum One) and monochromator HR460 from Jobin Yvon-Spex were used to disperse and detect the ZnO emission. Laser line with a wavelength of 266 nm from a diode laser (Coherent Verdi) pumped resonant frequency doubling unit (MBD 266) was used as excitation source.

3. Results and discussion

Although heterogeneous nucleation onto a foreign surface occurs easier compared to homogeneous nucleation [21], it is still difficult to control the nucleus with an

acceptable reproducibility concerning the nucleus density, size and distribution due to the random and complex nature of the nucleation on a foreign surface. But nucleation on substrates pre-coated with ZnO nanoparticles as crystal seeds is much easier. For this situation, the condition of ZnO nanoparticles layer on the substrates will directly influence the formation of ZNAs. Therefore, adjusting the density of ZnO nanoparticles on the pretreated substrates should be an effective way to control the diameter of the ZNAs. Therefore, a set of ZNAs were grown on the Si substrates pretreated with different density of ZnO nanoparticles. Fig.1 shows SEM images of ZNAs with different diameter and their corresponding AFM images of pretreated substrates. From AFM images at the right side of Fig.1, it can be seen that ZnO nanoparticles dispersed on the substrates, and their density can be determined to be $4.9 \times 10^7 \text{ cm}^{-2}$, $9.52 \times 10^8 \text{ cm}^{-2}$ and $2.51 \times 10^9 \text{ cm}^{-2}$ respectively from up to bottom. As corresponding results, it can be clearly seen from Fig.1 (b) and (c) that the well-aligned ZNAs uniformly covered entire surface with high density and all the top surfaces of the nanorods were hexagonal shape for all samples.

Combined SEM and AFM images in Fig.1, on one hand, the diameter of ZNAs decreased with increasing ZnO nanoparticles density on the substrates. In order to clearly see the relationship between ZNAs diameter and ZnO nanoparticles density on the pretreated substrates, the measured diameter of the ZNAs as a function of ZnO particles density was illustrated in Fig.2. It clearly indicates that the ZNAs diameter linearly decreased with increasing ZnO nanoparticles density. According to our experiment results, when the density of ZnO nanoparticles on the pretreated substrates is lower than $2.3 \times 10^8 \text{ cm}^{-2}$, the diameter is much larger and orientation is bad, as shown in Fig.1(a). When the density is higher than this value, the diameter and orientation can be well

controlled from 150nm to 40nm. This kind of well-controlled mechanism could be attributed to the competition growth mechanism between (0001) crystal planes and non-polar side planes. It is well known that the hexagonal wurtzite ZnO crystal is typical polar crystal with a dipole moment in the direction of c-axis. So, in comparison with a non-polar side plane, the growth rate along a polar (0001) crystal plane is relatively fast. Once the density is higher than the value of $2.3 \times 10^8 \text{ cm}^{-2}$, the growth of non-polar planes will be apparently suppressed due to higher density so that the diameter of ZNAs can be controlled through adjusting the density of ZnO nanoparticles on the substrates.

On the other hand, the orientation of ZNAs also became better with increasing ZnO nanoparticles density on the substrates as shown in Fig.1 (a) and Fig.1 (b) , which can be further testified by XRD results. Fig.3 gives the XRD patterns of these two ZNAs. Usually, the relative intensity ratio between (002) and (101) diffraction peak is used to characterize the orientation of ZnO nanorods. Only (002) diffraction peak in Fig.3 (b) provides further evidence that the nanorods are preferentially oriented in the c-axis direction. The explanation can be expressed as follows: For single nanorod, when it grows along a direction deviating from c-axis, it will easily meet other nanorods and be obstructed by them due to the higher density during the growth process. The more deviation away from c-axis, the more obstructions might be met, which implies that the nanorods departing from c-axis direction of substrate are very difficult to grow under such higher density. Therefore, the nanorods are apt to grow along the c-axis on the basis of competition and optimization rules.

In general, the diameter and density of ZnO nanoparticles on the substrates are restrained each other in the fixed area. It is very difficult to distinguish which one finally

determines the diameter of ZNAs. In order to make the growth mechanism clear, the as-pretreated substrates were further annealed under 500°C and 600°C respectively in order to increase the diameter of ZnO nanoparticles on the substrates. The SEM images of ZNAs and corresponding AFM of these pretreated substrates were shown in Fig.4. According to AFM images from Figure 4(a) to Figure 4(c), it can be determined that the density of ZnO nanoparticles is $2.02 \times 10^9 \text{ cm}^{-2}$, $1.38 \times 10^9 \text{ cm}^{-2}$ and $1.35 \times 10^9 \text{ cm}^{-2}$, and also the average diameter of ZnO nanoparticles is 35nm, 47nm and 60nm, respectively. It indicates that the density of ZnO nanoparticles decreases and diameter obviously increases after further annealing. As corresponding results of Fig.4 (a) and 4(b), the diameter of ZNAs grown on the 500°C further treated substrates is larger than that grown on the as-pretreated substrates as shown in SEM images. Since the density of ZnO nanoparticles decreases and the size of ZnO nanoparticles increases in Fig. 4(b) in comparison with Fig.4 (a), it is difficult to see whether the density or size of ZnO nanoparticles has more influence on the diameter of ZNAs. However, compared Fig. 4(b) and Fig.4(c), the diameters of ZNAs are the same (70nm) when the density of ZnO nanoparticles shows a similar value while the diameter of ZnO nanoparticles in Fig. 4(c) is larger than that of Fig. 4(b). From this result, it indicates that the diameter of ZNAs mainly depends on the density of ZnO nanoparticles. Taking into account all information in Fig.2 and Fig.4, we believed that both diameter and density of ZnO nanoparticles on the substrates determined the size of ZNAs. But when the density is higher than the value of $2.3 \times 10^8 \text{ cm}^{-2}$, the density will become the dominant factor to determine the diameter of ZNAs.

In order to determine the quality of the ZNAs, the PL measurements and TEM were performed. Insets in Fig.5 show a typical high resolution image TEM and the selected-area electron diffraction pattern. They clearly indicate that the ZnO nanorods arrays have a single crystalline structure and they grow along c-direction. From the PL measurements, all samples show a similar PL feature. Fig.5 shows the PL spectrum at the room temperature from the ZNAs grown on the pretreated Si substrates with a diameter of 40nm. The spectrum only consists of a strong UV peak at 385 nm in wavelength, which was related to a near band-edge transition of ZnO, namely, the recombination of the free excitons. Only UV peak in the spectrum indicated that as-synthesized sample has low density of the deep level defects such as Zn and O vacancies that often result the so-called green emission band with center wavelength around 510 nm.

4. Conclusion

In summary, we have presented, for the first time to the best of our knowledge, an effective way to control the diameter of well-aligned ZNAs grown on Si (100) substrates with two-step CBD method. The diameter of ZNAs can be well controlled from 150nm to 40nm with an excellent orientation. Our results offer an effective way to solve the existing problems, such as reproducibility, size control and orientation of ZNAs, in CBD methods. Therefore, this study can not only provides a method for large-scale fabrication of ZnO nanorods with a low cost, but also open a way to the size-controlled fabrication of other materials by a hydrothermal approach.

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Figure captions:

Fig.1. SEM images of ZNAs with different diameter and their corresponding AFM images of the pretreated substrates. The density of ZnO nanoparticles and diameter of ZNAs are respectively (a) $4.9\times 10^7\text{cm}^{-2}$, 200nm; (b) $9.52\times 10^8\text{cm}^{-2}$, 90nm; (c) $2.51\times 10^9\text{cm}^{-2}$, 40nm.

Fig.2. Dependence of ZNAs diameters on ZnO particles density of the pretreated substrates.

Fig.3. XRD patterns of ZNAs grown on the pretreated substrates with different density of ZnO nanoparticles. The density of ZnO nanoparticles and diameter of ZNAs are respectively (a) $4.9\times 10^7\text{cm}^{-2}$, 200nm; (b) $9.52\times 10^8\text{cm}^{-2}$,90nm.

Fig.4. SEM images of ZNAs grown on the pretreated substrate with further annealing under different temperature. The annealing temperature, density of ZnO nanoparticles and diameter of ZNAs are respectively (a)As pretreated, $2.02\times 10^9\text{cm}^{-2}$, 50nm; (b) 500°C, $1.38\times 10^9\text{cm}^{-2}$, 70nm; (c) 600°C, $1.35\times 10^9\text{cm}^{-2}$,70nm.

Fig.5. Room temperature PL spectrum of ZNAs. The diameter of ZNAs and ZnO nanoparticles density is 40nm and $2.51 \times 10^9 \text{ cm}^{-2}$ respectively.

Fig.1

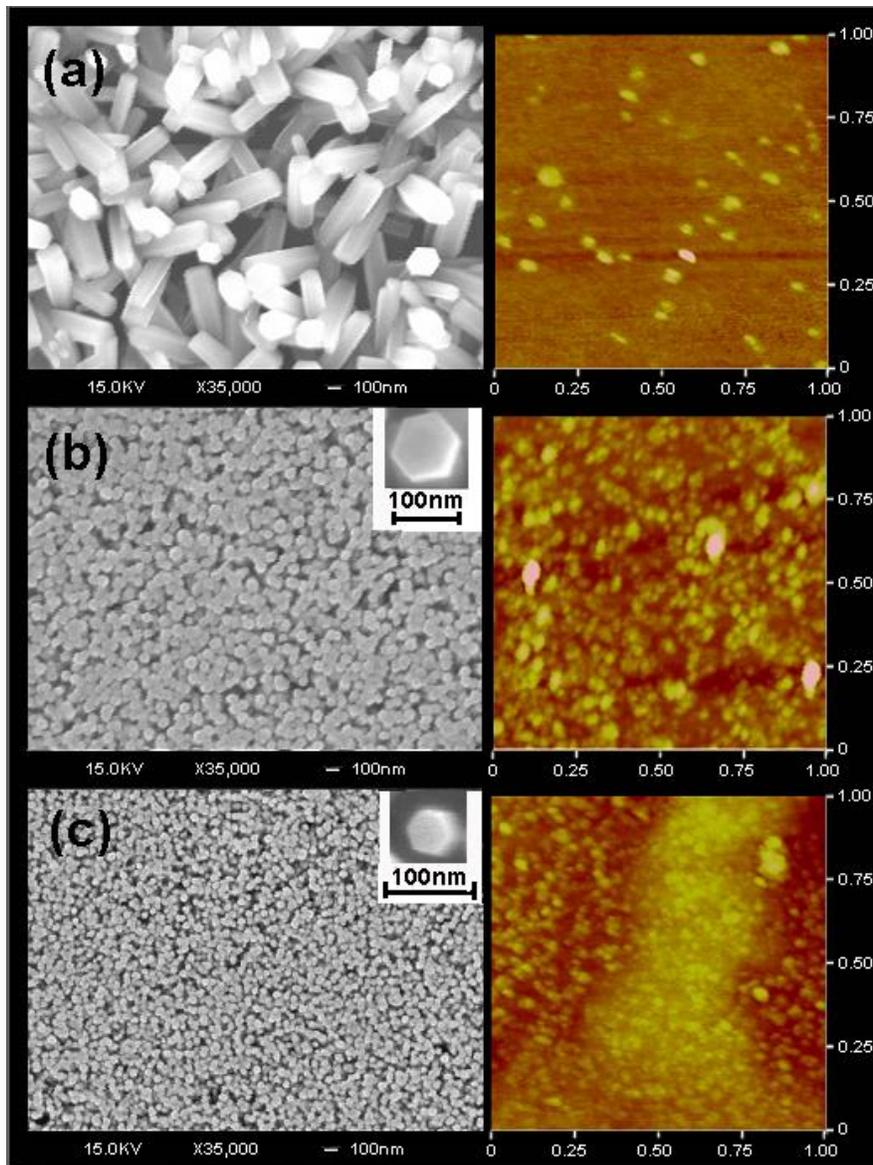


Fig.2

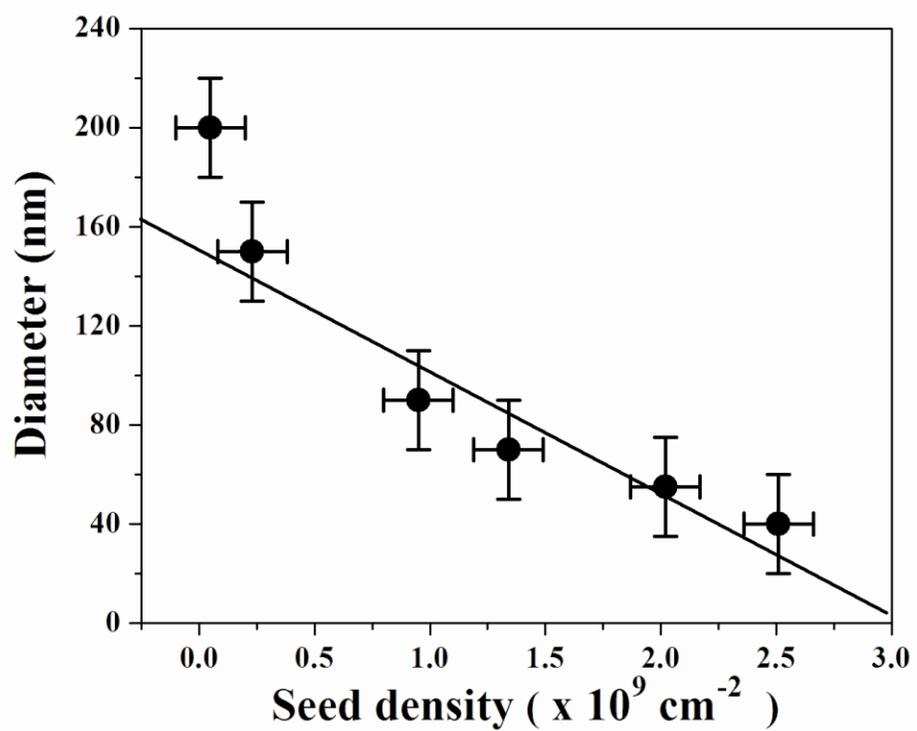


Fig.3

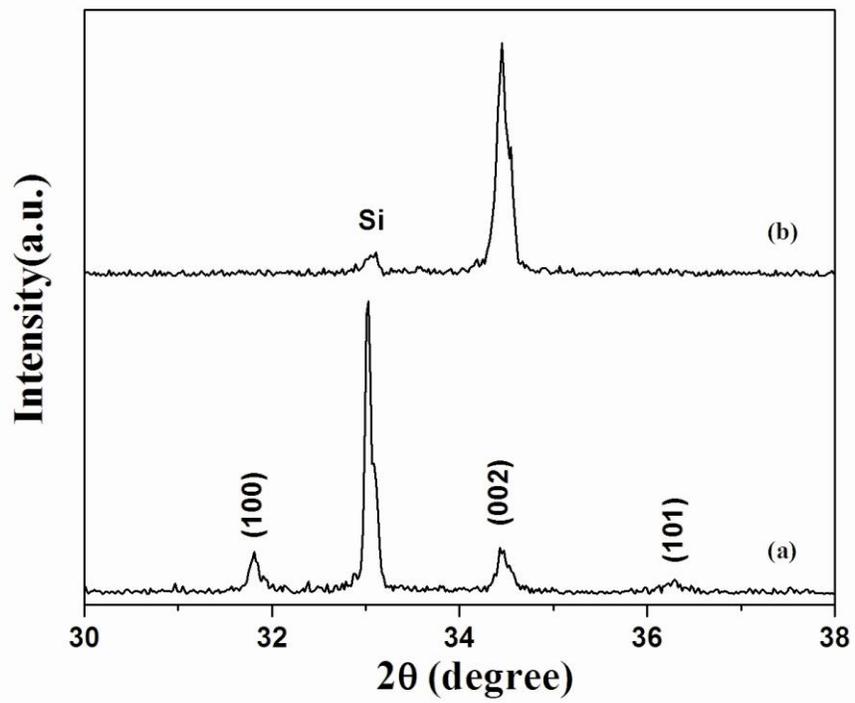


Fig.4

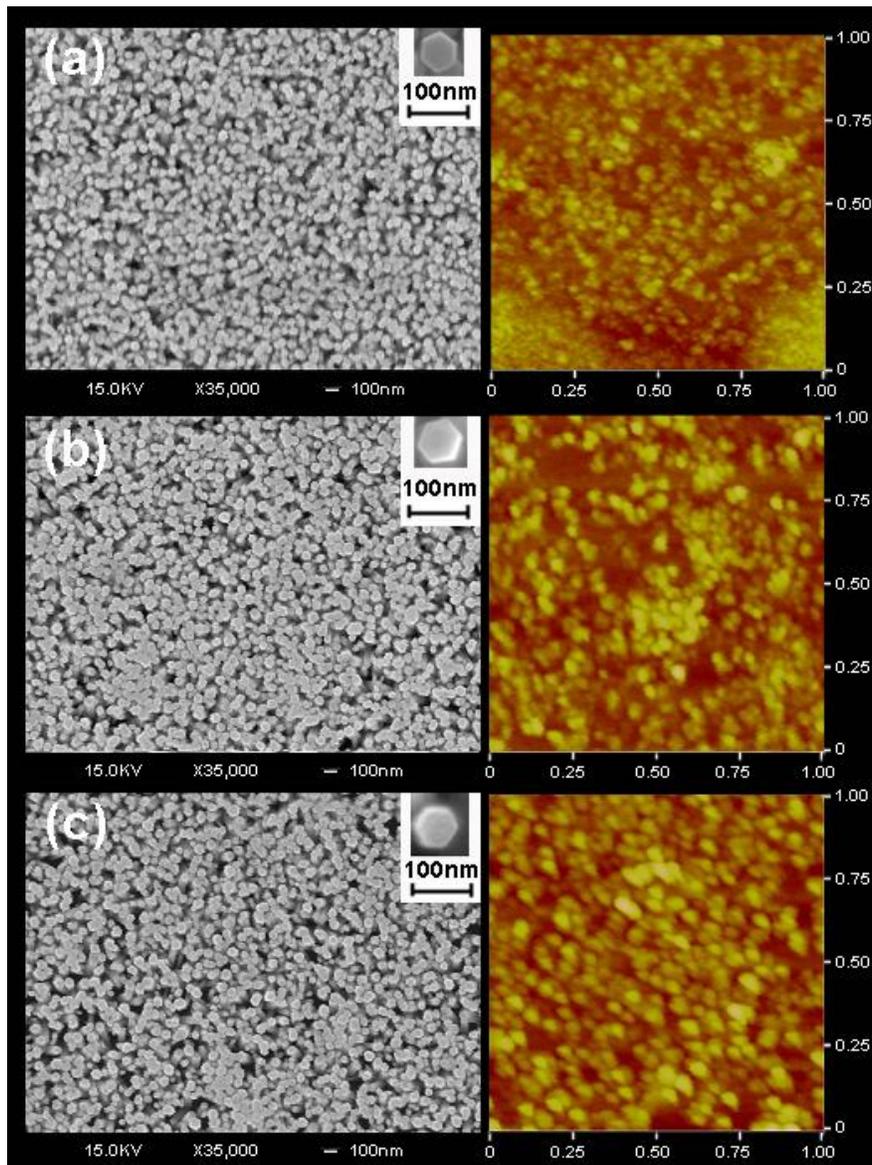


Fig.5

