Supporting Information

Enhanced Ferromagnetism from Organic-Cerium Oxide hybrid Ultrathin Nanosheets

Guangyuan Yan,[†,§] Yizhan Wang,[†] Ziyi Zhang,[†] Jun Li,[†] Corey Carlos,[†] Lazarus N. German,[†] Chenyu Zhang,[†] Jingyu Wang,[†] Paul M. Voyles,[†] and Xudong Wang*,[†]

[†]Department of Material Sciences and Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA. E-mail: xudong@engr.wisc.edu

[§]Key Laboratory of Solidification Control and Digital Preparation Technology (Liaoning Province), School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, PR China

S1. Figures and Captions

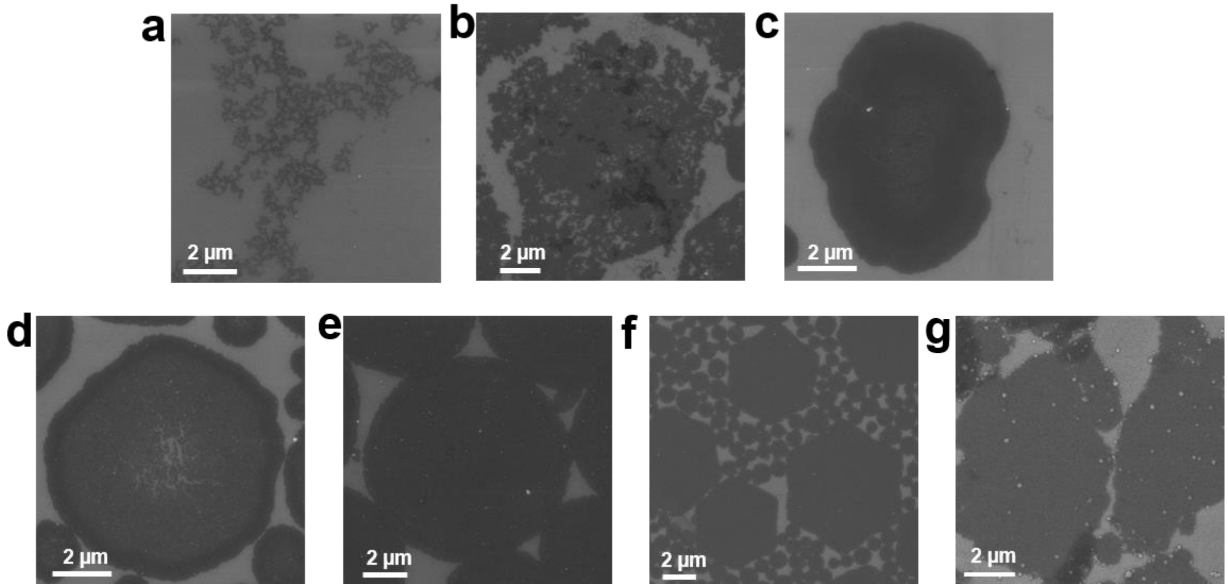

Figure S1. Influence of the surfactants ratio (SA:OAM, vol%) on the morphology of hy-CeO_{2-x} nanosheets. (a) 0:10. (b) 1:9. (c) 3:7. (d) 5:5. (e) 7:3. (f) 9:1. (g) 10:0.

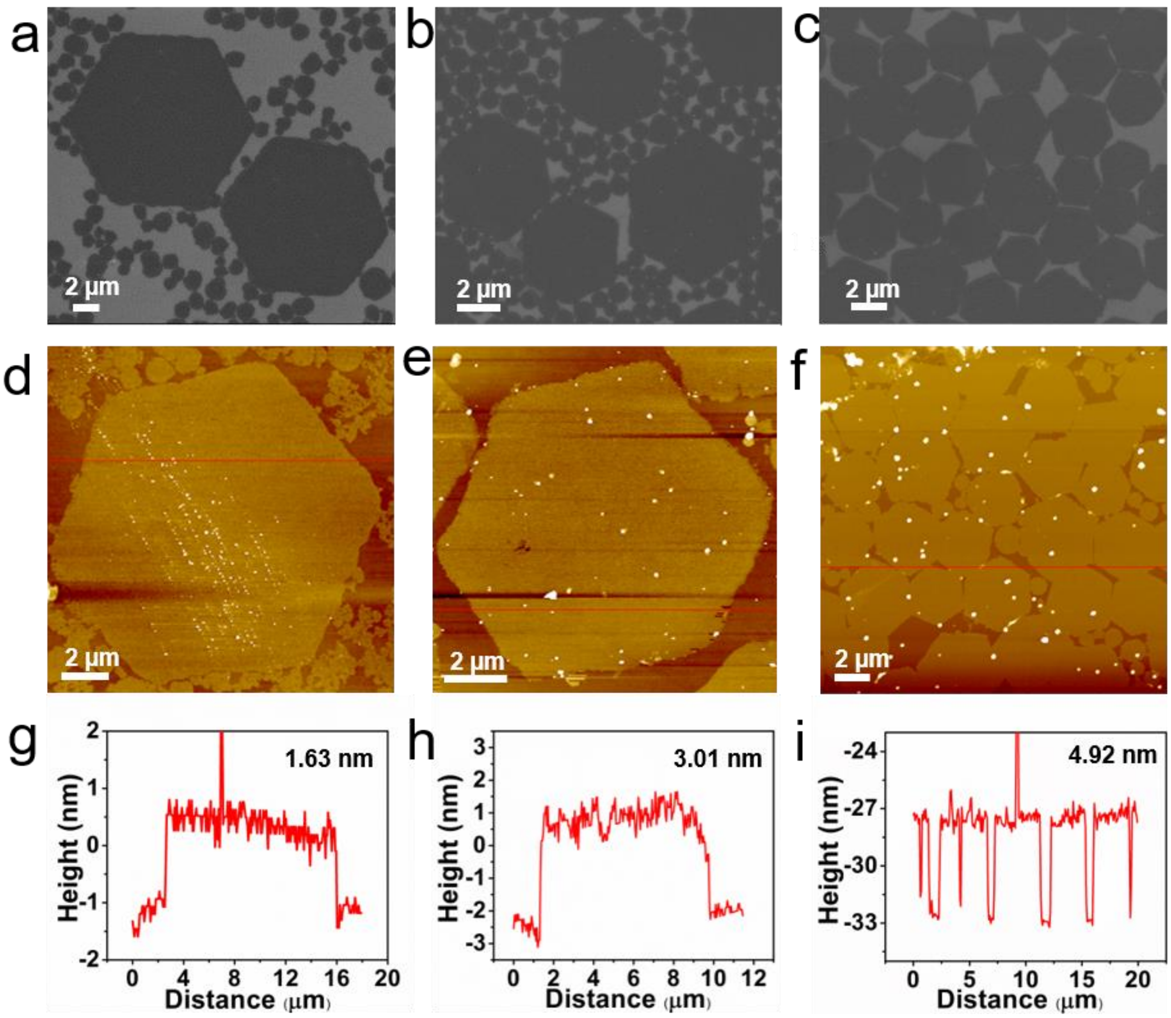

Figure S2. Influence of the $Ce(NO_3)_3$ concentration on the thickness of hy-CeO_{2-x} nanosheets. (a−c) SEM images, (d−f) AFM topography images, and (g−i) height profiles along the red dashed lines in corresponding AFM topography images of nanosheets grown with aqueous solution containing 2 mM HMTA and (a, d, g) 0.2 mM, (b, e, h) 1 mM, (c, f, i) 1.5 mM $Ce(NO_3)_3$.

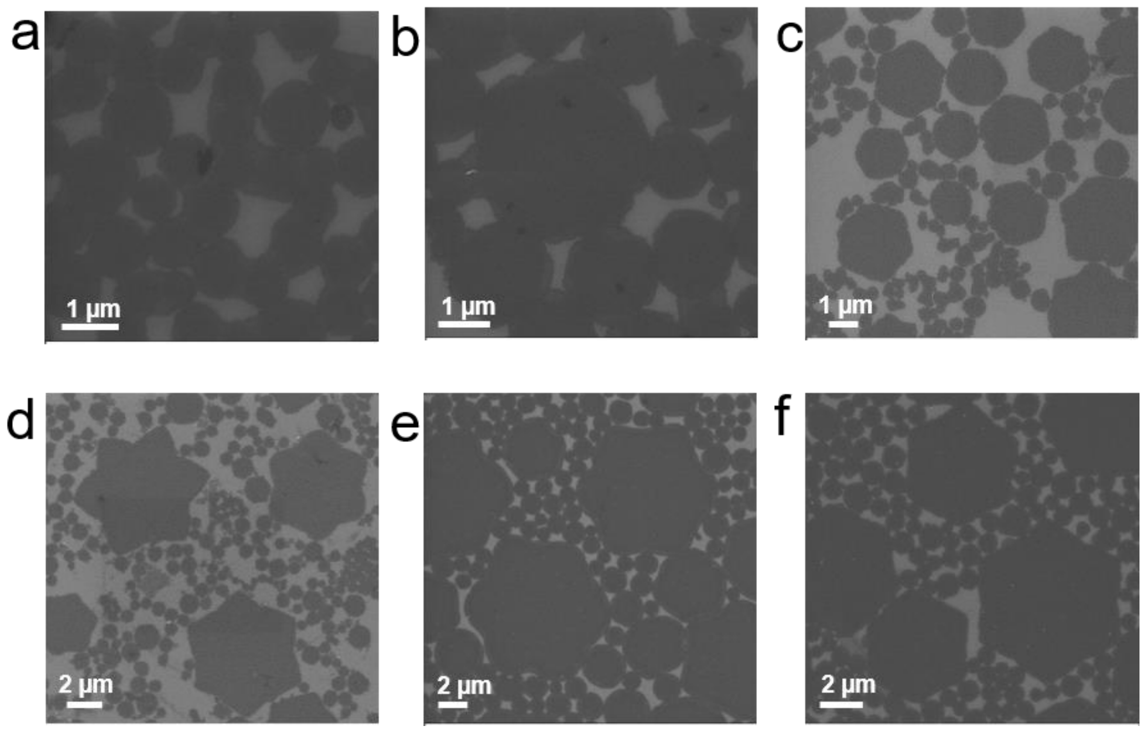

Figure S3. Influence of the growth time on the morphology of hy-CeO_{2-x} nanosheets. (a) 20 min. (b) 40 min. (c) 1 h. (d) 1 h 20 min. (e) 1 h 30 min. (f) 1 h 40 min.

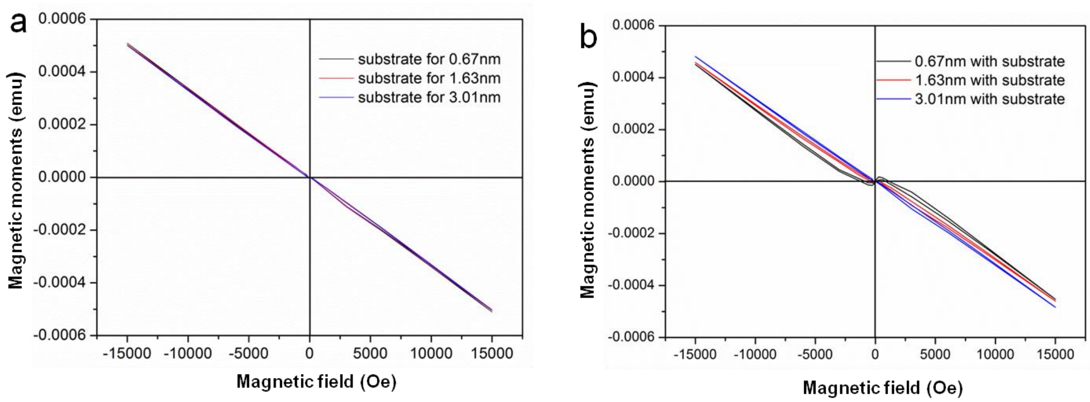

Figure S4. (a) M-H curves measured at 300 K from pure substrates for 0.67 nm, 1.63 nm, and 3.01 nm hy-CeO_{2-x} nanosheets respectively. (b) M-H curves measured at 300 K from 0.67 nm, 1.63 nm, and 3.01 nm hy-CeO2-x nanosheets with substrate.

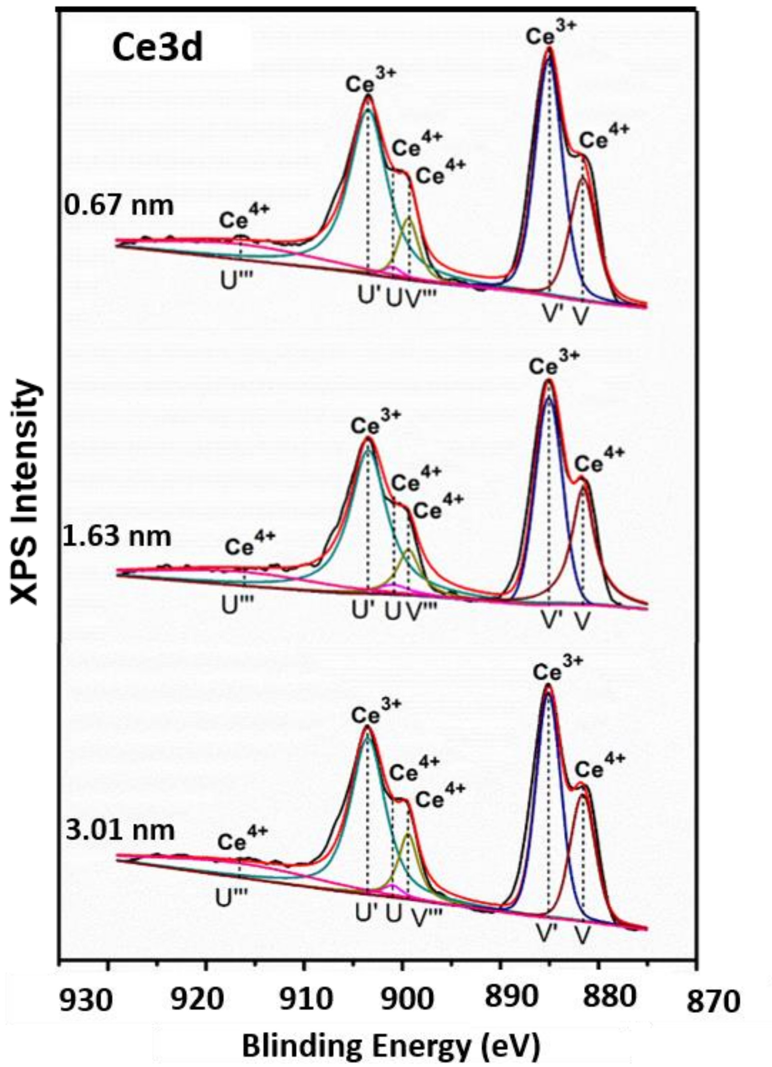

Figure S5. XPS spectrum of characteristic X-ray peak of Ce Ce3$d_{3/2}$ and Ce3$d_{5/2}$ from hy-CeO_{2-x} nanosheets with 0.67-nm, 1.63-nm and 3.01-nm thickness.

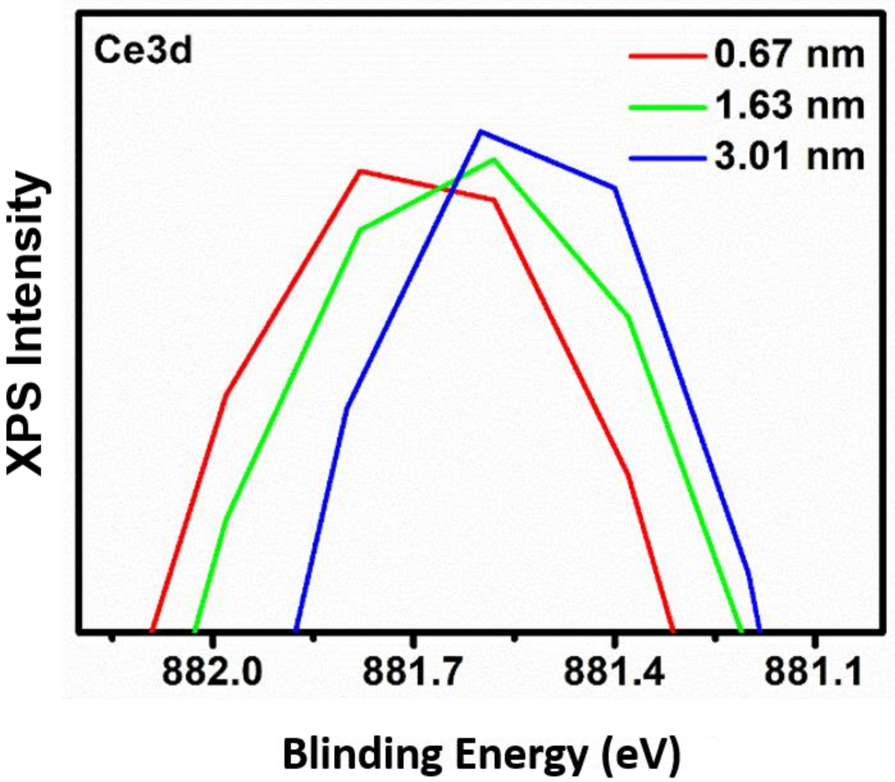

Figure S6. Ce3d$_{5/2}$ peak V XPS spectrum of hy-CeO_{2-x} nanosheets with 0.67-nm, 1.63-nm and 3.01-nm thickness.

S2. Calculation of theoretical stoichiometry O content X and actual stoichiometry O content X'

It is assumed that the total O content is the sum of the required O to fully oxidize Ce^{4+} and Ce^{3+} and to form CeO_2 and Ce_2O_3, respectively. Then, taking into account that the theoretical stoichiometry X = [O]/[Ce] is equal to 2 for CeO_2 and 1.5 for Ce_2O_3, the ratio of the required oxygen to fully oxidize Ce^{4+} and Ce^{3+} to the total concentration $[Ce^{4+}] + [Ce^{3+}]$ is determined from the concentrations $[Ce^{4+}]$ and $[Ce^{3+}]$ according to the following Equations:[1,2,3]

$$X = \frac{[O]}{[Ce]} = \frac{3}{2} \times [Ce^{3+}] + 2 \times [Ce^{4+}] \quad (1)$$

$$[Ce^{3+}] = \frac{A_{u'} + A_{v'}}{A_{u'''} + A_{u'} + A_{u} + A_{v'''} + A_{v'} + A_{v}} \quad (2)$$

$$[Ce^{4+}] = \frac{A_{u'''} + A_{u} + A_{v'''} + A_{v}}{A_{u'''} + A_{u'} + A_{u} + A_{v'''} + A_{v'} + A_{v}} \quad (3)$$

where A_i the integrated area of peak "i". While the actual stoichiometry O content X' = O1s/Ce3d can be determined directly from XPS integrated areas of the O1s and Ce3d XPS peaks according to the following Equation:

$$X' = \frac{O1s}{Ce3d} = \frac{A_O}{A_{Ce}} \times \frac{S_{Ce}}{S_O} \quad (4)$$

where A_O and A_{Ce} are the XPS integrated areas of the O1s and Ce3d peaks, and S_{Ce} (7.399) and S_O (0.711) are sensitivity factors of Ce and O atoms, respectively.

Table S1 shows the integrated areas of individual XPS fitting peaks of the Ce3d and O1s in Figure S4, and concentrations of Ce^{3+} and Ce^{4+} ions calculated by Equation (2) and (3) of hy-CeO_{2-x} nanosheets with different thickness.

Table S1. Integrated areas of individual XPS peaks of the Ce3d and O1s, and concentrations of Ce^{3+} and Ce^{4+} ions from the 0.67-nm, 1.63-nm and 3.01-nm thick hy-CeO_{2-x} nanosheets.

Sample	$Ce3d_{3/2}$			$Ce3d_{5/2}$			O1s	$[Ce^{3+}]$	$[Ce^{4+}]$
	U’’’	U’	U	V’’’	V’	V			
0.67 nm	10598.63	34989.69	2200.43	6898.64	25830.84	18272.73	13480.45	0.616	0.384
1.63 nm	19016.51	55000.00	2016.52	10016.35	46000.09	23623.00	21242.99	0.657	0.343
3.01 nm	20016.17	60000.00	3000.00	15016.15	50011.00	28523.15	24094.71	0.634	0.366

Table S2. Integrated areas of individual XPS peaks of the Ce3d and O1s, and concentrations of Ce^{3+} and Ce^{4+} ions from the 1.63-nm hy-CeO_{2-x} nanosheets after ALD coating, H_2 annealing and air annealing.

Sample	$Ce3d_{3/2}$			$Ce3d_{5/2}$			O1s	$[Ce^{3+}]$	$[Ce^{4+}]$
	U’’’	U’	U	V’’’	V’	V			
Initial 1.63nm	19016.51	55000.00	2016.52	10016.35	46000.00	23623.00	21242.99	0.657	0.343
ALD coated 1.63nm	21397.10	64140.00	2499.00	16052.15	53460.50	23759.60	23190.37	0.649	0.351
H_2 annealed 1.63nm	23424.60	58905.00	1655.60	10727.70	49266.00	19394.50	27148.30	0.662	0.338
Ar annealed 1.63nm	19293.63	54581.43	2045.43	10162.23	45650.40	23967.89	21111.85	0.652	0.348
Air annealed 1.63nm	16257.50	50319.90	3979.80	14473.50	47055.20	43410.00	28062.69	0.555	0.445

References

(1) Meng, F. M.; Zhang, C.; Fan, Z. H.; Gong, J. F.; Li, A. X.; Ding, Z. L.; Tan, H. B.; Zhang, M.; Wu, G. F. Hydrothermal Synthesis of Hexagonal CeO_2 Nanosheets and Their Room Temperature Ferromagnetism. *J. Alloys Compd.* **2015**, 647, 1013-1021.

(2) Fernandes, V.; Mossanek, R. J. O.; Schio, P.; Klein, J. J.; de Oliveira, A. J. A.; Ortiz, W. A.; Mattoso, N.; Varalda, J.; Schreiner, W. H.; Abbate, M.; Mosca, D. H. Dilute-defect Magnetism: Origin of Magnetism in Nanocrystalline CeO_2. *Phys. Rev. B* **2009**, 80, 035202.

(3) Fernandes, V.; Schio, P.; de Oliveira, A. J. A.; Ortiz, W. A.; Fichtner, P.; Amaral, L.; Graff, I. L.; Varalda, J.; Mattoso, N.; Schreiner, W. H. Ferromagnetism Induced by Oxygen and Cerium Vacancies above the Percolation Limit in CeO_2. *J. Phys.: Condens. Matter* **2010**, 22, 216004.