Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Self-Assembled Vertically Aligned Ni Nanopillars in CeO_2 with Anisotropic Magnetic and Transport Properties for Energy Applications

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Experimental

The Ni-CeO_2 nanocomposite target was prepared by a conventional solid-state mixing, followed by sintering process. Specifically, high-purity Ni and CeO_2 powders were mixed and pressed into a pellet (d=0.5 in), then it was sintered at 1200 °C for 6 hours, with inflowing Ar. The Ni-CeO_2 nanocomposite films were deposited by a single composite target and the YBCO film was grown by a YBCO target. All the films were deposited on single crystal STO (001) substrates, using a pulsed laser deposition (PLD) system with a KrF excimer laser (Lambda Physik, λ = 248 nm). The laser energy density was 3 J/cm^2 and the base pressure for all the depositions reached less than 1×10^{-6} Torr in vacuum with the target-substrate distance kept at 4.5 cm. The deposition conditions for the nanocomposite films are as follows: temperature of 700 °C, laser frequency of 5 Hz and the vacuum of ~10^{-6} Torr. The deposition recipe for YBCO matrix was optimized based on previous studies, e.g. 200 mTorr of oxygen at 780 °C during deposition followed by a post-annealing process under 200 Torr of oxygen at 550 °C for 30 min to maintain the oxygen stoichiometry in YBCO films.

The crystal structure and microstructure of the films was conducted by X-ray diffraction (XRD) (PANalytical X'Pert X-ray diffractometer) and transmission electron microscopy (TEM) (FEI Talos-200X). Scanning transmission electron microscopy (STEM) imaging and energy-dispersive X-ray spectra (EDS) chemical mapping were also conducted using FEI Talos-200X. The magnetization, critical transition temperature (T_c) and critical current density were measured by a physical property measurement system (PPMS 6000, Quantum Design). The magnetic field was applied either perpendicular (out-of-plane, OP) or parallel (in-plane, IP) to the film surface. J_c *(H//c)* were measured under applied field from 0 to 5T at 75K and 65K by the vibrating sample magnetometer (VSM) in PPMS. Electrochemical Impedance Spectroscopy (EIS) was measured with Gamry G300 Potentiostat from 50 mHz to 1 MHz for both out-of-plane and in plane

geometry. For the out-of-plane measurements, the films were deposited on $SrRuO_3$ (SRO) buffered STO substrates, where SRO is used as bottom electrode. Platinum was sputtered as contacts for EIS measurement and two contacts were deposited around 3 cm apart on film surface for in plane measurement and a bottom electrode was deposited under the film for through plane measurement.

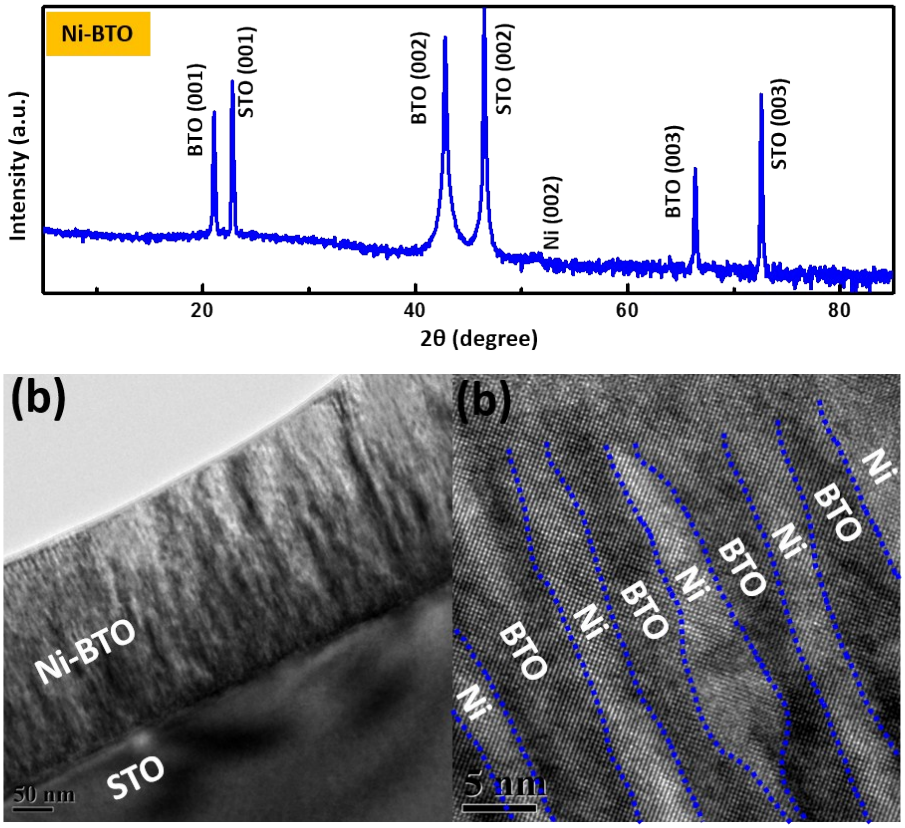

Figure S1. Crystallinity and microstructure characterizations of Ni-BTO nanocomposite thin film. (a) θ-2θ XRD scan; (b) low-mag cross-sectional TEM image; and (c) high-resolution TEM image to show the Ni and BTO phase separation.

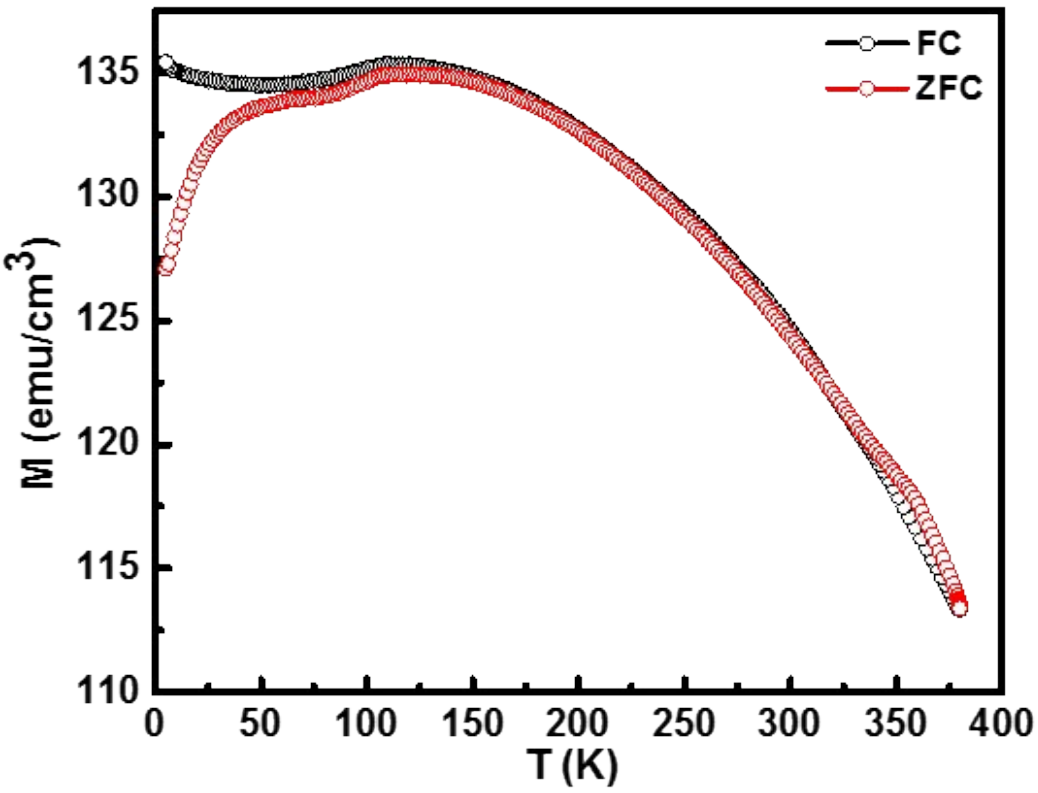

Figure S2. Temperature-dependence of magnetization of Ni-CeO_2 nanocomposite thin film measured from 5 K to 380 K. Magnetic field of 1000 Oe was applied in the IP direction during measurement.

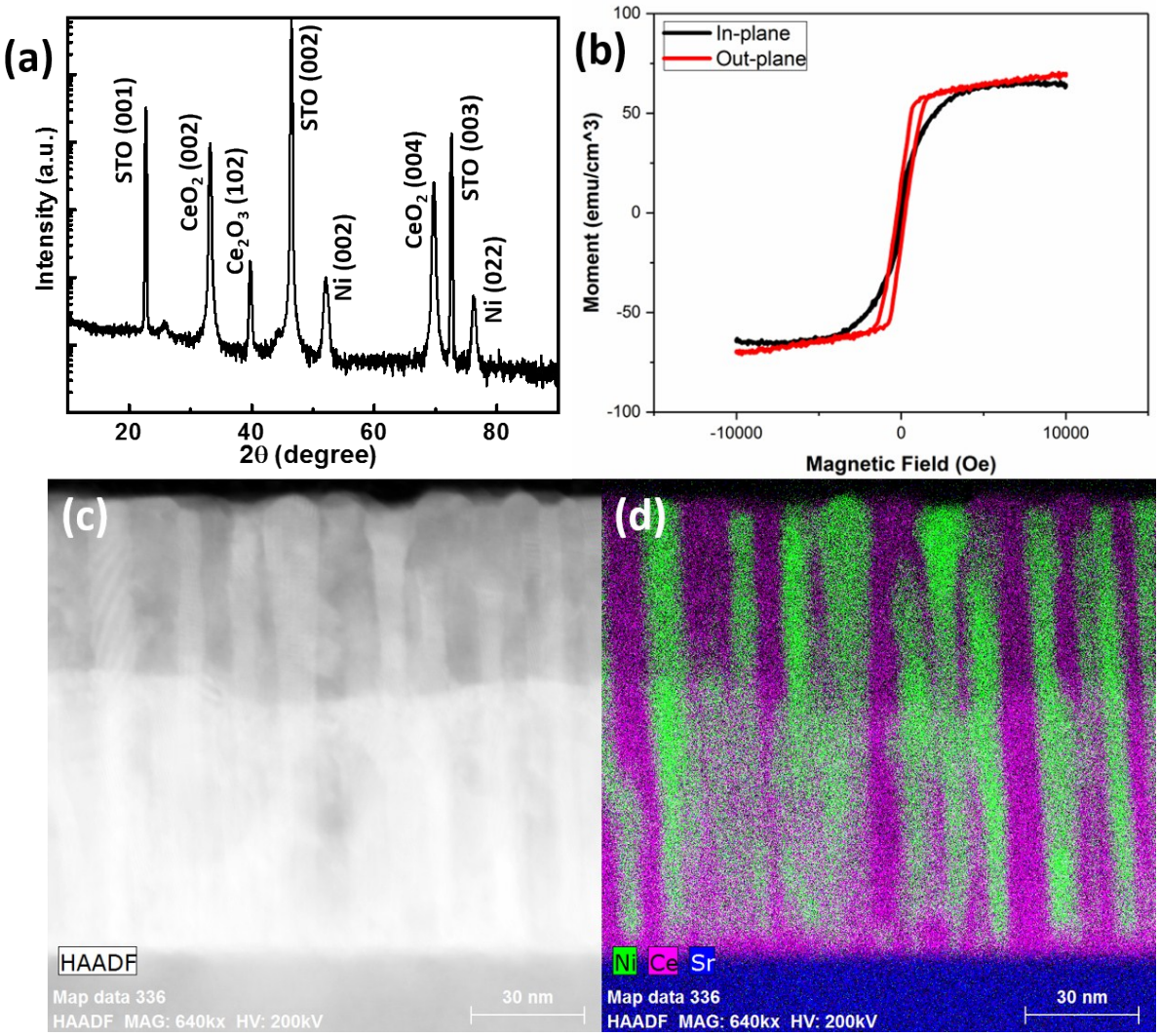

Figure S3. Characterizations of the Ni-CeO_2 nanocomposite film deposited at 750 °C. (a) θ-2θ XRD plot; (b) M-H hysteresis loops for in-plane and out-of-plane measurements; (c) STEM image and (d) corresponding EDS mapping.

To investigate the tunability of the ratio of Ni (002) and Ni (022) in the nanocomposite thin films, Ni-CeO_2 was also grown at a higher temperature of 750 °C. Fig. S3(a) presents the θ-2θ XRD scan of the sample. More interestingly, comparing to the film deposited at 700 °C, the Ni (022) peak in this sample is much stronger, which indicates more Ni (022) phase exists. The different ratio of Ni (002) and Ni (022) consequently affects the magnetic response, as shown in Fig. S3(b). However, the overall microstructure of the film is similar to the one in the main text, as shown in the STEM image in Fig. S3(c) and corresponding EDS mapping in Fig. S3(d). It is noted that an extra Ce_2O_3 (102) peak is also observed due to this higher growth temperature of 750 °C.

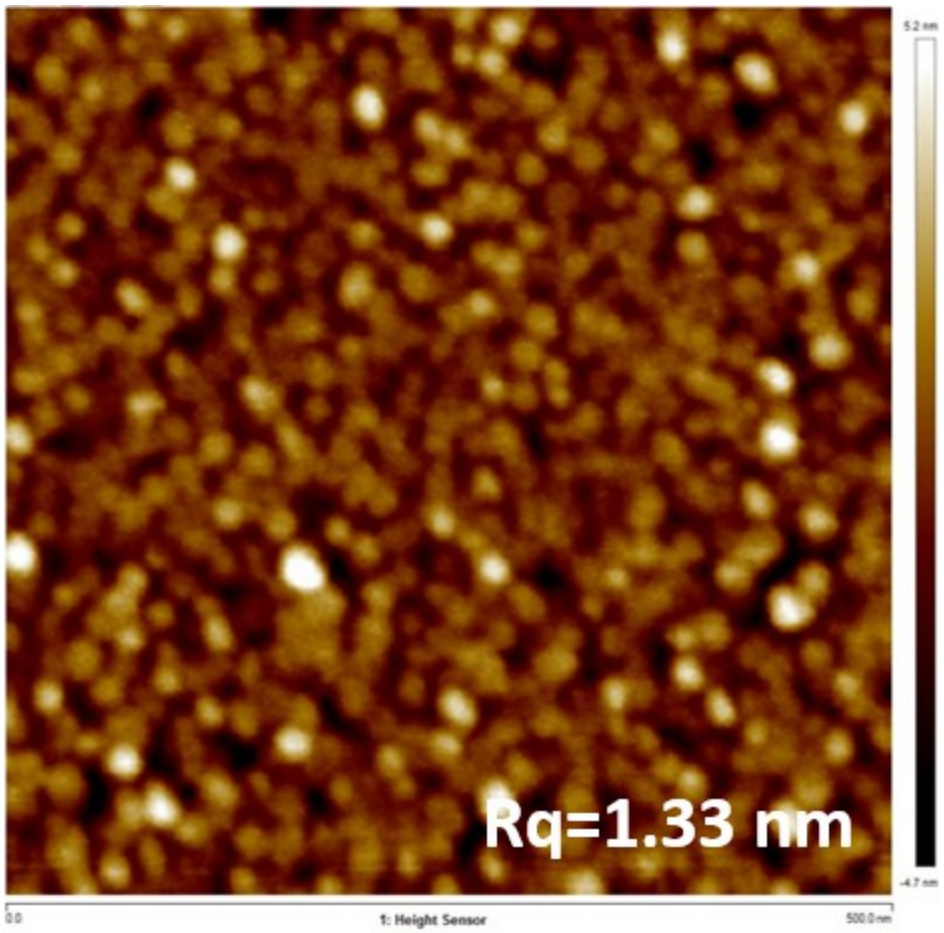

Figure S4. AFM image of the Ni-CeO2 nanocomposite thin film.

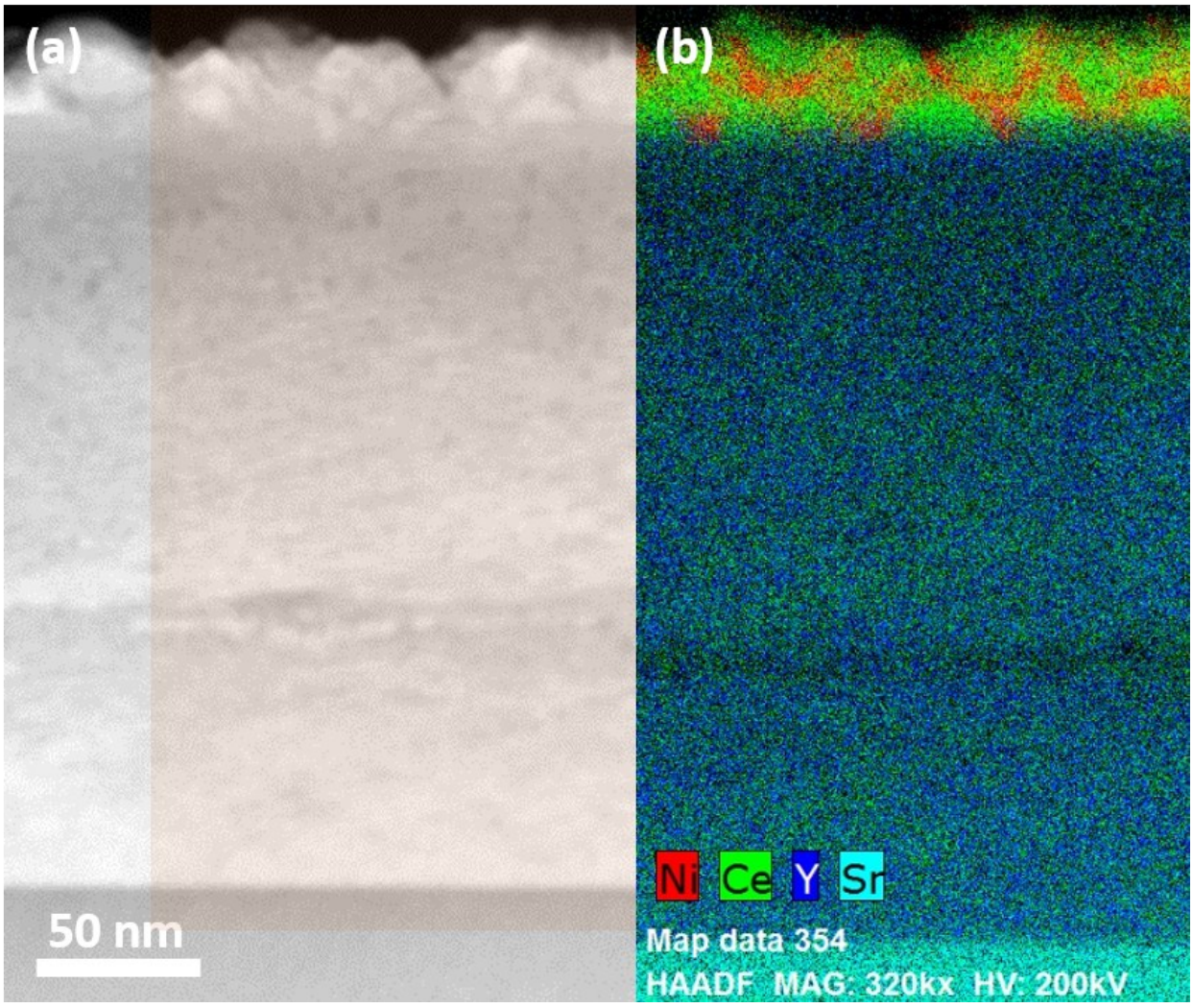

Figure S5. Microstructure characterization of Ni-CeO_2/YBCO bilayer. (a) Low-mag STEM image and (b) corresponding EDS mapping.

The microstructure of Ni-CeO2/YBCO film is carried out. A relative clean interface is observed, which indicates no or very limited inter-diffusion between the nanocomposite layer and YBCO layer.

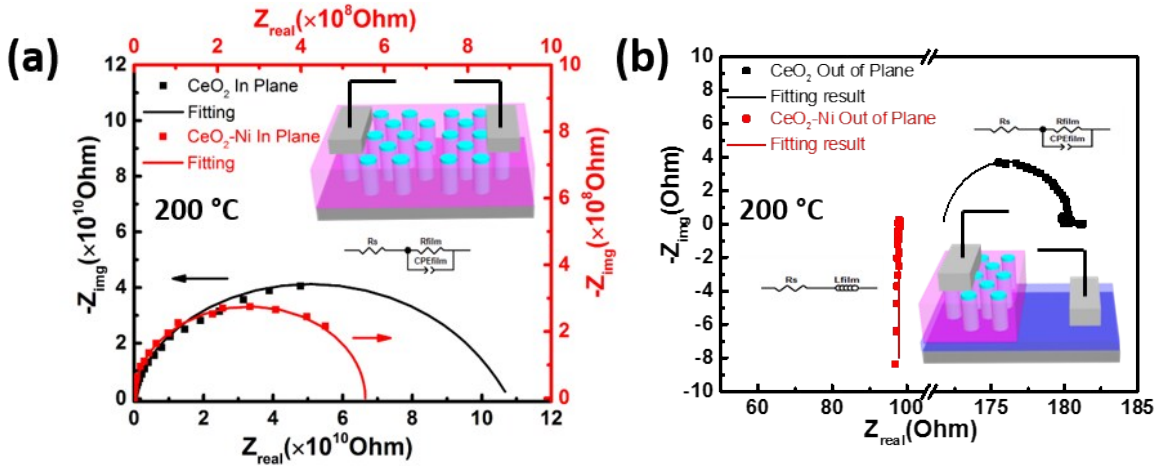

Figure S6 (a) In-plane and (c) out-of-plane EIS data and fitting result of pure CeO_2 and Ni-CeO_2 composite and their responding equivalent circuits model.