Electronic Supplementary Material (ESI) for Nanoscale.

Designing Shape Anisotropic $SmCo_5$ Particles by Chemical Synthesis to Reveal Morphological Evolution Mechanism

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Experimental Procedures

Synthesis of SmCo-C_2O_4: The precursor was synthesized *via* co-precipitation of samarium chloride hexahydrate ($SmCl_3 \cdot 6H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and sodium oxalate ($Na_2C_2O_4$) with Sm : Co molar ratio of 1 : 3.2. In a typical synthesis, 0.5000 g of $Co(NO_3)_2 \cdot 6H_2O$, and 0.1959 g of $SmCl_3 \cdot 6H_2O$ were dissolved in 70 ml of deionized water. Then, the mixture was loaded into a 250 ml three-neck bottle with vigorous mechanical stirring. 0.3719 g of $Na_2C_2O_4$ (10% excessive) was dissolved in 30 ml of deionized water. At room temperature, under mechanical stirring and ultrasonic concussion, $Na_2C_2O_4$ solution was added to the solution dropwise for 5 min. After the reaction ran for 1 h, the mixture was centrifuged at 5000 rm for 3 min. The precipitate was twice rinsed in deionized water to wash away sodium chloride (NaCl) or sodium nitrate ($NaNO_3$) and extra $Na_2C_2O_4$. The precipitate was further washed with anhydrous alcohol and dried at room temperature to obtain a mixture of $Sm_2(C_2O_4)_3 \cdot 10H_2O$ and $CoC_2O_4 \cdot 2H_2O$.

Synthesis of SmCo-C_2O_4/CaC_2O_4: A similar procedure was operated like the preparation of SmCo-C_2O_4, and the difference is the extra addition of 0.5000 g $Ca(NO_3)_2 \cdot 4H_2O$. In a typical synthesis, 0.5000 g of $Co(NO_3)_2 \cdot 6H_2O$, 0.1959 g of $SmCl_3 \cdot 6H_2O$ and 0.5000g $Ca(NO_3)_2 \cdot 4H_2O$ were dissolved in 70 ml of deionized water in a 250 ml three-neck bottle. 0.6840 g of $Na_2C_2O_4$ was dissolved in 30 ml deionized water. The co-precipitation, with the assistance of ultrasonic concussion, was carried out to obtain a mixture of $Sm_2(C_2O_4)_3 \cdot 10H_2O$, $CoC_2O_4 \cdot 2H_2O$, and $CaC_2O_4 \cdot 2H_2O$ with a Sm/Co ratio of 1:3.2. To prepare SmCo-C_2O_4/CaC_2O_4 with different Sm/Co ratios, the amount of $SmCl_3$ was changed while keeping the amounts of $Co(NO_3)_2$ and $Ca(NO_3)_2$ constant at 0.5000 g. Quantities of 0.2506 g, 0.2089 g, 0.179 g, 0.1567 g, 0.1253 g and 0.0895 g

$SmCl_3 \cdot 6H_2O$ were used to synthesize SmCo-C_2O_4/CaC_2O_4 with Sm/Co ratios of 1:2.5, 1:3.0, 1:3.5, 1:4, 1:5 and 1:7, respectively.

Synthesis of $SmCo_5$ particles: For the synthesis of $SmCo_5$ particles, previously prepared precursor powders were mixed with 3.0 g of calcium (Ca) powders and 1.0 g of anhydrous potassium chloride (KCl). Subsequently, the mixture was transferred to a tungsten crucible which was then moved into a steel tube and degassed three times to remove air and moisture. The tube was flushed with Ar and heated to different temperatures (890 °C, 910 °C, 930 °C and 950 °C) at a rate of 8 °C·min^{-1}. The reaction was maintained for 90 min before cooling down to room temperature within 1 h. Afterwards, the product was washed with deionized water and 5% chlorhydric acid to dissolve CaO, KCl, and extra Ca. A black powder was obtained by centrifuging at 8000 r/min for 3 min. The powder was further washed with deionized water and ethanol and dried under vacuum for further usage.

Annealing of SmCo-C_2O_4: SmCo-C_2O_4 precursors with Sm/Co of 1:3.2 without addition of Ca and KCl were placed in alumina boat and the boat was put in tube furnace which was degassed for 3 times to remove air and moisture. The temperature was raised to 500 °C and 700 °C at a heating rate of 8 °C·min^{-1} and kept for 1.5 h under an Ar atmosphere. After cooling the mixture down to room temperature, the mixture of Co and Sm_2O_3 was obtained.

Characterization: The crystallographic structure was identified by X-ray diffraction (XRD, D/MAX 2200 PC) with Cu-K_α radiation (λ=0.15418 nm). The microstructure and morphology of the above samples were investigated using scanning electron microscopy (SEM, ZEISS - SUPRA55) and transmission electron microscopy (TEM, Tecnai G2 F20). The magnetic properties were measured at room temperature using a Physical Property Measurement System (PPMS) under

a maximum applied field of 70 kOe. To obtain aligned samples, the cylindrical samples were prepared by mixing the as-prepared $SmCo_5$ powders with epoxy, which would solidify slowly when the samples were aligned in static magnetic field of 2.2 T.

Supplemental Data

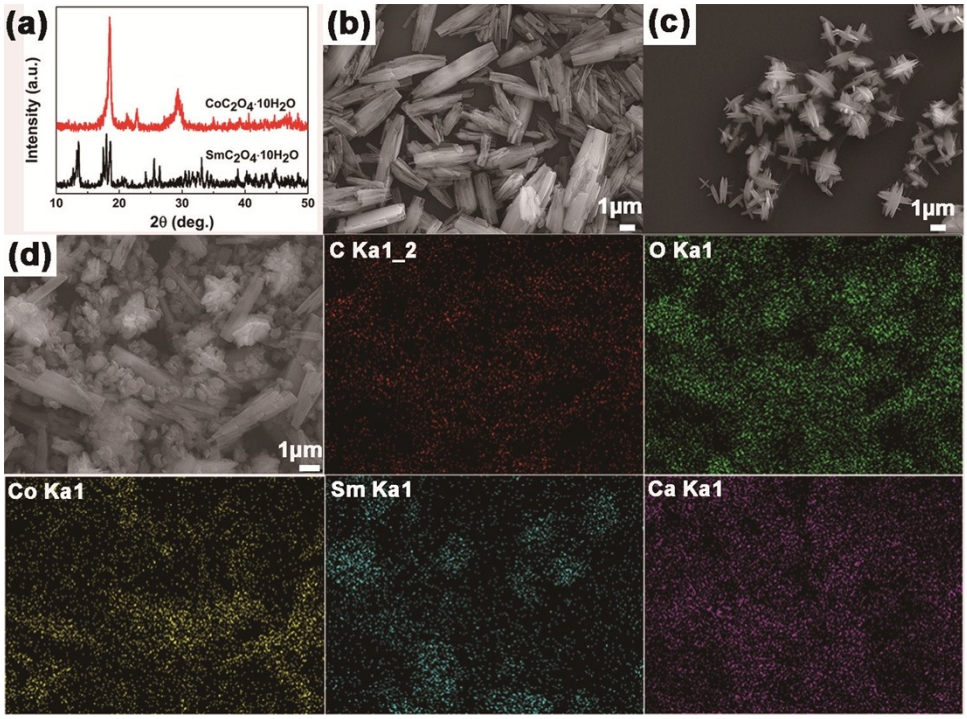

Fig. S1 (a) XRD patterns of single $Sm_2(C_2O_4)_3·10H_2O$ and $CoC_2O_4·2H_2O$; (b) SEM image of $CoC_2O_4·2H_2O$; (c) SEM image of $Sm_2(C_2O_4)_3·10H_2O$; (d) SEM image of SmCo-C_2O_4/CaC_2O_4 and corresponding elemental mapping.

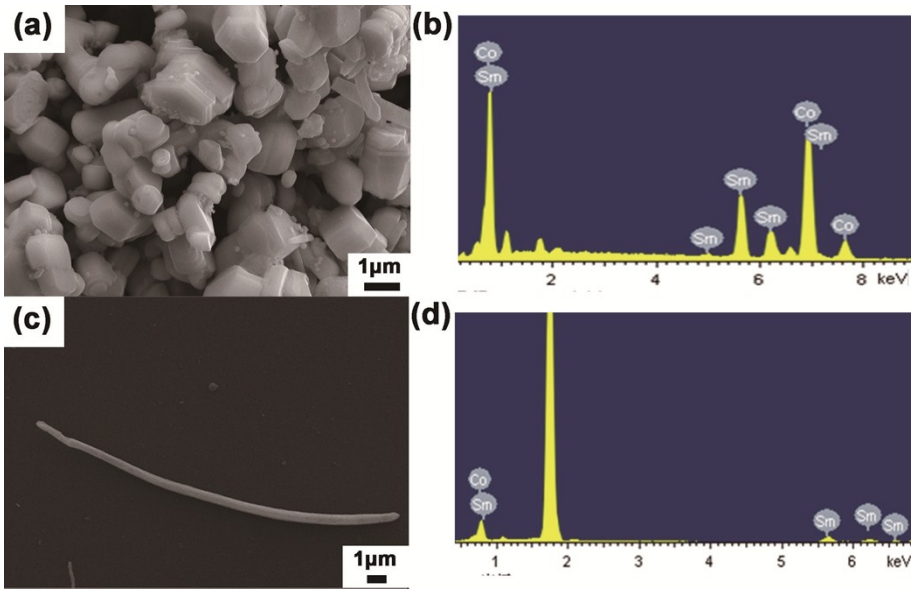

Fig. S2 (a) SEM images of hexagonal$SmCo_5$particles prepared by reductive annealing of SmCo-C_2O_4/CaC_2O_4 with Sm/Co ratio of 1:3.2; (b) corresponding EDS of (a) with measured Sm/Co ratio of 1:4.21; (c) single $SmCo_5$ rod in another view; (d) corresponding EDS of (c) with measured Sm/Co ratio of 1:4.3.

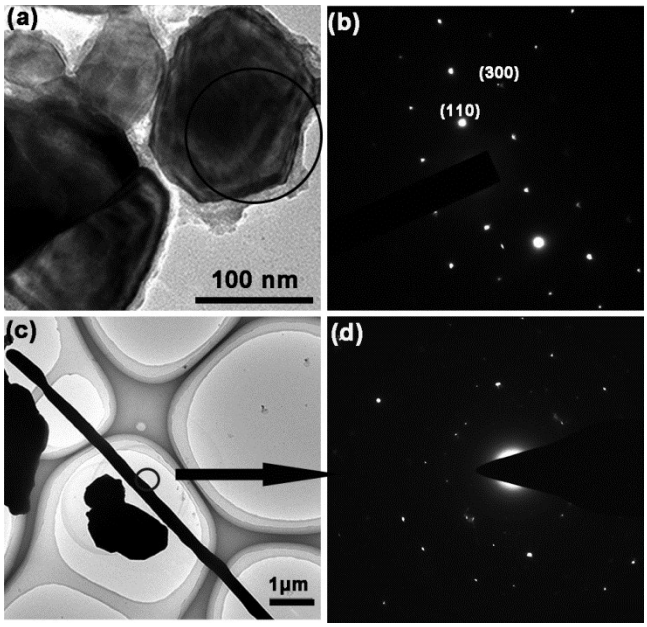

Fig. S3 (a) TEM images of hexagonal particles in $SmCo_5$ prepared by reductive annealing of $SmCo\text{-}C_2O_4/CaC_2O_4$ with Sm/Co of 1:3.2; (b) corresponding SAED of (a), which exhibitssymmetric hexagonal diffraction spotand implies single structure, suggesting hexagonal planes perpendicular tothe direction of the *c*-axis; (c) $SmCo_5$ rod in another view; (d) corresponding SAED of (c), demonstrating polycrystalline structure in circled field of (c).

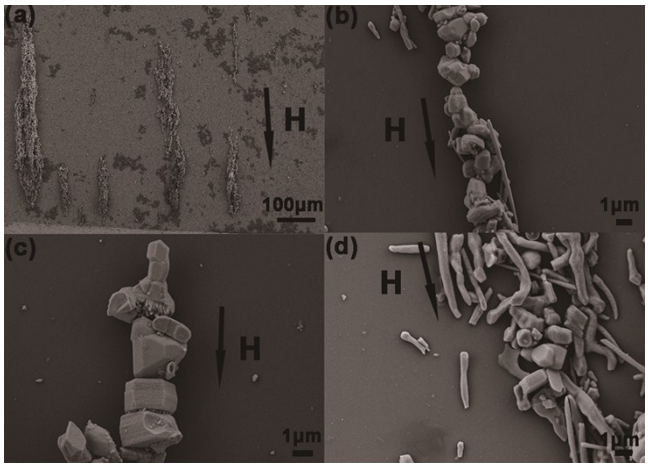

Fig. S4 SEM images of magnetically aligned $SmCo_5$ particles. (a) low-magnification image; (b) high-magnification image which implies that hexagonal particles and rodsare well-arrayed along the magnetic field direction; (c) high-magnification image in different view which describes well-arrayed $SmCo_5$ hexagonal particles; (d) high-magnification image in different view which demonstrates that most of rods have uniform directions along the magnetic field direction.

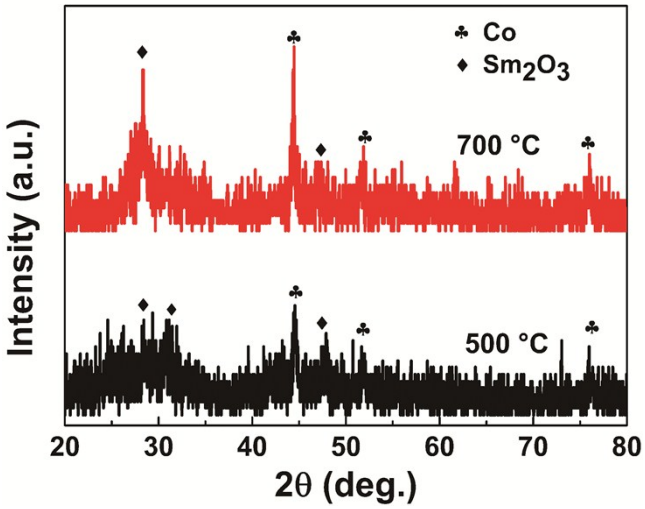

Fig. S5 XRD patterns of SmCo-C_2O_4, without Ca addition, annealed at different temperatures.

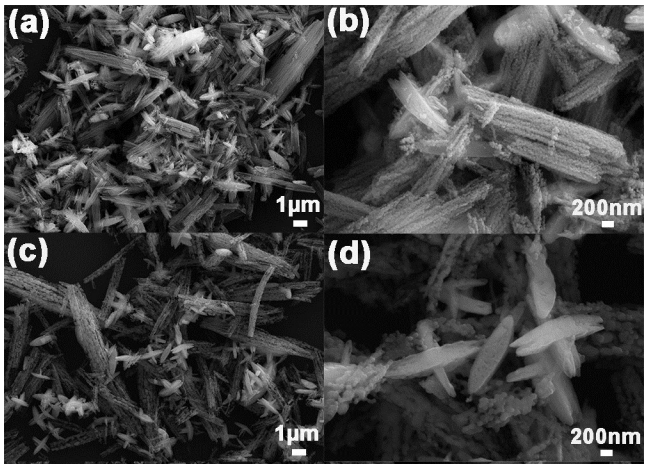

Fig. S6 SEM images of SmCo-C_2O_4, without Ca addition, annealed at different temperatures: (a)-(b) 500 °C; (c)-(d) 700 °C.

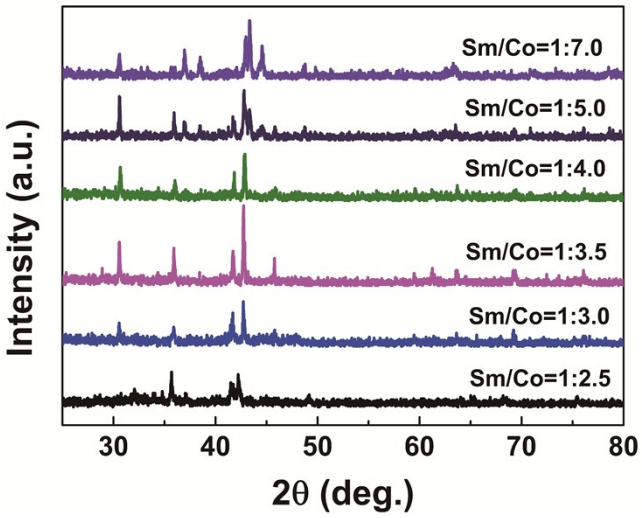

Fig. S7 XRD patterns of SmCo alloys prepared by reductive annealing of SmCo-C_2O_4/CaC_2O_4 with different Sm/Co ratios at 930 °C.

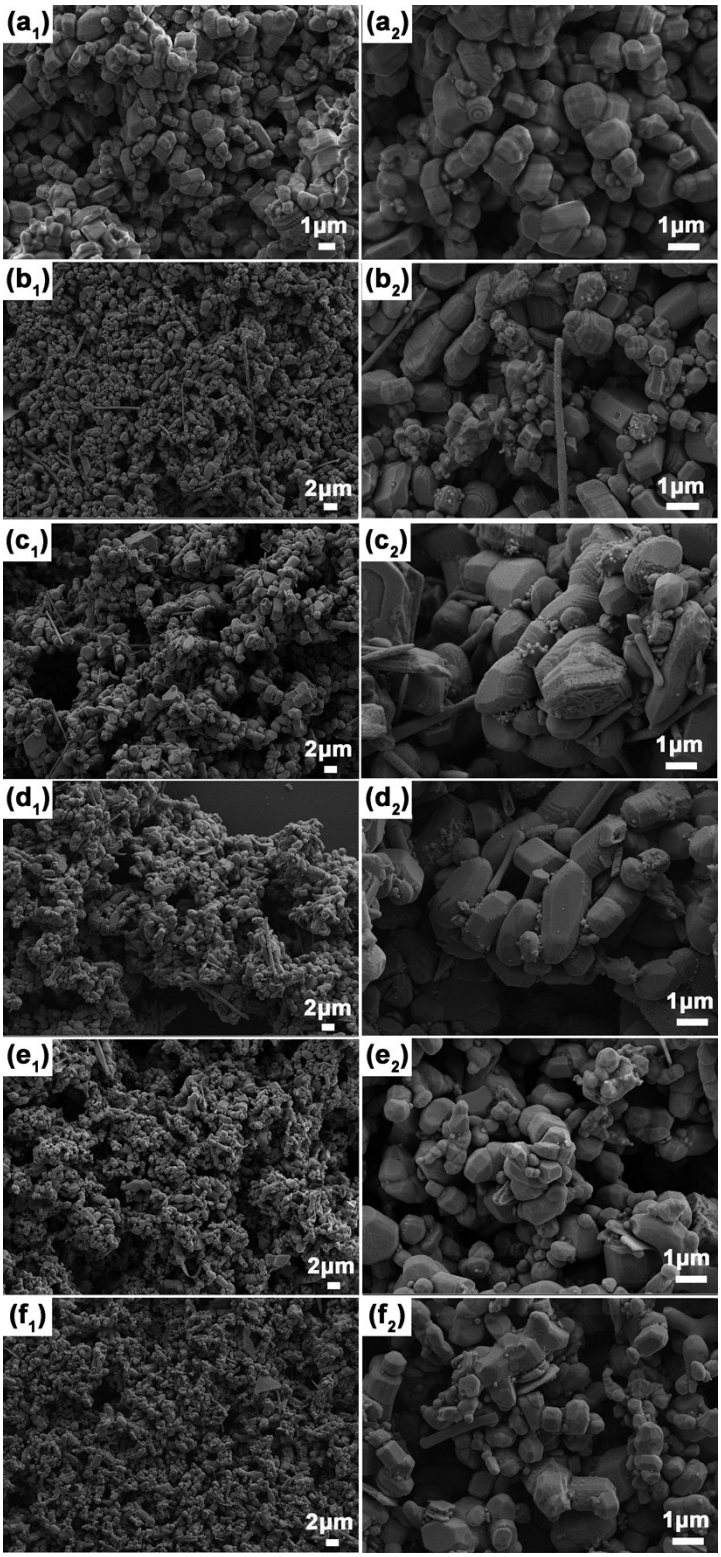

Fig. S8 SEM o of SmCo alloys prepared by reductive annealing of SmCo-C_2O_4/CaC_2O_4 with different Sm/Co ratios at 930 °C: (a1) 1:2.5; (b1) 1:3.0; (c1) 1:3.5; (d1) 1:4.0; (e1) 1:5.0; (f1) 1:7.0, where (a2)-(f2) is the corresponding magnified images of (a1)-(f1), respectively.

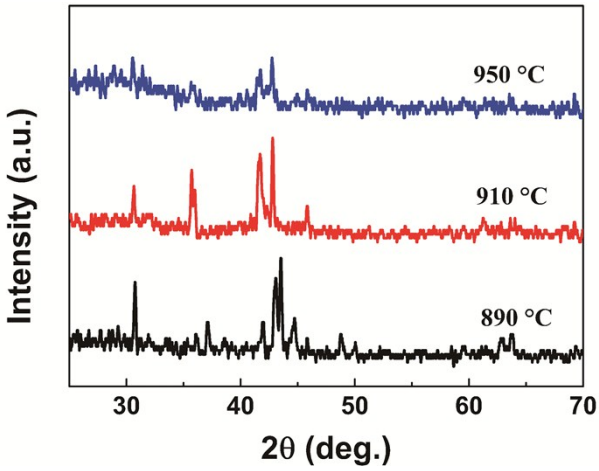

Fig. S9 XRD patterns of SmCo alloys prepared by reductive annealing of SmCo-C_2O_4/CaC_2O_4 with Sm/Co of 1:3.2 at different temperatures.

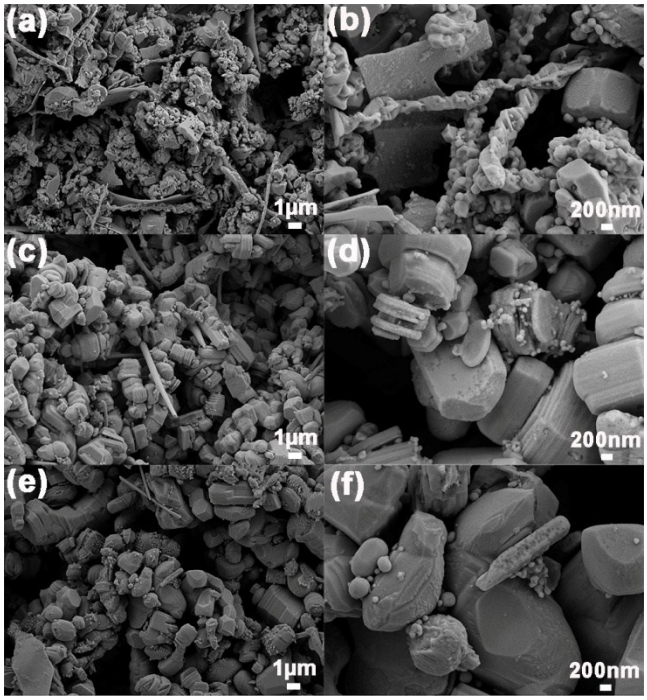

Fig. S10 SEM images of SmCo alloys prepared by reductive annealing of SmCo-C_2O_4/CaC_2O_4 with Sm/Co of 1:3.2 at different temperatures: (a)-(b) 890 °C; (c)-(d) 910 °C; (e)-(f) 950 °C.