

## *Supporting Information*

### **Significantly improved hydrogen storage properties of NaAlH<sub>4</sub> catalyzed with Ce-based nanoparticles**

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The morphologies and size distribution of the synthesized Ce-based nanoparticles were investigated by TEM analysis. The as-synthesized CeB<sub>6</sub> is in size of 6-12 nm, as shown in Fig. S1(a). Some particles are agglomerated due to the high surface energy for nanoparticles. The structural details are revealed by high resolution TEM (HRTEM, Fig. S1(b)), CeB<sub>6</sub> particles are single crystals and the measured lattice fringes of ~0.41 nm correspond to the (100) plane of the CeB<sub>6</sub> simple cubic structure. This observation is in good agreement with the estimated crystallite size obtained from the XRD patterns (~ 8 nm).

Only Ce and B can be detected in the EDX results of nanoparticles (Fig. S2), implying high purity of synthesized nanoparticles. In the solution condition, the crystallization of CeB<sub>6</sub> is triggered at relatively mild temperatures, and the excessive grain and particle growth can be avoided, resulting in a narrow particle size distribution. Fig. S1(c) is the TEM image of CeF<sub>3</sub>, which exhibits a cake shape with

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size of 5-15 nm. Selected area electron diffraction (SAED) pattern exhibits diffraction rings with a hexagonal structure, in line with the XRD findings. The HRTEM image (Fig. S1(d)) shows one particle consists of more than one crystallite, in agreement with smaller grain size estimated by XRD patterns (~ 6 nm). Comparing to the well dispersion of  $\text{CeB}_6$  and  $\text{CeF}_3$ , the particles of  $\text{CeO}_2$  are more easily agglomerate, shown in Fig. S1(e) and (f), the size of which is about 6-10 nm.

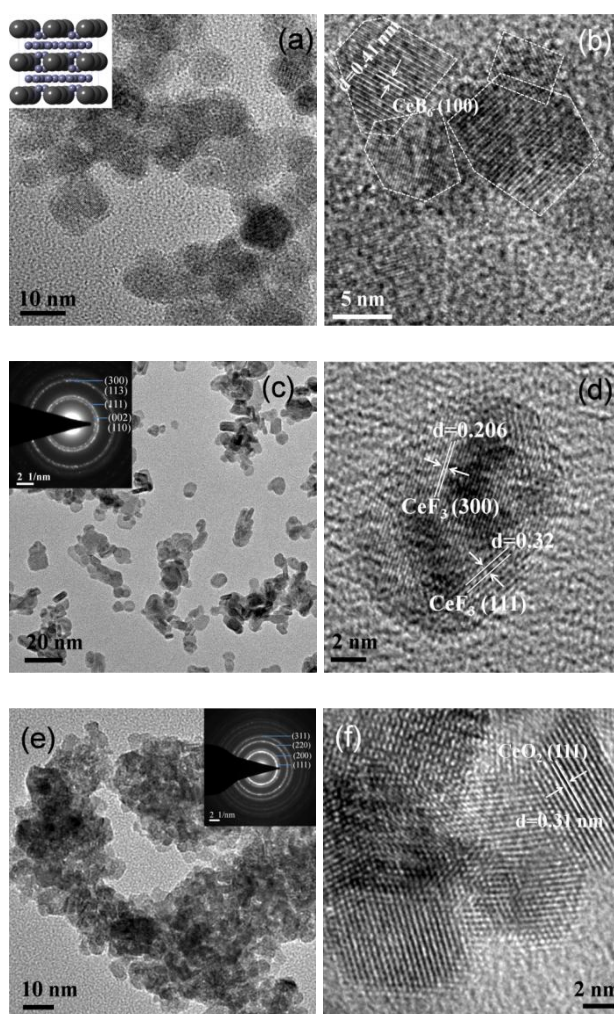


Figure S1. TEM micrographs of as-synthesized Ce-based nanoparticles: (a) bright field image of  $\text{CeB}_6$ , (b) HRTEM of  $\text{CeB}_6$ , (c) bright field image of  $\text{CeF}_3$ , (d) HRTEM of  $\text{CeF}_3$ , (e) bright field image of  $\text{CeO}_2$ , (f) HRTEM of  $\text{CeO}_2$ . Schematic depiction in (a) shows the cubic structure of  $\text{CeB}_6$ . The insets in (c) and (e) are the corresponding selected area electron diffraction (SAED) patterns.

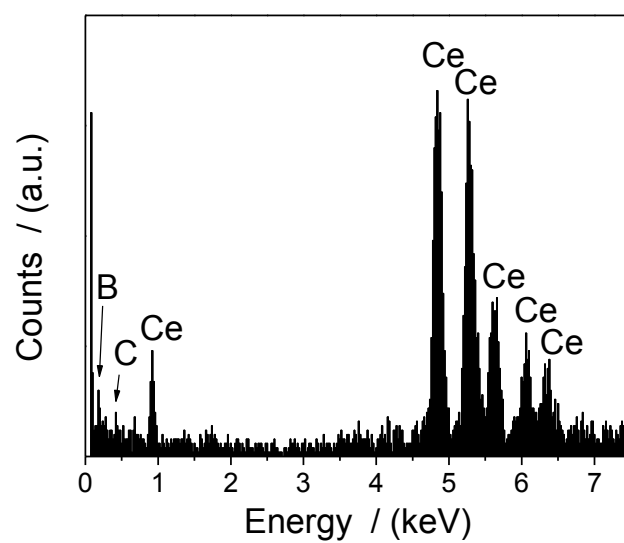
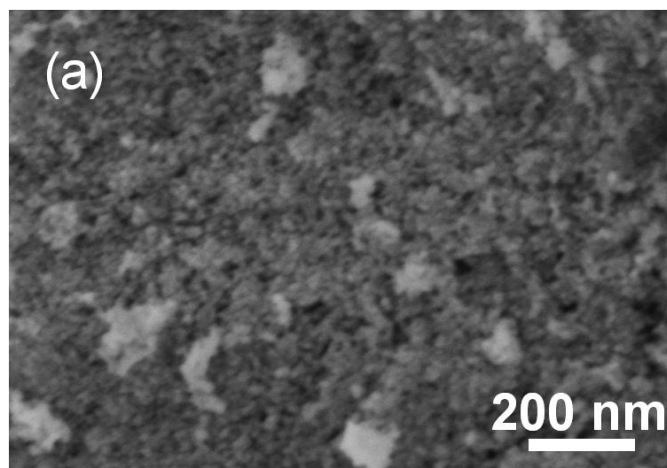


Figure S2. EDS results of  $\text{CeB}_6$  nanoparticles. The signal of carbon originates from carbon supporting film.



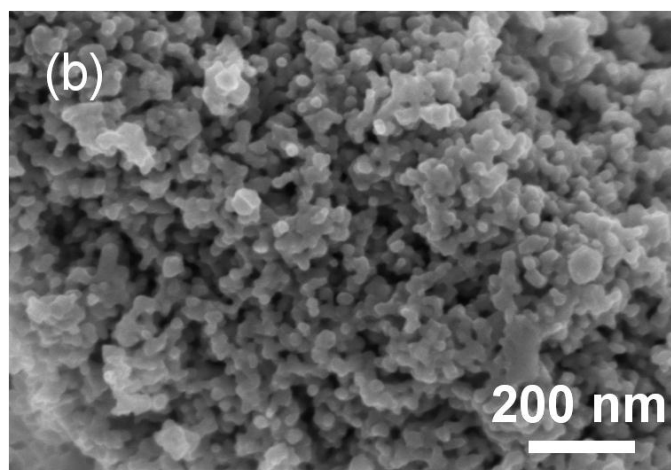
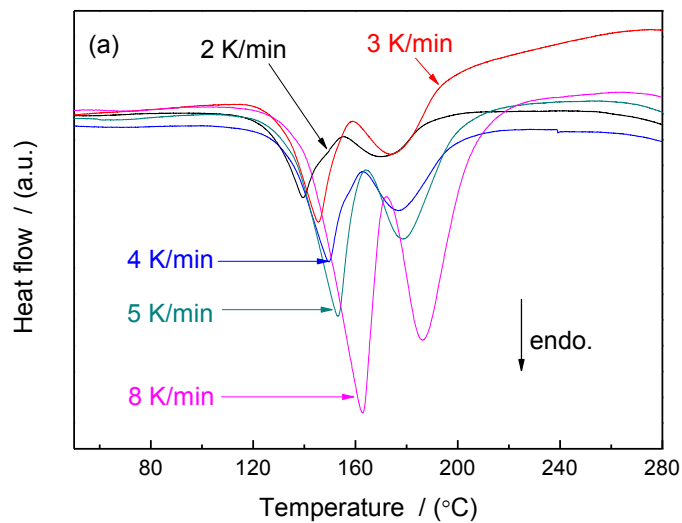


Figure S3. SEM micrographs of synthesized nano CeB<sub>6</sub> with size of about: (a) 10 nm;  
(b) 30 nm.



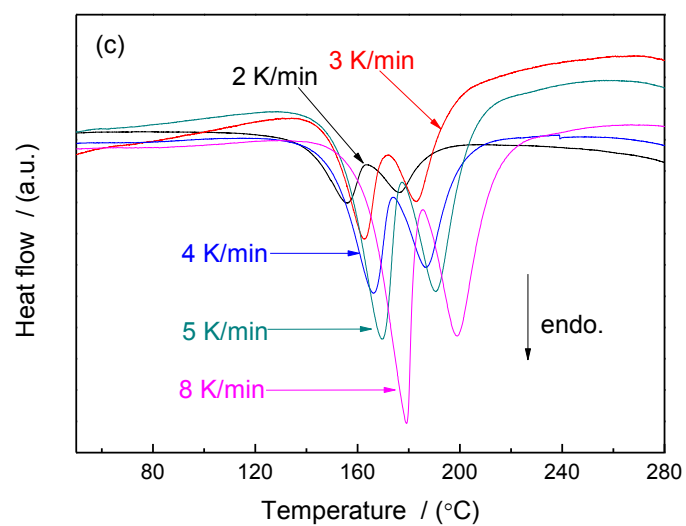
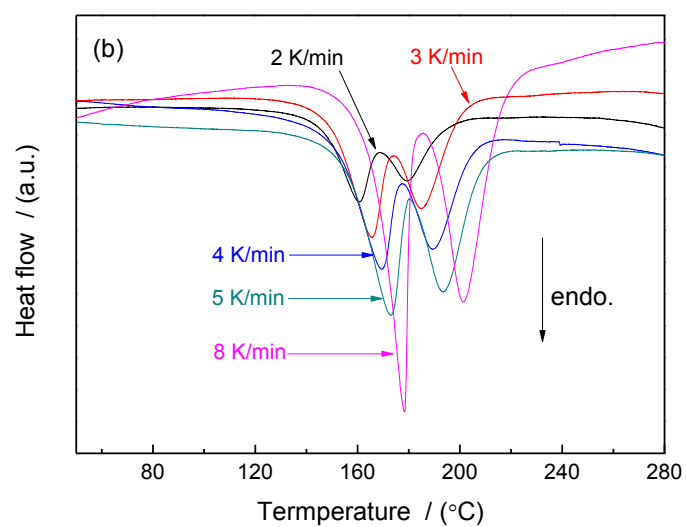


Figure S4. DSC curves of NaAlH<sub>4</sub> doped with (a) nano-CeB<sub>6</sub>; (b) nano-CeF<sub>3</sub>; (c) nano-CeO<sub>2</sub>.

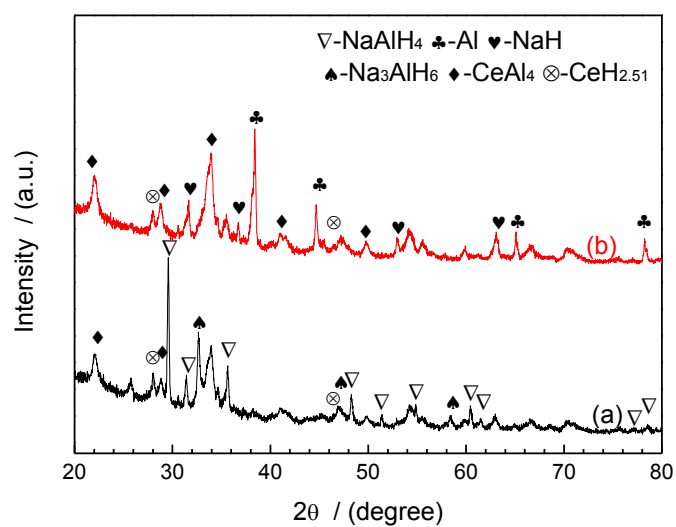
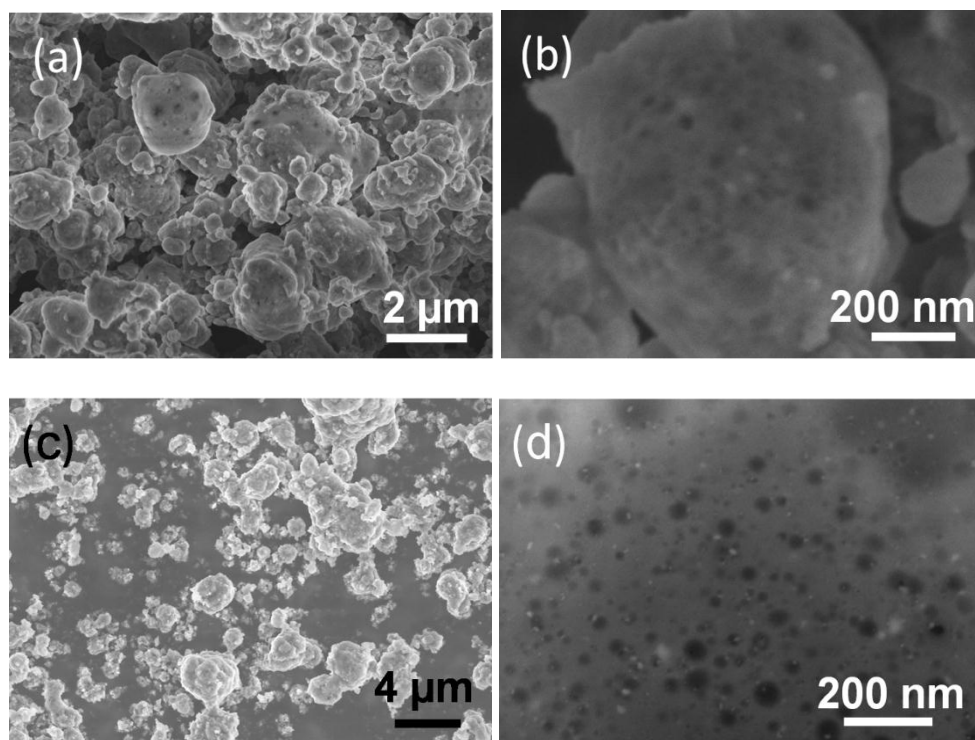


Figure S5. XRD patterns of  $\text{NaAlH}_4$  doped with 10 mol% nano- $\text{CeO}_2$ : (a) after 10<sup>th</sup> hydrogenation; (b) after 15<sup>th</sup> dehydrogenation.



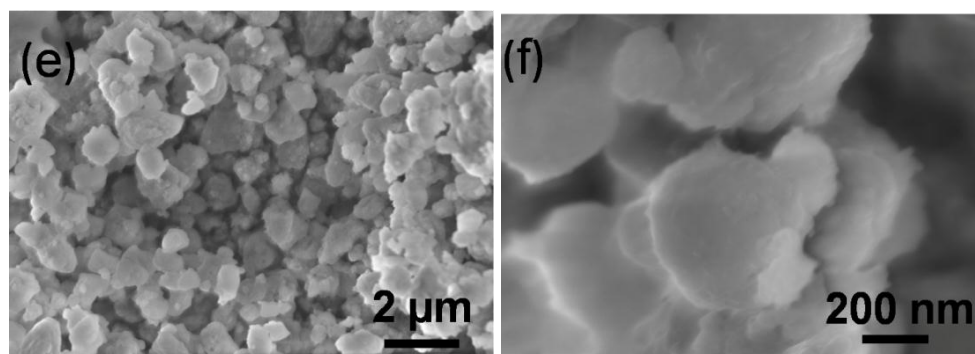


Figure S6. SEM micrographs of the samples doped with Ce-based nanoparticles (10 nm) after 5<sup>th</sup> hydrogenation at various magnifications: (a) and (b) CeB<sub>6</sub>-doped NaAlH<sub>4</sub>; (c) and (d) CeF<sub>3</sub>-doped NaAlH<sub>4</sub>; (e) and (f) CeO<sub>2</sub>-doped NaAlH<sub>4</sub>.