Metal-semiconductor hybrid nanostructure Ag-Zn_{0.9}Co_{0.1}O:

synthesis and room-temperature ferromagnetism

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Supporting Online Materials

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1. XRD, XPS, EDX, and TEM measurements of Ag-Zn_{0.9}Co_{0.1}O hybrid nanostructure and Zn_{0.9}Co_{0.1}O nanorods

(1) Material preparation and characterization

In a typical synthesis, 10 mmol of Zn(Ac)₂·2H₂O and 1.11 mmol of Co(Ac)₂·4H₂O were dispersed into 100 mL ethanol with stirring. A well-controlled amount of 0.1 mol/L ethanol solution of AgNO₃ was carefully added to the above suspension which was then mixed with 50 mL of 1 mol/L NaOH solution in ethanol under magnetically stirring at room temperature. The mixture was sealed in 25 mL Teflon-lined stainless steel autoclaves and to react at 120 °C for 2 hours. When the reactions were complete, the final products were sufficiently washed and then dried at ambient conditions.

The parallel experiment was performed under identical condition, which was conducted as follows: 10 mmol of Co(Ac)₂·4H₂O were dispersed into 100 mL ethanol, which was mixed with a well-controlled amount of 0.1 mol/L ethanol solution of AgNO₃. 50 mL of 1 mol/L NaOH was added into the above suspension under magnetic stirring at room temperature. The mixture was sealed in 25 mL Teflon-lined stainless steel autoclaves and to react at 120 °C for 2 hours.

For comparative study of the origin of the room-temperature ferromagnetism of hybrid nanostructure, films of Zn_{0.9}Co_{0.1}O nanorods with a diameter of 6 nm and thickness of 1 nm were physically coated with Ag by a thermal evaporation method under a vacuum of 5×10⁻³ Pa at a baking temperature of 63 °C.

The structures of the samples were determined by x-ray diffraction (XRD) with Cu K α radiation at room temperature. Nickel, with a purity of 99.99%, was used as the internal standard for peak position determinations. The morphologies and microstructures of the samples were investigated by a transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) on a JEM-2010 apparatus with an acceleration voltage of 200 kV. The chemical compositions of the samples were examined with an energy-dispersive X-ray spectrometer (EDX) analysis. The optical absorption spectra of the samples were obtained using a Lambda 900 UV/VIS spectrophotometer. The magnetic properties of the samples were measured using a Quantum Design PPMS-7 magnetometer. The valence states of Co ions in our samples were determined by x-ray photoelectron spectroscopy (XPS) on an ESCA-LAB MK II X-ray photoelectron spectrometer (VG Co.) with Al K α radiation. The base pressure is 5×10⁻⁹ Pa. The C1s signal was used to correct the charge effects on the sample surfaces.

(2) XRD

Figure S1 XRD patterns of Ag-Zn_{0.9}Co_{0.1}O hybrid nanostructure with given Ag contents. Peaks marked by (●) are indexed to the fcc silver. Lattice parameters of the primary phase of our hybrid nanostructures were calculated using Retica Rietveld program. It is found that the cell dimensions were slightly smaller than those of pure ZnO, e.g., the lattice parameters for 1%Ag-Zn_{0.9}Co_{0.1}O are $a=0.32520(2)$ nm, $c=0.52066(3)$ nm, and $V=0.04769(3)$ nm³, which compare to those of $a=0.32527(3)$ nm, $c=0.52093(2)$ nm, and $V=0.04773(1)$ nm³ for pure ZnO. This observation is consistent with the ionic size consideration, since Co²⁺ has an ionic radius of 0.058 nm which is slightly smaller than 0.060 nm for Zn²⁺ in 4-fold coordination. In combination with our EDX analyses (Figure S4), the semiconductor of our hybrid nanostructure is a solid solution Zn_{0.9}Co_{0.1}O.

(3) XPS

Figure S2 Co₂p core level XPS of hybrid nanostructure Ag(1%)-Zn_{0.9}Co_{0.1}O and nanorods Zn_{0.9}Co_{0.1}O. Both XPS spectra are characterized by Co₂p_{3/2} peak at 779.4 eV. It is noted that no any apparent signal was observed at about 778 eV for metallic Co. The difference in binding energy between Co₂p_{3/2} and Co₂p_{1/2} is about 15.4 eV, which is very close to that for standard Co²⁺ [J. F. Moulder, W. F. Stickle, et al., in Handbook of X-ray Photoelectron Spectroscopy (Ed: J. Chastain), Perkin Elmer, Eden Prairie, MN 1992, p83]. These results confirmed the absence of metallic Co in our samples. It should be mentioned that, owing to the lower concentration and smaller scattering ability of Co²⁺ ions, the XPS data of our hybrid nanostructures are generally showing a somewhat high noise.

(4) TEM

Figure S3 (a) TEM images showing various individual metal-semiconductor hybrid nanostructures and (b) HRTEM image of an enlarged individual hybrid nanostructure. The interplanar spacing of 0.285 nm for Zn_{0.9}Co_{0.1}O nanorod is close to that between two adjacent (100) planes of pure ZnO, and that of 0.236 nm for rod Ag tip is compatible with the separation of Ag (111) planes.

(5) EDX

(a)

(b)

Figure S4 EDX line scanning (a) and spot analysis (b) of Ag-Zn_{0.9}Co_{0.1}O hybrid nanostructure.

2. M-H and χ_g -T curves of hybrid nanostructure and nanorods

Figure S5 (a) Experimental magnetization curves and (b) ferromagnetic and paramagnetic components of $\text{Ag}(1\%)\text{-Zn}_{0.9}\text{Co}_{0.1}\text{O}$ at 300K (blue), 110K (red), and 50K (green). (c) Temperature dependence of paramagnetic susceptibility obtained by nonlinear least-square fit of the initial magnetization curve of $\text{Ag}(1\%)\text{-Zn}_{0.9}\text{Co}_{0.1}\text{O}$ using Langevin equation. Open hysteresis loops in Figure (a) are clearly seen to show a “potbelly” shape, which indicates the presence of ferromagnetic component intermixed with a paramagnetic one (Figure b). Susceptibility data exactly followed the Curie-Weiss law from 50 to 335K (Figure c). Curie-Weiss constant listed in Figure

(c) suggested that the paramagnetic component is intrinsic for $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods. Susceptibility data $<50\text{K}$ deviated from Curie-Weiss law, which is probably associated with a magnetic transition as indicated in Figure S6 (a).

Figure S6. (a) Temperature dependence of mass susceptibility of $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods and the corresponding magnetization curves measured at (b) 300 K and (c) 5 K. The reciprocal of mass susceptibility in Figure (a) is linearly dependent on temperature ($50\text{K} < T < 300\text{K}$), indicating a paramagnetic nature as is confirmed by magnetization

curve of Figure (b). Based on the Curie-Weiss law, $\chi_g = C_g / (T - \theta)$, the Curie-Weiss temperature, θ , and constant, C_g , are obtained and listed in Figure (a). The effective moment of Co^{2+} was calculated to be $3.73\mu_B$, which is close to the theoretical value of $3.87\mu_B$. As the temperature decreased to 5K, the magnetization curve exhibited a super-paramagnetic behavior (Figure c). It is also noted from Figure (a) that the susceptibility data deviated from the Curie-Weiss law at lower temperatures, which is most likely due to the paramagnetic-superparamagnetic transition. In addition, the films of $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods physically coated with Ag also showed a paramagnetic curve as observed in Figure (b) for bare $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods.

3. Schematic level diagram of hybrid nanostructure and nanorods

Figure S7 Schematic level diagram for Ag, $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods, and $\text{Ag-Zn}_{0.9}\text{Co}_{0.1}\text{O}$ hybrid nanostructure