A method for covering a substrate with highly-oriented single crystalline hexagonal zinc structures under ambient pressure and room temperature[†]

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We report a novel method for covering a substrate with highly-oriented single crystalline hexagonal zinc structures under atmospheric pressure and room temperature without an external source of electric current, any templates or the use of epitaxial growth on the substrate.

Metal nano- and microstructures have been extensively used in many applications, including photonics, electronics, optoelectronics, information storage, photography, catalysis, biological and chemical sensing, surface-enhanced Raman scattering (SERS), and the formation of magnetic ferrofluids.¹ To integrate such nanostructures into a more regular form in order to enhance device performance, various methods have been employed to fabricate vertically or horizontally oriented nanostructures,² such as homo- or hetero-epitaxial growth and template assisted growth. In the epitaxial crystal growth methods, the choice of substrate is restricted due to crystal lattice matching considerations, while the templating methodology approach has the disadvantage that it requires an additional template-elimination process. Generally, the metal nano- or microstructure synthesis methods reported to date require high temperatures (>100 °C) and pressure control. Thus, a synthetic method for fabricating metal nanostructures under mild conditions is still required to meet economic and industrial needs. In addition, it is highly desirable to develop total chemical syntheses that operate near room temperature under normal atmospheric pressure for the purposes of mimicking natural mineralogical or biological processes.³

Zinc (Zn) is an important material in batteries. For example, a rechargeable alkaline Zn-air battery with a porous Zn/ZnO electrode has been fabricated.⁴ Zn is a conventional type-I superconductor with a transition temperature of 0.85 K (at H = 0 Oe) and a critical magnetic field of 50 Oe (at T = 0 K), and its superconductivity is tunable when the wire diameter is less than 70 nm.⁵ Thin Zn nanostructures with diameters less than 15 nm have been found to have an enhanced thermopower that is related to their temperature-dependent electrical and magnetic resistances.⁶ Zn is also an important precursor for the preparation of other Zn-based semiconductors

such as ZnO, ZnS, ZnSe, and ZnTe, which have extensive applications in electronics, photoelectronics, and phonics.⁷

In this communication, we report a novel method for covering a substrate with highly-oriented single crystalline hexagonal zinc structures under atmospheric pressure and room temperature without an external source of electric current, any templates or the use of epitaxial growth on the substrate.

A substrate coated with an Al film was immersed in an aqueous ammonia solution containing Zn ions and maintained at 25 °C for 6 h. Details of experimental procedures and Al film characterizations are provided in ESI⁺. Fig. 1(a) and (b) show the XRD pattern of the substrate before and after the reaction at 25 °C for 6 h, respectively. The XRD pattern before the reaction (Fig. 1(a)) contains four peaks that correspond to Al (111), (200), (220), and (311) planes in addition to the Si peak (JCPDS No. 04-0787). After the reaction (Fig. 1(b)), the Al peaks have disappeared and new peaks have emerged that are indexed as hexagonal Zn crystal planes (JCPDS No. 04-0831). The Zn (002) and Zn (004) peaks are much stronger than the other Zn plane peaks, indicating that the Zn crystals are highly oriented. The Zn (002) planes are parallel to the planar substrate. No diffraction peaks due to other crystals are present in the XRD pattern except for the Si substrate peaks; hence, we conclude that pure hexagonalphase Zn crystals were formed on the Si substrate and that Zn–Al alloys or crystals that contain Al atoms did not form.

We used a FESEM to investigate the morphology of the substrate surface after the reaction. Fig. 2(a) and (b) show SEM images of the Zn structures that formed as a result of the reaction at 25 °C for 6 h. The substrate surface is covered with hexagonal plates with lateral sizes of 500-1200 nm. Almost no overlapping of hexagonal plates is observed. Note that the hexagonal structures are highly oriented and that the Zn (002) planes are parallel to the substrate, consistent with the XRD results. The average thickness of the plates is ~ 50 nm. Higher magnification images of the hexagonal structures were obtained using a HR-STEM. Fig. 2(c) shows a bright-field TEM image of a hexagonal Zn plate that has been detached from the substrate after synthesis. To investigate the crystalline nature of the synthesized materials, selected-area electron diffraction (SAED) patterns and HR-TEM images were obtained. The inset of Fig. 2(c) shows the SAED pattern of the area marked by a triangle in Fig. 2(c). The SAED patterns lie on the [001] zone axes and their regular spots are indicative of the good crystallinity and single crystalline nature of this material; they are also consistent with the hexagonal phase indexed from the XRD reflections. HR-TEM images of the separated areas indicated by the circles (circles 1 and 2) in

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 [†] Electronic supplementary information (ESI) available: (A) Materials and experimental procedures; (B) characterizations; (C) Al film characterizations; (D) XPS analysis of hexagonal zinc structures; (E) high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image. See DOI: 10.1039/b911773c



Fig. 1 XRD patterns of the Al-coated substrate (a) before and (b) after the reaction with the aqueous ammonia solution containing Zn ions at 25 $^{\circ}$ C for 6 h.

Fig. 2(c) are shown in Fig. 2(d) and (e). The HR-TEM images show that the areas have a single crystalline nature with a lattice spacing of about 0.23 nm, which corresponds to the distance between the {100} planes in the hexagonal Zn crystal lattice, and have the same crystal orientations, which confirms that the hexagonal structure is a single crystal and preferentially grows parallel to the (002) plane. The two corresponding fast Fourier transform (FFT) images (insets of Fig. 2(d) and (e)) have almost the same regular spots, providing further strong evidence that the hexagonal structure is a single crystal. The compositions of the synthesized materials were investigated with energy dispersive X-ray spectroscopy (EDX). The EDX pattern (Fig. 2(f)) indicates that the structures are composed only of Zn; the C and Cu signals are attributed to the carbon coated copper mesh used in HR-TEM. No evidence of other impurities was found. After the reaction, no precipitate was present in the bulk solution. The XPS spectrum of the reaction products is provided in ESI[†] (Fig. S2).

To investigate the mechanism of formation of the hexagonal Zn structures, we characterized the products formed during the early stage (20 min) of the reaction.

Fig. 3(a) shows an SEM image of structures obtained after reaction for 20 min. At this time point, the structures are not yet well-defined hexagonal structures. Fig. 3(b) shows a TEM image of a Zn structure after 20 min of reaction, while Fig. 3(c) shows a more magnified image of the area marked by the circle in Fig. 3(b), and Fig. 3(d) shows an even higher magnification image. The high magnification image in Fig. 3(c) and a HAADF image (Fig. S3 in ESI[†]) show that the structures are composed of nanoparticles, and the higher magnification image in Fig. 3(d) establishes that the nanoparticles share the same single crystallographic orientation. Thus, these findings indicate that the Zn crystals formed after reaction for 20 min are almost single crystalline, a finding that is confirmed by the corresponding FFT image (see the inset in Fig. 3(d)).



Fig. 2 (a) and (b) SEM images of the substrate surface after reaction with an aqueous ammonia solution containing Zn ions at 25 $^{\circ}$ C for 6 h. (c) TEM image of a hexagonal structure that was detached from the substrate after synthesis. The inset shows the SAED pattern of the area marked by a triangle in (c); (d) and (e) HR-TEM images of the areas indicated by the circles 1 and 2 in (c), respectively. The insets are the corresponding FFT images; (f) EDX pattern of the hexagonal Zn structure.



Fig. 3 (a) SEM image of the substrate surface after the reaction with an aqueous ammonia solution containing Zn ions at 25 °C for 20 min. (b) TEM image of a nanostructure obtained from the 20 min reaction and then detached from the substrate; (c) HR-TEM image of the areas indicated by the circle in (b); (d) higher magnification HR-TEM image. The inset shows the corresponding FFT image of (d).



Fig. 4 Schematic illustration of the proposed mechanism for the formation of the hexagonal Zn structures.

These results for the early growth stage provide strong evidence that oriented attachment is an important mechanism underlying the formation of single crystalline Zn structures.⁸

When a Si wafer without an Al layer was used as the substrate in a control experiment, crystal structures did not form on the substrate surface after immersing the substrate in aqueous ammonia solution at 25 °C for 6 h. Because zinc cannot be reduced under these conditions, an aluminium layer was chosen and used as the reductant. Replacement reactions, in which the more reactive component is consumed without any external electron source, have been demonstrated to provide a general and effective method for preparing metallic nanostructures.⁹ We propose that the following reactions occur in the system comprising an aqueous ammonia solution and an Al layer:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$
(1)

$$Zn^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4^{2+}$$
 (2)

$$2Al(s) + 3Zn(NH_3)_4^{2+} + 8OH^-$$

$$\rightarrow 3Zn(s) + 2Al(OH)_4^- + 12NH_3 \qquad (3)$$

The proposed mechanism of formation of the hexagonal Zn structures is illustrated in Fig. 4. The standard reduction potentials of an Al(OH)₄⁻/Al pair and a $Zn(NH_3)_4^{2+}/Zn$ pair are -2.33 V and -1.04 V, respectively,¹⁰ which indicates that reaction (3) is spontaneous in aqueous media, and does not require any external electron source. Zn nanoparticles are formed by Zn²⁺ reduction processes near the Al layer through reaction (3). The Zn nanoparticles then diffuse on the surface and become attached to other Zn nanoparticles. Jiggling of these nanoparticles via Brownian motion enables adjacent particles to rotate to find the lowest-energy configuration, resulting in a coherent particle-particle interface.¹¹ As a result of the oriented attachment of nanoparticles, hexagonal nanostructures form on the substrate surface. The driving force of this spontaneous oriented attachment is the elimination of high-energy surfaces.^{11,12} As the reaction proceeds, the $Zn(NH_3)_4^{2+}$ concentration, the amount of Al metal and the number of Zn nanoparticles decrease. As time progresses, the hexagonal crystals formed via oriented attachment are transformed into regular and smooth hexagonal plates (Fig. 2) through the coarsening process known as Ostwald ripening.¹³

In summary, we report a novel method for covering a substrate with highly-oriented single crystalline hexagonal zinc structures under atmospheric pressure and room temperature. On the basis of the results, we propose a mechanism for the spontaneous growth of such highly-oriented hexagonal single crystalline Zn structures. The present method should be applicable to the synthesis of other single crystalline metal structures and provides an alternative method for the synthesis of highly-oriented metal nanostructures.

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