

Template synthesis of highly ordered hydroxyapatite nanowire arrays

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Highly ordered hydroxyapatite (HA) nanowire arrays were synthesized using porous anodic aluminum oxide (AAO) template from sol-gel solution containing P_2O_5 and $Ca(NO_3)_2$. The results of transmission electron microscopy (TEM) and scanning electron microscopy (SEM) revealed that the obtained HA nanowires had a uniform length and diameter and formed highly ordered arrays, which were determined by the pore diameter and the thickness of the applied AAO template. The results of X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) demonstrated that the major component was HA. The selected-area electron diffraction (SAED) results indicated that HA was a polycrystalline structure. This novel method of preparing highly ordered HA nanowires with a large area might be important for many applications in biomaterials. © 2005 Springer Science + Business Media, Inc.

1. Introduction

Many methods for the fabrication of nanoparticles have been developed ranging from lithographic techniques to chemical methods [1]. The method termed template synthesis for the preparation of a variety of micro- and nano-materials has been explored [2–7]. This process involves synthesizing desired materials within the pores of a nanoporous membrane. The template membrane employed contains cylindrical pores, with mono-dispersed diameters, which extend through the entire thickness of the membrane. The diameter of this nanocylinder is determined by the diameter of the pores in the template. Because of their restricted size and high surface area, one-dimensional nanomaterials exhibit novel physical properties and play important roles in fundamental research as well as practical application. We have used this approach to synthesize nanowires or nanotubules of metals [8–12], metal oxides [13], semiconductors [14], copolymers [15–17] and carbons [18, 19].

Sol-gel chemistry has recently evolved as a powerful approach for preparing inorganic materials such as glasses and ceramics [20]. This method for the synthesis of inorganic materials has a number of advantages over more conventional synthetic procedures. For example, high-purity materials can be synthesized at a lower temperature. In addition, homogeneous multi-component systems can be obtained by mixing precursor solutions. This allows for easy chemical doping of

the materials prepared. Finally, the rheological properties of the sol and the gel can be utilized in processing the materials, by dip coating of thin films, spinning of fibers, etc. [21].

Synthetic hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is a very important biomaterial used for many applications in medicine such as a bulk ceramic, a ceramic coating and as one of the components of composites. It is also used as a catalyst for the water gas shift reaction [22], the decomposition of tetrachloromethane [23] and so on. Although there are many studies on the preparation and properties of nanostructural HA powders and whiskers, few papers have been concerned with the preparation of HA nanowires.

In this paper, we have combined the concepts of sol-gel synthesis and template preparation of nanomaterials to yield a new general route for fabricating highly ordered HA nanowire arrays, which was distinctly different from the results of conventional methods. This was accomplished by conducting sol-gel synthesis within the pores of nanoporous membrane, and mono-dispersed HA nanowire arrays were obtained.

2. Experiments

2.1. Membrane preparation

High purity Aluminum foil (99.999%) was ultrasonically degreased in acetone for 10 min, etched in 1.0 mol/L NaOH at room temperature for 3 min to

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remove the native oxide, washed thoroughly with distilled water, electropolished in a mixed solution of $\text{HClO}_4:\text{CH}_3\text{CH}_2\text{OH} = 1:4$ (V/V) for 5 min to provide a smooth surface and promptly rinsed with distilled water. Afterwards, the resulted clean aluminum foil was anodized at 80 V_{dc} for 2 h in 0.5 mol/L phosphoric acid solution. Each sample was then placed into saturated HgCl_2 solution for 1 h to separate the template membrane from the aluminum substrate. The membrane was rinsed with distilled water and immersed in 0.5 mol/L H_3PO_4 solution for about 15 min at 55°C in order to dissolve the barrier-type part of nanoholes on the bottom. The obtained AAO template had a highly ordered porous structure with very uniform and nearly parallel pores, which could be organized in an almost precise hexagonal structure. The AAO template was characterized by using atomic force microscopy (AFM, SOLVER P47, Russia) and SEM (JSM-5600LV, Japan).

2.2. Preparation of HA nanowire arrays

Hydroxyapatite nanowire arrays were prepared by using a sol-gel method with $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and P_2O_5 as two precursors [24]. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (A.R) and P_2O_5 (A.R) were weighed with a Ca/P molar ratio of 1.67 and dissolved by the same volume of alcohol until complete dissolution, respectively. The HA sol was obtained by mixing the above two alcohol solutions and stirring with a magnetic force machine for 0.5 h.

The AAO template membrane was immersed into this sol for the desired amount of time and allowed to dry in air at 50°C for 3 h. Excess sol on the membrane surface was carefully wiped off using a laboratory tissue and then heat treated at 600°C for 6 h in the open furnace. HA nanowire arrays were formed inside the pores of AAO template.

2.3. Characterization of HA nanowire arrays

The structure and morphology properties of HA nanowire arrays were characterized by several techniques. The SEM samples were obtained as following: the alumina membrane was attached to a SEM sample stub with carbon conductive paint and then several drops of 3 mol/L NaOH were added to the sample to dissolve the partial membrane. Prior to characterization, Au was sputtered onto the sample surface in order to increase their conductivity. TEM images were obtained using a Hitachi-600 microscope. The samples were obtained as following: Before TEM observation, the alumina template membrane was dissolved by using 3 mol/L NaOH, and then diluted with distilled water for three times. Droplets of solution containing HA nanowires were dropped onto the copper grids. XRD patterns for HA nanowires were collected using a Rigaku D/Max-2400 diffractometer with $\text{Cu K}\alpha$ radiation. XPS data were obtained with a V. G. ESCA Lab. 2201-XL photoelectron spectrometer with $\text{Mg K}\alpha$ source, a concentric hemispherical analyzer operating in fixed analyzer transmission mode and a multi-channel detector. The pressure in the analysis chamber was less than 2×10^{-10} Torr. The spectra were acquired with a 50 eV pass energy and a 1 mm^2 spot (large area mode without using XL lens). The binding energy was

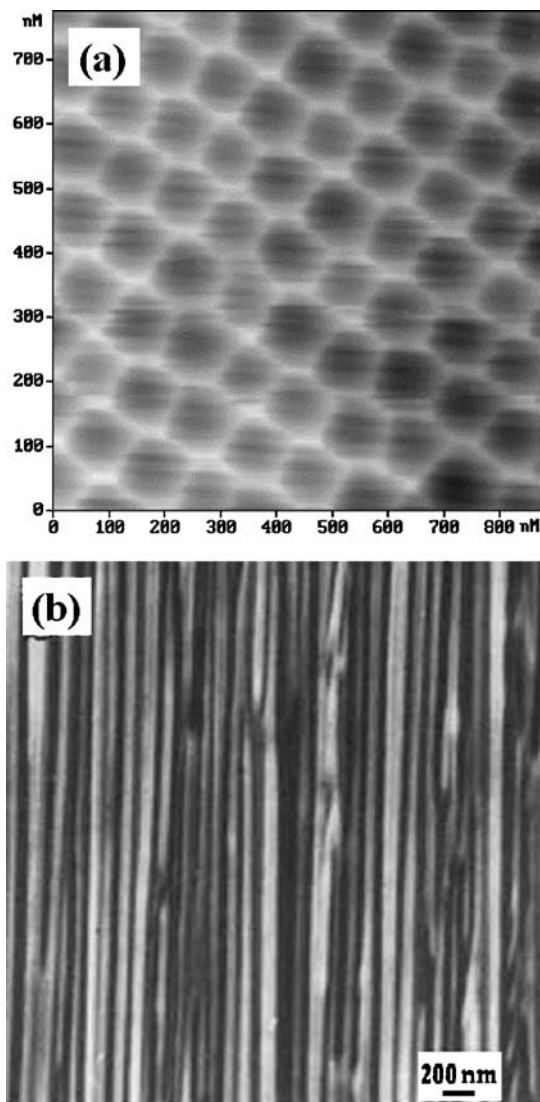


Figure 1 (a) AFM image of the surface of AAO template under tapping mode and (b) SEM image of cross-section of AAO template.

calibrated with reference to the C 1s level of carbon (285.0 eV).

3. Results and discussion

3.1. SEM and TEM analysis

When anodized in an acidic electrolyte, aluminum forms a porous oxide with very uniform and parallel pores open at one end and sealed at the other [8, 9, 25]. Its structure is described as a close-packed array of columnar cells, each containing a central pore of which the side and the interval can be controlled by changing the forming conditions [8, 9, 25]. As indicated in Fig. 1a, the pores in the membrane are arranged in a regular hexagonal lattice. Perfect hexagonal pore arrays can be observed within domains of microsize, which are separated from neighboring aluminum oxide domains with a different orientation of the pore lattice by grain boundaries. Fig. 1b depicts the cross-section of the AAO template with pores parallel to each other and perpendicular to the surface of the membrane. Here, the pores of the membrane are about 100 nm in diameter and about 50 μm in length with a pore density of about 10^{11} – 10^{12} cm^{-2} .

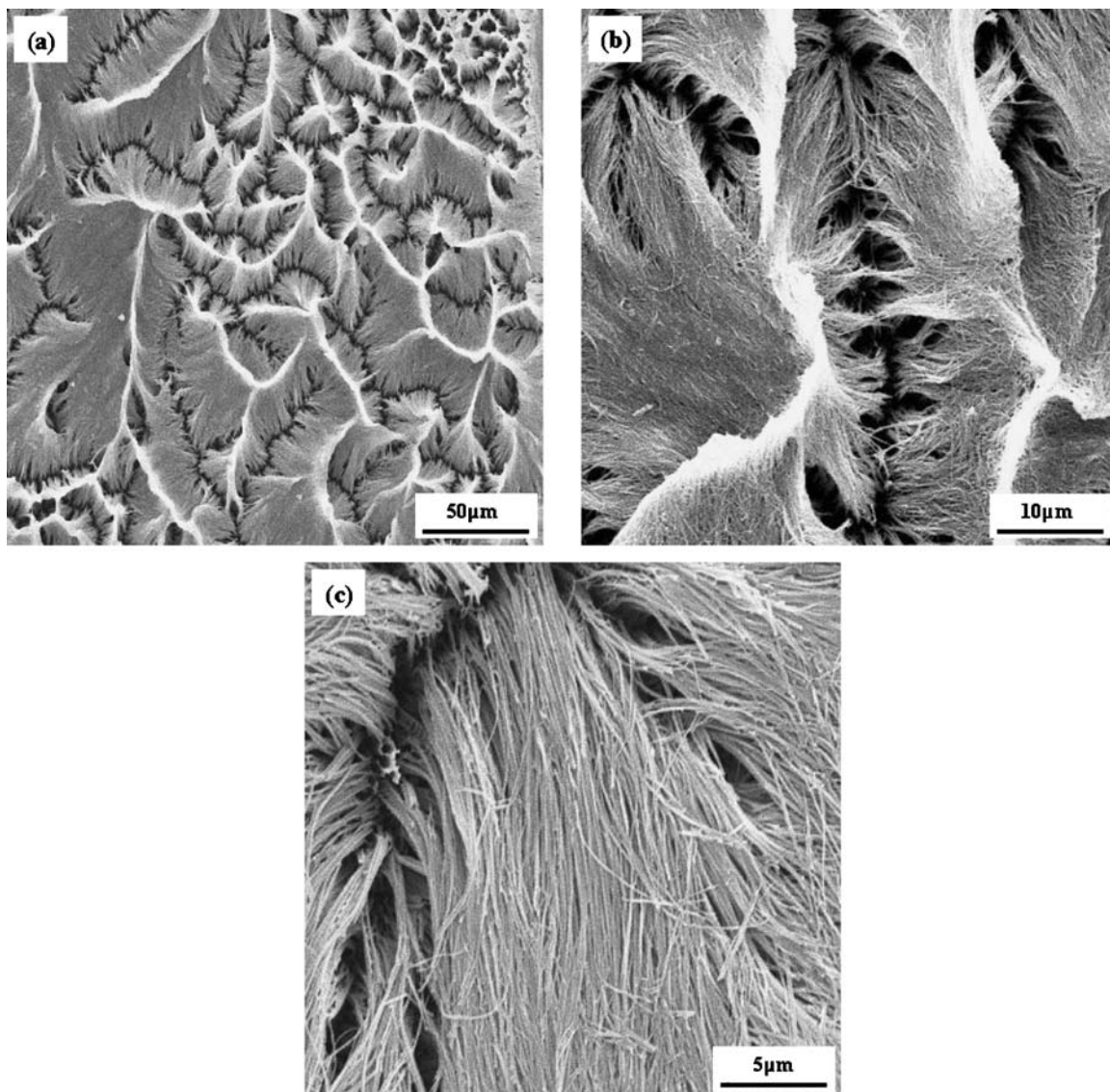


Figure 2 SEM images of HA nanowire arrays with the AAO template partly dissolved: (a) top view in low magnification, (b) cross-section view and (c) top view in high magnification.

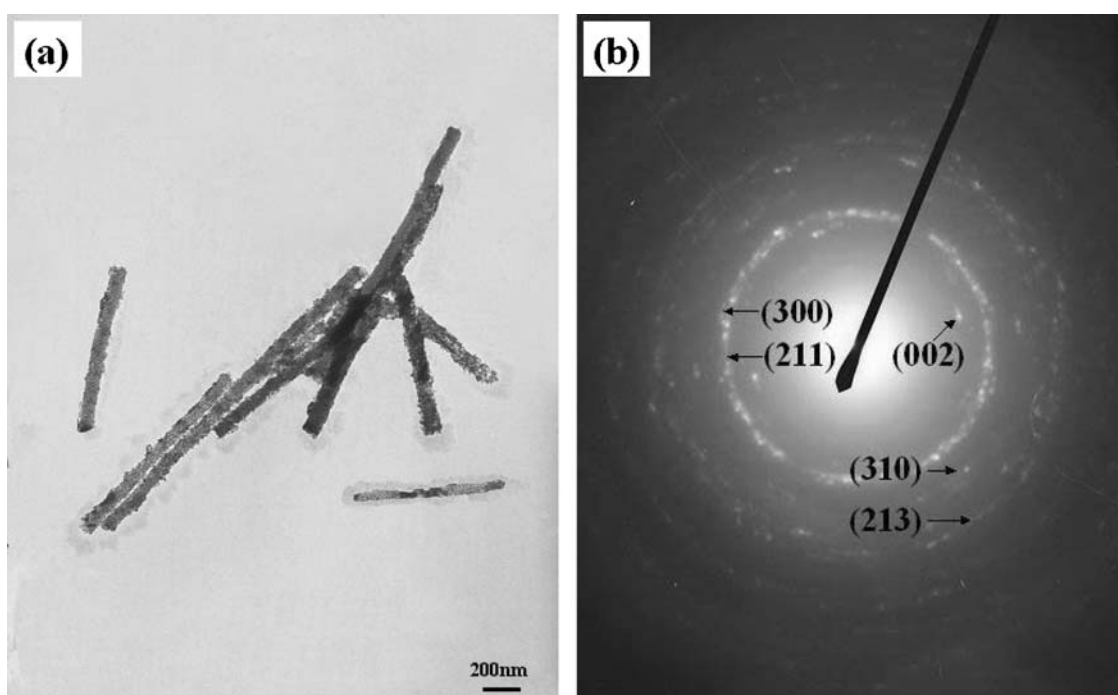


Figure 3 (a) TEM image of several HA nanowires after removing AAO and (b) selected-area electron diffraction for HA nanowires.

Fig. 2a–c shows SEM images of HA nanowires grown in AAO template. These photographs show that the nanowires are uniformly distributed, highly ordered, parallel to each other. Few microscopic defects are found in these wires. Fig. 2a is a platform from which we can find several clusters of nanowires. The clusters can result from the situation in which the nanowires are uncovered from the framework of the AAO template but freestanding incompletely. When the top alumina of the AAO template is dissolved away, the nanowires embedded in the template release gradually and incline to agglutinate together. It is conceivable that the surface energy of the nanowires causes this interesting phenomenon. Fig. 2a also shows that HA nanowires are abundant, uniform and highly ordered in the large area. Fig. 2b reveals a cross-section where the alumina matrix of the AAO template has been partially dissolved away. It can be seen that the nanowires deposited inside the nanochannel of the AAO template are parallel, tidily aligned and uniformly distributed. It is correlative to that the AAO template had an array of densely parallel nanoholes arranged in a hexagonal fashion. Fig. 2c shows a split where the alumina matrix of the AAO template has been dissolved away and large quantities of HA nanowires remain. We can see that these nanowires have a fiber-brush aspect. From these figures it can be estimated that the length of HA nanowires is about 50 μm . It is corresponding with the thickness of the AAO template used. At the same time the outside diameters of these wires are about 100 nm, which are equivalent to the pore diameter of the template membrane.

TEM images of HA nanowires formed within the AAO template are shown in Fig. 3a and b. Fig. 3a shows several HA nanowires, in which some of these nanowires cross and overlap with each other. This image also shows that the diameter of HA nanowires is about 100 nm. Its diameters approximately equal to those of the nanochannels of the employed AAO template. These nanowires are uniformly distributed, which indicates that the alumina matrix is dissolved completely. Fig. 3b shows the corresponding selected area electron diffraction (SAED) pattern taken from HA nanowires. Lots of individual HA nanowires were characterized and we always observed diffraction rings. The SAED results indicate that HA nanowires are polycrystalline. Generally, the nanowires prepared by

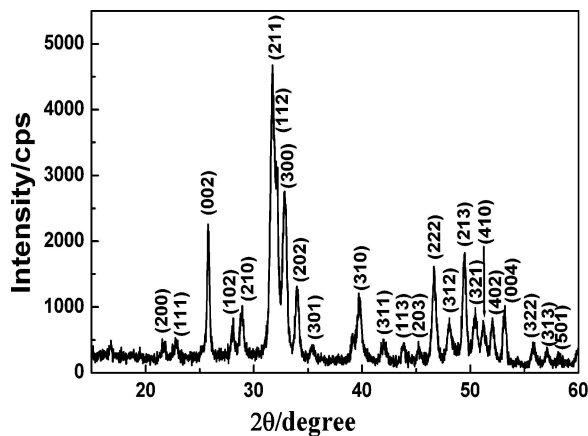


Figure 4 XRD patterns of HA nanowires.

the sol-gel method with the AAO templates are polycrystal [26, 27]. The rings are sharp and continuous, which shows that the nanowires are highly crystalline. According to the electron-diffraction formula, the diffraction spots correspond to the (002), (211), (300), (310) and (213) diffraction planes of HA crystalline.

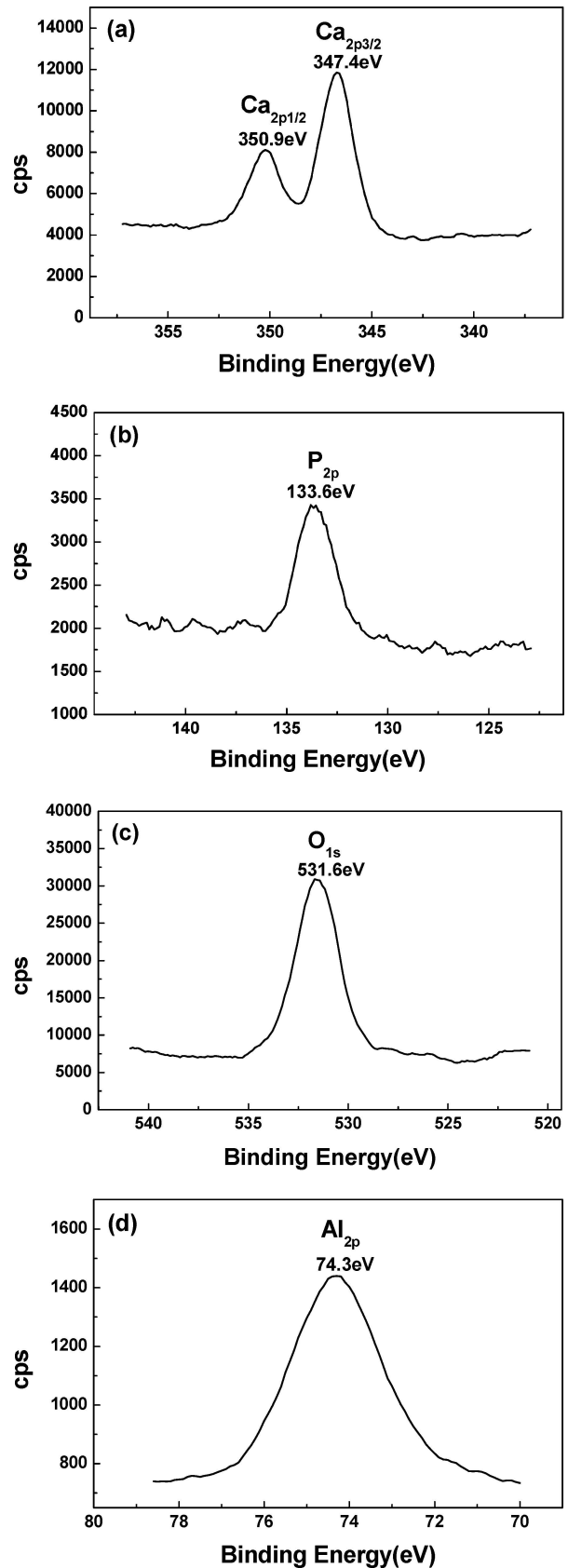


Figure 5 XPS spectra of (a) Ca 2p; (b) P 2p; (c) O 1s and (d) Al 2p core levels for HA/AAO membrane.

3.2. XRD analysis

Fig. 4 shows the X-ray diffraction patterns of HA nanowire arrays after heat treatment at 600°C for 6 h. The peak positions and their relative intensities are consistent with the standard powder diffraction patterns of HA (JCPDS, card number: 09–0432). Fifteen observed major peaks with 2θ values of 25.87, 28.12, 28.87, 31.73, 32.18, 32.93, 34.02, 39.75, 46.67, 48.07, 49.47, 50.47, 51.23, 52.05 and 53.21 degree, respectively correspond to the (002), (102), (210), (211), (112), (300), (202), (310), (222), (312), (213), (321), (410), (402) and (004) planes diffraction peaks of crystalline HA.

3.3. XPS analysis

Fig. 5 shows the XPS patterns of HA nanowire arrays embedded in AAO template. The oxidation state of principal elements of HA in the pores of AAO can be determined by XPS, the binding energies obtained in the XPS analysis are standardized for specimen charging using C 1s as the reference at 285.0 eV. Fig. 5a–d display the XPS spectra of Ca 2p, P 2p, O 1s and Al 2p core levels for the HA/AAO system, respectively. The peaks located at 346.6 eV and 350.2 eV (Fig. 5a) are attributed to the spin–orbit splitting of the Ca (2p) components, Ca (2p_{3/2}) and Ca (2p_{1/2}), respectively. The line of the P 2p core level has a binding energy located at 133.4 eV (Fig. 5b). The line shape of the core levels O 1s and Al 2p are Gaussian-like with a binding energy of 531.6 eV (Fig. 5c) and 74.3 eV (Fig. 5d), respectively. The binding energy values for principal elements of HA in the pores of AAO are in good agreement with those of HA in literatures [28, 29]. XPS spectra shown in Fig. 5a–d further confirm the main composition of the nanowires in the pores of AAO is HA.

4. Conclusion

In summary, highly ordered HA nanowire arrays were successfully fabricated by a sol-gel template process. We also applied TEM, SEM, XRD and XPS techniques to characterize the structure of HA nanowires. HA nanowires have a uniform length and diameter and form highly ordered arrays, which is determined by the pore diameter and the thickness of the applied AAO template. XRD and XPS results indicated that HA was the major component. The result of SAED demonstrated that HA was a polycrystalline structure. We have succeeded in providing a meaningful method to design artificial nano-structures of HA. It was expected that the novel and effective technique might be extended to fabricate other biomaterials nanowire arrays.

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