Nanoscale



View Article Online

PAPER



Cite this: Nanoscale, 2014, 6, 13710

Received 28th April 2014, Accepted 9th September 2014 DOI: 10.1039/c4nr02287d

www.rsc.org/nanoscale

1. Introduction

Magnetic nanocrystals have attracted great research interest for decades because of their remarkable shape-, size-, surfacedependent physical and chemical properties,^{1,2} for example, nanoscale confinement, blocking behavior, and nanomagnetism.³ The change in shape is proven to be an effective way to modify their electronic states and physical characteristics.⁴ Recently, considerable efforts have been devoted to synthesize various shape-controlled nano-architectures, including spherical,⁵ cubic,⁶ rod-like,⁷ hexagonal⁸ and branched nanostructures.⁹ Nanotetrapod is one member of the branched

Bimagnetic h-Co/h-CoO nanotetrapods: preparation, nanoscale characterization, three-dimensional architecture and their magnetic properties[†]

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Well-defined bimagnetic h-Co decorated wurtzite h-CoO nanotetrapods with uniform size have been successfully fabricated by a one-pot thermal decomposition method for the first time, and their threedimensional architecture, crystal structure, chemical phase and exchange bias effect are characterized at the nanoscale. It is found that individual bimagnetic h-Co/h-CoO nanotetrapods are made of a h-CoO nanotetrapod skeleton to which multiple nanocrystals of ferromagnetic metallic h-Co are directly attached. The chemical analysis shows that the mass ratio of h-CoO and h-Co is 65:35. The detailed investigations of the crystal structure reveal that both the h-CoO nanotetrapod skeleton and h-Co nanoparticles have hexagonal structure. The four pods of individual nanotetrapods are single crystals with the same [001] orientation along with their pod axes and grow together by twinning with (110) the twin interface and the 120° spatial boundary angle. The magnetic measurements reveal that the h-Co/h-CoO nanotetrapods have a surprisingly strong room temperature ferromagnetism and there exists a weak exchange coupling between the h-CoO nanotetrapod skeleton and the decorated h-Co tiny nanoparticles. It is believed that our new structural form of the bimagnetic h-Co/h-CoO nanotetrapods provides not only a smart functional 3D nanoarchitecture as building block in nanoelectronics and nanosensors, but also an ideal specimen for a further understanding of weak antiferromagnetic-ferromagnetic interaction

> nanostructure family, which consists of a central core/region with four nano-arms branching out at the tetrahedral angle from a central region.^{10,11} Its intriguing three-dimensional (3D) geometry provides unique promises of inducing novel physical properties and developing into versatile functional nanoelectronics/sensors, which are beyond the capability of spherical and rod-shaped nanomaterials.^{12–16} Diverse tetrapod nanocrystals, including II-VI semiconductors CdS,17 CdTe,15 ZnS,¹⁸ ZnO,¹⁹ precious metals PbS,²⁰ Pd,²¹ Au,²² Pt²³ and transition metal oxides MnO,²⁴ Fe₂O₃¹⁶ and cubic rocksalt CoO,¹⁰ have been experimentally synthesized. Among them, the controlled synthesis of transition metal oxide nanotetrapods are the most challenging. Therefore, to the best of our knowledge, as one of two stable phases, hexagonal wurtzite CoO nanotetrapods or their metal-decorated hybrids have not been reported earlier.

> CoO nanocrystals that are known as one member of the diluted magnetic semiconductor family have been observed to have superparamagnetic or weak ferromagnetic^{25–29} behavior at room temperature, while the bulk CoO is antiferromagnetic.²⁵ They are proven to have promising applications in

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[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/ c4nr02287d

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catalysts, magnetic data storage devices, lithium-ion battery materials and solid-state sensors.³⁰⁻³³ Their crystal structures typically have two stable phases: cubic rocksalt with the Co²⁺ cations occupying the octahedral sites and hexagonal wurtzite with Co²⁺ cations occupying the tetrahedral sites.^{26,33} Typically, the 180° Co-O-Co superexchange interactions in cubic CoO result in an antiferromagnetic coupling preponderance, and the latter forming tilted 110° Co-O-Co angle leads to an absence of magnetic ordering; therefore, behaves as paramagnetic or superparamagnetic at low temperatures.^{26,27} Keen research interest has been extended to explore the synthesis and magnetic properties of hexagonal CoO (h-CoO) crystals in recent years. Magnetism of several shape-controlled h-CoO nanocrystals, including nanoclusters,³⁴ size dependent pyramids,²⁹ and pencil-shaped nanorods,²⁵ have been investigated. However, the magnetism of bimagnetic h-Co/h-CoO nanotetrapods extremely lacks so far. The magnetism origins of the nanoscale CoO crystals are suggested to come from the multisublattice,²⁹ uncompensated spin at the surface³⁴ and the donor ferromagnetic impurity.²⁵ However, despite these efforts, a widely accepted magnetism origin of h-CoO nanocrystals and their hybrids is still lacking. More efforts need be devoted to further understand the origin of their intrinsic magnetism.

In this work, for the first time, we report on a straightforward synthesis and detailed nano-scale characterization of bimagnetic h-Co/h-CoO nanotetrapods via a one-pot thermal decomposition method. Individual bimagnetic h-Co/h-CoO nanotetrapods are made of a h-CoO nanotetrapod skeleton, to which multiple ferromagnetic nanocrystals of metallic h-Co are directly attached or embedded, which exhibit both physical and chemical properties of individual h-CoO nanotetrapods and h-Co nanocrystals, and display unique characteristics not observed in either of the two components. The morphological, 3D architectural, structural, chemical, and magnetic characterization of the h-Co/h-CoO nanotetrapods have been systemically investigated. It is believed that the new structural form of the bimagnetic h-Co/h-CoO nanotetrapods provides not only a smart functional 3D nanoarchitecture as building block in nanoelectronics and nanosensors, but also an ideal specimen further understanding weak antiferromagnetic-ferrofor

magnetic interaction, which is manifested by higher saturation magnetization, enhanced coercivity values and exchange bias.

2. Results and discussion

2.1. Morphological, and 3D architectural analysis of h-Co/h-CoO nanotetrapods

The morphologies of h-Co/h-CoO nanotetrapods were observed by transmission electron microscopy (TEM). Fig. 1a shows a representative TEM image of the synthesized h-Co/h-CoO nanotetrapods, revealing a well-controlled tetrapod shape with corn-like arms. The contrast of TEM image depends on the thickness and atomic number $Z^{4/3}$ of the specimen. In this image, the middle pod of each nanotetrapod viewed along the electron beam appears darker than the other three pods, revealing the nanotripod pseudomorphism. Individual nanotetrapods have a continuous structure and virtually uniform size and shape. The size statistics (seen in Fig. S1c and S1d†) reveals that the average width and length of the single pod on each nanotetrapod are 35.8 nm and 73.8 nm, respectively.

In comparison with TEM, a high angle annular dark field and scanning transmission electron microscopy (HAADF-STEM) has a considerably better spatial resolution because of a better view depth; thus, it is very useful to observe the spatial shape of nanomaterials. Fig. 1b shows a representative lowmagnification HAADF-STEM image of ten h-Co/h-CoO nanotetrapods, which provides a further insight into their shapes. It is observed that the size and shape of the individual nanotetrapods are uniform, which are in good agreement with the above TEM observation. Fig. 1c shows a high-magnification HAADF-STEM image of a single nanotetrapod, which provides a clearer view than Fig. 1a and 1b. It is clearly observed that the single nanotetrapod has three pods with a 120° angle between each other and has a very bright hexagonal nanoparticle located at the center of the three pods. The bright hexagonal particle is believed to be the projection view of the fourth pod of the nanotetrapod, which was aligned with the electron beam direction. In addition, it is also seen that tens of tiny nanoparticles are randomly interconnected or embedded into



Fig. 1 (a) Representative TEM image of four h-Co/h-CoO nanotetrapods. (b) HAADF-STEM image of ten h-Co/h-CoO nanotetrapods. (c) Highmagnification HAADF-STEM image of a single h-Co/h-CoO nanotetrapod.



Fig. 2 Selected TEM images of the three dimensional architecture experiment and the ideal 3D geometrical model: (a)–(i) projection views from the tilt series of the two nanotetrapods at 30°, 24°, 12°, 0°, -6° , -12° , -24° , -30° and -36° recorded using TEM; (j)–(l) the corresponding ideal 3D geometrical models of the (a), (d) and (i) projection views, respectively.

the pod bodies of each nanotetrapod, which forms a nanoparticles-attached-on-nanotetrapod-skeleton hybrid structure. The average diameter of these tiny nanoparticles is about 6 nm.

Although the HAADF-STEM image has a level of spatial resolution, it is still a 2D projection of an object. In order to confirm the 3D architecture of the h-Co/h-CoO nanotetrapods at the nanoscale, a TEM tomographic tile series of two h-Co/ h-CoO nanotetrapods was acquired from 36° to -36° with 2° increment to reconstruct their intrinsic 3D geometric morphology. Fig. 2a-2i shows nine selected 2D TEM projection images of the two nanotetrapods from the tilt series at 30°, 24°, 12°, 0°, -6° , -12° , -24° , -30° and -36° tilt angle. The acquired TEM images were spatially aligned to a visualization movie using Ulead Video Stutio software (ESI movie S1[†]). The ideal 3D geometrical model of a single nanotetrapod was subsequently reconstructed by Autodesk 3ds Max (ESI movie S2[†]). Fig. 2j-2l shows three volume rendered projection views generated from the reconstructed 3D architecture, of which projection directions are the same as Fig. 2a, 2d and 2i, respectively. Fig. 2k also represents the projection view of above Fig. 1a-1c, of which the fourth nanopod was nearly colinear with the view direction or electron beam direction. It is therefore observed that individual nanotetrapods are formed by four nanopods branching out at tetrahedral angles from a central region,^{10,11}

and each nanopod likes a corn with a hexagonal cross section along its long axis.

2.2. Chemical and structural analysis of the h-Co/h-CoO nanotetrapods

The chemistry of the h-Co/h-CoO nanotetrapods was characterized using XPS, EDX and STEM mapping on a 300 kV HRTEM. Fig. 3a shows a representative XPS spectrum of the h-Co/h-CoO nanotetrapods, of which Co 2p binding energy was calibrated with the C 1s peak (284.6 eV). The Co $2p_{3/2}$ peak located at 780.2 eV accompanying the prominent shake-up satellite peak (785.2 eV) and the Co $2p_{1/2}$ located at 796.3 eV combining with the shake-up satellite peak (802.5 eV) verify the presence of the CoO phase.^{35–37} The peaks located at 778.2 eV and 793.3 eV reveal the existence of metallic Co.^{38,39} Quantitative analysis of the XPS spectrum indicates a 65 : 35 mass ratio of CoO and Co.

Fig. 3b shows a representative EDX spectrum obtained from a single h-Co/h-CoO nanotetrapod. The Co and O peaks come from the h-Co/h-CoO nanotetrapods, which further prove the existence of cobalt and oxygen elements. The C and Cu peaks are believed to be from the holey carbon coated copper grid, which was confirmed by the measurement of an EDX baseline of an empty holey carbon coated copper grid. The chemical distributions of individual h-Co/h-CoO nanotetrapods were



Fig. 3 Chemical characterization of the h-Co/h-CoO nanotetrapods: (a) a representative XPS spectrum; (b) EDX spectrum; (c) TEM image of the single h-Co/h-CoO nanotetrapod used for elemental mapping analysis; (d) cobalt mapping; (e) oxygen mapping.

subsequently studied by EDX elemental mapping analysis techniques. Fig. 3c shows a TEM image of the single h-Co/h-CoO nanotetrapod used to carry out the elemental mapping experiment. Fig. 3d and 3e show the corresponding EDX elemental mappings of cobalt (K_{α} , 6.93 keV) and oxygen (K_{α} , 0.52 keV) elements, respectively. The elements Co and O are nearly evenly distributed throughout the whole nanotetrapod, revealing a uniform CoO chemical phase. This data is not expected. According to above observation of metallic Co nanoparticles randomly decorated on the CoO nanotetrapod skeleton, the Co elemental distribution should appear randomly highlight spots where metallic Co nanoparticles were attached or embedded. The reason is believed to originate from the resolution limitation of the EDX elemental mapping technique. The resolution limitation of our EDX hardware in this work is 20 nm, which is not sensitive enough to detect the 6 nm Co nanoparticles.

The crystalline structures of the h-Co/h-CoO nanotetrapods were characterized in detail using SAED, XRD and high-resolution TEM (HRTEM). Fig. S2a[†] shows a representation SAED of tens of h-Co/h-CoO nanotetrapods. The rings can be indexed to two sets of lattice planes: (100), (002), (101), (102), (110), (103) and (112) planes of hexagonal CoO structure marked by white letters; (100), (101) and (102) planes of hexagonal Co structure marked by red letters. The XRD spectrum (ESI Fig. S2b[†]) is a further proof that hexagonal CoO and hexagonal Co structure co-exist in the prepared nanotetrapods, consistent with the above findings of the TEM studies. Therefore, the prepared sample in this work can be named as bimagnetic h-Co/h-CoO nanotetrapods after extensive consideration of the above morphological, 3D architectural, chemical and structural analyses.

Fig. 4b shows the HRTEM image of the middle pod (marked by blue square A) of the single h-Co/h-CoO nanotetrapod in Fig. 4a, of which the long axis is along the incident electron beam. The interplanar spacing was measured to be 2.79 Å, corresponding to the (100) serial planes distance of hexagonal wurtzite CoO structure. The bottom-left inset shows the FFT image of the lattice pattern in Fig. 4b, revealing a hexagonal close packing (hcp) structure with [001] orientation. The other three pods from the same nanotetrapod shown in Fig. 4a have also been analyzed, of which lattice resolution TEM images are shown in Fig. 4c-4e, respectively. The interplanar spacings were measured to be 2.62 Å (marked by red square B), 2.62 Å (marked by yellow square C) and 2.61 Å (marked by green square D), which agree well with the same (002) plane distance of hexagonal wurtzite CoO structure. Further experiments show that each pod of individual nanotetrapods is a single crystal with the same [001] orientation along with pod axis.

The tiny nanoparticles randomly attached on the nanotetrapod skeleton were also examined. Fig. 4f shows a typical HRTEM image of the nanoparticle E marked by the purple square in Fig. 4a. The interplanar spacing was measured to be 2.05 Å, matching with the (002) plane of hexagonal Co metal.



Fig. 4 Structural analysis of the h-Co/h-CoO nanotetrapods: (a) TEM of a chosen h-Co/CoO nanotetrapod; (b), (c), (d) and (e) lattice-resolution TEM images of the areas from four pods of the nanotetrapod in (a) marked by square blue A, red B, yellow C and green D, respectively; (f) the lattice fringe of an embedded tiny particle in (a) marked by purple E and the corresponding FFT image shown in the inset.

Its corresponding FFT image shown in the bottom-right inset of Fig. 4f reveals that the zone axis of this Co nanoparticle is [011]. The size of this Co nanoparticle is about 6 nm, consistent with above HAADF-STEM observations (Fig. 1b). More HRTEM observations (Fig. S3†) confirm that individual Co nanoparticles are single crystals with hcp structure and have an average 6 nm diameter.

The interfaces located at the joint of the four legs of individual h-Co/h-CoO nanotetrapods were further characterized. Fig. 5a shows a lattice resolution TEM image of the interface between two neighbouring pods in Fig. 3c (marked by red square A), revealing a clear (110) twin interface (red line) with a 120° boundary angle. For future analyzing the grain boundaries among four pods, this h-Co/h-CoO nanotetrapod was then tilted at 30°, and the HRTEM image of the interface of the four nanopods is shown in Fig. 5b. Its corresponding FFT image shown in Fig. 5c consists of three obvious sets of diffraction spots marked by blue gridlines A, red gridlines B and yellow gridlines C, which can be indexed as [010], [011] and [010] orientations of the wurtzite structure CoO.

Fig. 5d–5f show the lattice-resolution TEM images of the three square areas marked by blue A, red B and yellow C in Fig. 5b, respectively. The interplanar distances are measured to be 2.60 Å and 2.78 Å for area A, matching with (002) and (100) planes of hexagonal CoO; 2.61 Å for area B, matching with (002) plane of hexagonal CoO; 2.61 Å and 2.79 Å for area C, matching with (002) and (100) planes of hexagonal CoO. This result indicates that the zone axes of the three projection

pods in this nanotetrapod are along the [010], [011] and [010] directions of the h-CoO nanocrystal, respectively. Their corresponding FFT images of the three areas, A (Fig. 5d), B (Fig. 5e) and C (Fig. 5f), are displayed in Fig. 5g–5i, which can be well indexed into [010], [011] and [010] crystallographic orientations of h-CoO. This result is matched with the theoretical crystal diffraction patterns of h-CoO structure with zone axes of [010], [011] and [010] as shown in Fig. S4.†

2.3. Magnetic properties of the h-Co/h-CoO nanotetrapods

The magnetic properties of the h-Co/h-CoO nanotetrapods were measured by VSM at room temperature and SQUID at 2 K. Fig. 6a shows a typical hysteresis loop of the h-Co/h-CoO nanotetrapods measured by VSM at room temperature, displaying a 33.3 emu g⁻¹ saturation magnetization (M_s) and 1241.5 Oe coercivity. This result clearly reveals that the h-Co/h-CoO nanotetrapods have a surprisingly strong room temperature ferromagnetism. As determined by the above morphological and chemical characterization, our specimen has a nanoskeleton of h-CoO terapod with four 35.8 nm diameter and 73.8 nm length pods, and multiple tiny metallic Co nanoparticles with around 6 nm diameter directly attached or embedded to the nanoterapod skeletons at the atomic scale. It is reported that the nanoscale hexagonal CoO nanocrystals behave with weak ferromagnetism or superparamagnetism in addition to its intrinsic antiferromagnetism at room temperature,^{20,28,29,34,40} and Co nanoparticles with 6 nm diameter display room temperature superparamagnetism.41,42 There-



Fig. 5 Lattice resolution TEM images of the grain boundaries of a single nanotetrapod: (a) twin interface between two neighbour pods in Fig. 3c; (b) grain boundaries among four pods after the specimen in Fig. 3c has been tilted 30° ; (c) the corresponding FFT image of Fig. 5b; (d)–(f) the HRTEM images of the three square areas marked by blue A, red B and yellow C in Fig. 5b, respectively; (g)–(i) the corresponding FFT images of Fig. 5d–5f.

fore, it is seen that our h-Co/h-CoO nanotetrapods display different magnetic properties from its two components, either h-CoO tetrapod skeletons, or Co tiny particles.

It is reported that the experimental $M_{\rm s}$ of approximate 6 nm Co is 91 emu g⁻¹ (ref. 43) and that of h-CoO is 2.22 emu g^{-1,29} As determined by the above XPS measurement, the mass ratio of CoO and Co in this study is 65:35. Therefore, a calculated $M_{\rm s}$ of the bimagnetic h-Co/h-CoO can be estimated to be 33.29 emu g⁻¹, which is nearly the same as the earlier measured value of 33.3 emu g⁻¹. This result confirms the accuracy of our above XPS and VSM measurements. This 33.3 emu g⁻¹ $M_{\rm s}$ is nearly ten times of that reported for 38 nm hexagonal pyramid-shaped CoO nanoparticles.²⁹

The coercivity value of the h-Co/h-CoO nanotetrapods is larger than that of Co/iron oxide with the same structure and similar size (but different skeleton composition; 150 ± 20

Oe),¹⁶ and that of 67 nm pyramid-shaped h-CoO nanoparticles (484 Oe),²⁹ but smaller than that of 6 nm Co/CoO core–shell structure (5 kOe at 5 K temperature).⁴⁴ A possible reason that the h-Co/h-CoO nanotetrapods show the strong room temperature ferromagnetism may originate from the exchange interactions induced by the interfaces between the anti-ferromagnetic (AFM) h-CoO nanotetrapod skeletons and ferromagnetic (FM) Co nanoparticles.

In order to experimentally measure the exchange coupling effect, we measured the hysteresis loops at 2 K. Fig. 6b shows representative hysteresis loops measured by SQUID at 2 K after zero field cooling (ZFC) and field cooling in a field of 50 kOe, revealing a symmetrical ZFC loop (blue hysteresis) and slightly shifted FC loop (red hysteresis). It is known that the coercivity $H_{\rm C}$ can be obtained from ZFC loops, which is equal to $(H_{c2}^{\rm ZFC} - H_{c1}^{\rm ZFC})/2$. In this study, $H_{c1}^{\rm ZFC}$ and $H_{c2}^{\rm ZPC}$ are measured to be



Fig. 6 Magnetic properties of the h-Co/h-CoO nanotetrapods: (a) a representative hysteresis loop of the h-Co/h-CoO nanotetrapods measured at room temperature; (b) hysteresis loop of the h-Co/h-CoO nanotetrapods measured at 2 K by SQUID after cooling in 50 kOe FC or zero field cooling ZFC. Inset shows the enlarged view of the central part which reveals the shift of the hysteresis loop.

-1434.7 Oe and 1432.3 Oe as shown in blue curves in Fig. 6b, respectively; therefore, a 1433.5 Oe coercivity is calculated. This value is larger than that of 6 nm pure Co nanopaticles (700 Oe) at 2 K.⁴⁵ The exchange bias field $H_{\rm E}$, which is equal to $(H_{c1}^{FC} + H_{c2}^{FC})/2$, can be obtained from FC loops. As shown in the red curve in Fig. 6b, H_{c1}^{FC} and H_{c2}^{FC} are read to be -1518 Oe and 1351 Oe, respectively, an exchange bias field $H_{\rm E}$ of -83.5 Oe under 50 kOe cooling field at 2 K temperature is obtained for our bimagnetic h-Co/h-CoO nanotetrapods. This result proves that there are exchange interactions between the h-CoO nanotetrapod skeleton and the decorated Co tiny nanoparticles. The negative $H_{\rm E}$ value indicates the shift direction of the hysteresis loop is opposite with the cooling field. However, the $H_{\rm E}$ value in our bimagnetic h-Co/h-CoO nanotetrapods is small in comparison with the reported 10.2 kOe H_E in Co/CoO core-shell cluster,44 revealing that the exchange coupling induced by the interfaces between the h-CoO nanotetrapod skeletons and h-Co nanoparticles is not strong. The reason for the weak exchange coupling could be the poor interfacial

layers because the tiny h-Co nanoparticles are randomly attached or embedded on the h-CoO nanotetrapod skeleton as observed above, which is different from the reported Co/CoO core-shell structures⁴⁴ which formed high-qualified interfacial layers because the CoO layers were directly oxidized from the surfaces of the Co nanoparticles.

Although the exchange bias field is experimentally proven to be weak, the strong room temperature ferromagnetism of the h-Co/h-CoO nanotetrapods indicates that the exchange coupling at the AFM-FM interfaces induce uniaxinal anisotropy, eventually leading to magnetization stability. Above crystal structural analysis has proven that both individual Co nanoparticles and the CoO nanotetrapod skeleton are good single crystals with hcp structure, which are in favor of inducing an extra uniaxinal anisotropy for the decorated Co nanoparticles because the crystal structure matches and the crystallinity is good. In order to quantitatively understand the influence of the exchange coupling at AFM-FM interfaces on the magnetization stability of the bimagnetic h-Co/h-CoO nanotetrapods, the calculation of the blocking temperature $(T_{\rm B} \approx KV/k_{\rm B}\ln(\tau/\tau_0))^{46}$ is adapted. Considering the coupling energy in this study, KV has been modified to $KV_{FM} + \Delta E \times 2\pi R^2$. Typically, the interface energy ΔE for a Co–CoO system⁴⁷ is about 0.4–3.5 erg cm⁻² at 10 K, which is considerably larger at 2 K. The anisotropy constant K is 4.5×10^5 J m⁻³.⁴¹ The volume V is 113.0 nm³ for 6 nm Co nanoparticles. The blocking temperature for a h-Co/h-CoO nanotetrapod is calculated to be 289 K, which is in good agreement with our experimental measurement of the strong room temperature ferromagnetism at room temperature, 1241.5 Oe coercivity and 33.3 emu $g^{-1} M_s$ at room temperature.

The deduced coercive field can be further estimated by the formula $\mu_0 H_C = \Delta E/M_S V.^{48}$ In this study, M_S is 33.3 emu g⁻¹ and *V* is 113.0 nm³ for 6 nm Co nanoparticles. A coercivity $\mu_0 H_C$ can be obtained to be 0.178 T (equal to 1780 Oe). If considering the uncertain parameters during the estimated calculation, this value is in a satisfied agreement with the measured value of 1433.5 Oe. Therefore, it is concluded that the strong room temperature ferromagnetic behavior of the bimagnetic h-Co/h-CoO nanotetrapods should come from beating the superparamagnetic limit of the decorated Co nanoparticles with exchange bias.

3. Conclusion

In conclusion, we have demonstrated a fabrication of welldefined bimagnetic h-Co/h-CoO nanotetrapods using a onepot thermal decomposition method. Individual h-Co/h-CoO nanotetrapods are formed by four nanopods branching out at tetrahedral angles from a central region, to which multiple tiny Co nanoparticles are randomly interconnected or embedded into. The h-CoO nanotetrapod skeletons and Co particles both are proved to be hexagonal in structure. Each pod of individual nanotetrapods is a single crystal with the same [001] orientation along with pod axis and the four pods

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grows together by twinning with a (110) twin interface and 120° spatial boundary angle. The saturated magnetization and coercivity of the bimagnetic h-Co/h-CoO nanotetrapods are measured to be 33.3 emu g^{-1} and 1241.5 Oe at room temperature, revealing a surprisingly strong room temperature ferromagnetism. SQUID experiments proved that there is weak exchange coupling (-83.5 Oe exchange bias field) induced by the interfacial layers between h-CoO nanotetrapod skeletons and the decorated Co tiny nanoparticles. Theoretical analysis indicate that the strong room temperature ferromagnetic behavior should originate from beating the superparamagnetic limit of the Co nanoparticles decorated on the CoO nanotetrapod skeleton with exchange bias. This work provides not only a smart functional 3D nanoarchitecture of novel bimagnetic h-Co/h-CoO nanotetrapods as building block in nanoelectronics and nanosensors, but also an ideal specimen for a further understanding of weak antiferromagnetic-ferromagnetic interaction.

4. Experimental section

4.1. Synthesis of h-Co/h-CoO nanotetrapods

2 mmol cobalt(II) acetylacetonate (Co(acac)₂, 99%, Aldrich, USA) and 10 mmol 1,2-dodecanediol (90%, TCI, Japan) were dissolved in 20 ml 1-octadecene (90%, Alfa, USA) and magnetically stirred under a flow of argon. The mixture was heated to 120 °C for 1 h to dehydrate, and then heated to 200 °C and 320 °C and maintained at the temperature for 1 h and 2 h, respectively, while magnetically stirred under a flow of argon during the entire procedure. Finally the reaction solution was cooled to room temperature. The materials were separated *via* centrifugation (13 000 rpm, 6 min) with isopropyl alcoholhexane (1:1 vol) for several times to purify the products. The final products were removed from solvent and re-dispersed in hexane.

4.2. Characterization

The morphological, crystal structural and chemical characterization of the h-Co/h-CoO nanotetrapods were analyzed at the nanoscale using high-resolution field emission transmission electron microscopy (HRTEM, Tecnai[™] G² F30, FEI), high angle annular dark field and scanning transmission electron microscope (HAADF-STEM), selected area electron diffraction (SAED), EDX mapping and X-ray diffraction (XRD) instrument using Cu K α radiation (λ = 1.5418 Å) (X'pert powder, Philips). The three-dimensional architectures of the h-Co/h-CoO nanotetrapods were dynamically observed by a high angle tilting experiment with TEM. The chemical composition and atomic bonding states were analyzed by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD, Japan). The magnetic properties were measured by a vibrating sample magnetometer (VSM, Microsence VSM EV9, USA) at room temperature and superconducting quantum interference device (SQUID, MPMS-XL, Quantum Design, USA) magnetometer at 2 K after cooling in 50 kOe FC and zero field cooling ZFC.

4.3. Three-dimensional architecture investigation

A series of images was obtained by an angle tilting experiment using transmission electron microscope from -36° to 36° with 2° tilt increments at 49 000 times magnification with a 2048 × 2048 pixel CCD camera. The images were edited to a visualization video to investigate the 3D geometrical morphology.

Acknowledgements

This work was supported by National Basic Research Program of China (2012CB933104), National Natural Science Foundation of China (11274145 and 11034004), Program for Changjiang Scholars and Innovative Research Team in University (grant no. IRT1251), the Fundamental Research Funds for the Central Universities (lzujbky-2013-19, and 2022013zrct01).

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