Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supporting Information

$Ce_{0.9}Fe_{0.1}O_{1.97}$/Ag: A cheaper inverse catalyst with excellent oxygen storage capacity and improved activity towards CO oxidation

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Sample characterization

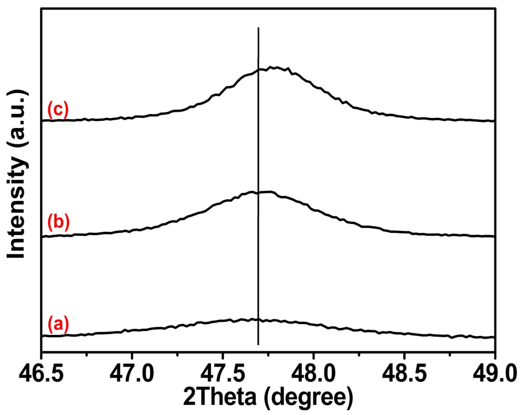

Fig. S1 Enlarged XRD patterns of (a) CeO_2, (b) CeO_2-Fe_2O_3, and (c) $Ce_{0.9}Fe_{0.1}O_{1.97}$ between theta of 46.5-49.0°.

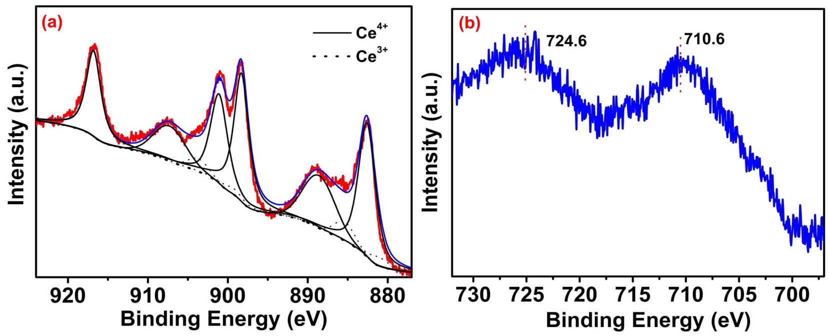

Fig.S2 XPS spectra of (a) Ce(3d) region, (b) Fe(2p) region of $Ce_{0.9}Fe_{0.1}O_{1.97}$. To determine the oxidation state of Ce and Fe in $Ce_{0.9}Fe_{0.1}O_{1.97}$, XPS spectra of Ce (3d) and Fe (2p) region were evaluated. By the method introduced by Hilaire et at.[3] three doublets from CeO_2 (solid lines in black) and two doublets from Ce_2O_3 could be identified as shown in Fig S3. More detailed information are given in Table. S2 and it could be indicated that the results agreed well with previous literature.[1-2,4] Amount of Ce^{3+} detected in the sample is about 8.38%. The binding energy of Fe(2p3/2, 1/2) is observed at 710.6 and 724.6eV (Fig S1(b)), corresponding to the 3+ oxidation state of Fe.[1,5] Thus it could be suggested that the formula of Ce-Fe solid solution is $Ce^{+4}_{0.825}Ce^{+3}_{0.075}Fe^{+3}_{0.1}O_{1.97}$.

Table S1. Assignment of Ce $3d_{3/2.5/2}$ components from XPS spectra collected for $Ce_{0.9}Fe_{0.1}O_{1.97}$.

Ionic state	*Spin-orbit doublet*	*components*	*BE (±0.2eV)*	*FWHM(±0.2eV)*	△E(±0.1eV)
Ce^{4+}	3d5/2	v	882.6	2.5	-34.2
		v’	888.6	4.3	-28.2
		v’’’	898.3	2.2	-18.5
	$3d_{3/2}$	u	901.1	2.5	-15.7
		u’	907.3	4.3	-9.5
		u’’’	916.8	2.2	0
Ce^{3+}	3d5/2	vo	881.1	2.9	-35.7
		v	885.4	3.0	-31.4
	$3d_{3/2}$	u	899.3	2.9	-17.5
		u’	903.7	3.0	-13.1

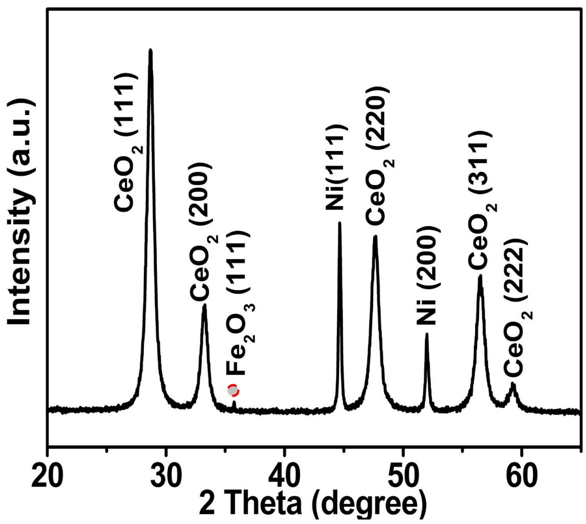

Fig. S3 XRD patterns of CeO_2-Fe_2O_3.

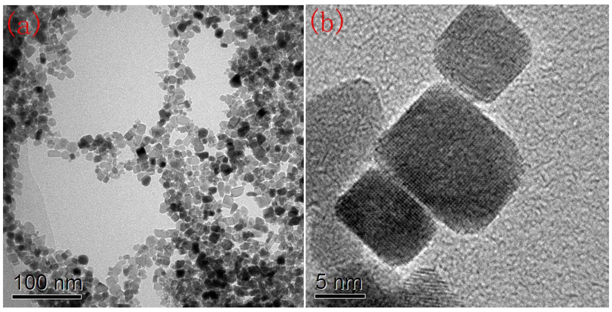

Fig. S4 TEM images of CeO_2. As indicated in Fig. S4, the primary morphology for CeO_2 was nanocube.

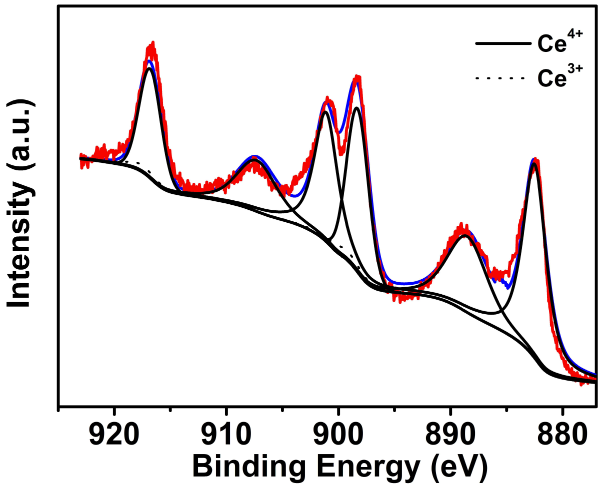

Fig.S5 XPS spectra of (a) Ce(3d) region of CeO_2. XPS spectra of Ce (3d) was evaluated to determine the oxidation state of Ce in CeO_2. The Ce 3d spectra composed of two multiplets (u and v), corresponding to she spin-orbit splitting of $3d_{3/2}$ and $3d_{5/2}$, respectively. [1] As shown in Fig. S2, six obvious peaks for Ce^{4+} were identified (in solid line), while signals for Ce^{3+} were quite weak (in dashed line). Further details on the evaluation of CeO_2 XPS spectra is shown in Table S1. By calculation, Ce^{3+} in CeO_2 is 0.70%, therefore the composition of ceria could be given as $Ce^{4+}_{0.993}Ce^{3+}_{0.007}O_{1.997}$.

Table S2 Assignment of Ce $3d_{3/2,5/2}$ components from XPS spectra collected for CeO_2.

Ionic state	*Spin-orbit doublet*	*components*	*BE (±0.2eV)*	*FWHM(±0.2eV)*	△E(±0.1eV)
Ce^{4+}	$3d_{5/2}$	v	882.5	2.5	-34.2
		v’	888.5	4.2	-28.2
		v’’’	898.3	2.3	-18.5
	$3d_{3/2}$	u	901.1	2.4	-15.7
		u’	907.3	4.2	-9.5
		u’’’	916.8	2.3	0
Ce^{3+}	$3d_{5/2}$	v	882.5	2.5	-34.2
		v’	888.5	4.2	-28.2
	$3d_{3/2}$	u	899.3	2.9	-17.5
		u’	903.7	3.0	-13.1

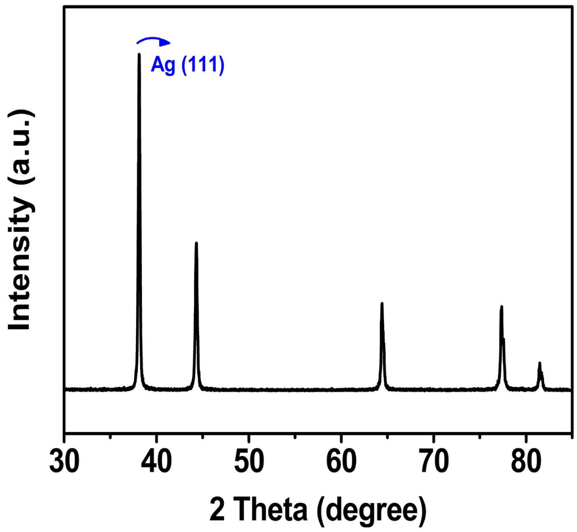

Fig. S6 XRD patterns of Ag. XRD pattern of Ag was shown in Fig.S6. The diffraction peaks indicated the formation of Ag with a crystallite size of 27nm.

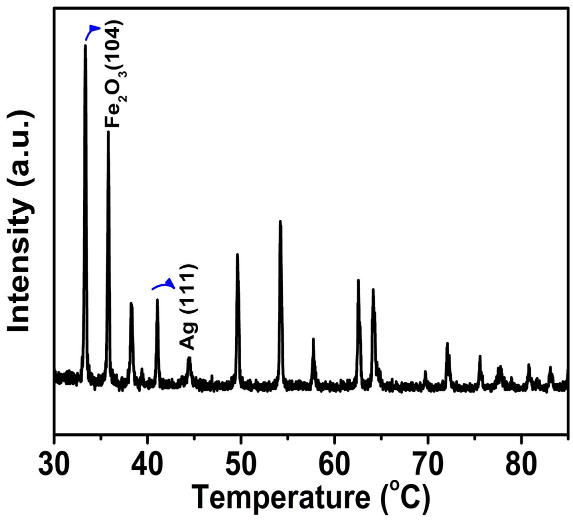

Fig. S7 XRD patterns of Ag-Fe_2O_3. XRD pattern of Ag-Fe_2O_3 was shown in and Fig.S7. The diffraction peaks fitted well with standard Fe_2O_3 and Ag pattern, which indicating the successful formation of Ag-Fe_2O_3.

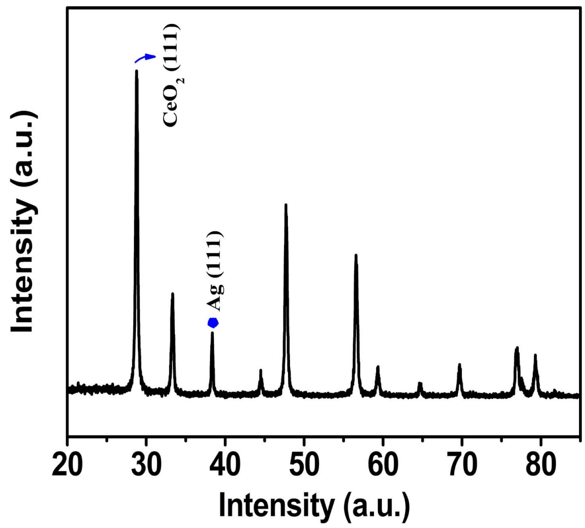

Fig.S8 XRD patterns of Ag-CeO_2. XRD pattern of Ag-CeO_2 was shown in and Fig. S8. The diffraction peaks fitted well with standard CeO_2 and Ag pattern, which indicating the successful formation of Ag-CeO_2.

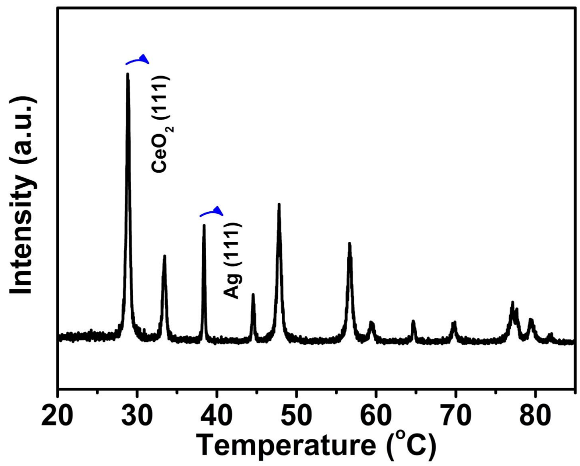

Fig.S9 XRD patterns of Ag-$Ce_{0.9}Fe_{0.1}O_2$-M. XRD pattern of Ag-$Ce_{0.9}Fe_{0.1}O_{1.97}$-M was shown in Fig.S9. The diffraction peaks fitted well with standard CeO_2 and Ag pattern, which indicating the successful formation of Ag-$Ce_{0.9}Fe_{0.1}O_{1.97}$-M.

Table S3. Specific surface area of the samples.

Sample	CeO_2	Fe_2O_3	CeO_2-Fe_2O_3	$Ce_{0.9}Fe_{0.1}O_{1.97}$	Ag	Ag-Fe_2O_3	Ag-CeO_2	Ag@CeO_2	Ag-$Ce_{0.9}Fe_{0.1}O_{1.97}$-M	$Ce_{0.9}Fe_{0.1}O_{1.97}$/Ag
S_{BET} (m^2/g)	58.71	35.82	52.02	69.13	8.09	29.89	45.18	30.18	32.06	29.04

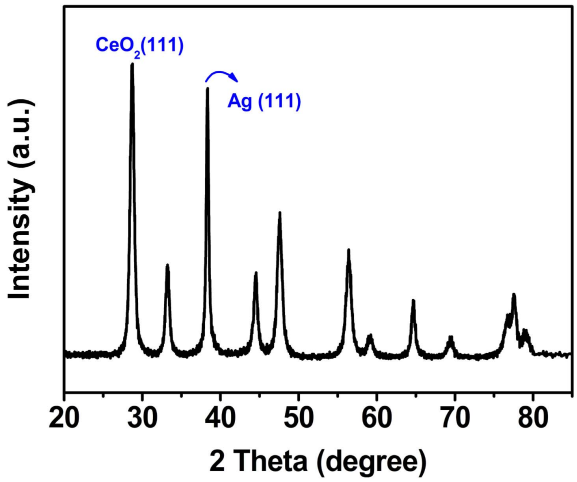

Fig.S10 XRD patterns of CeO_2/Ag. XRD pattern of CeO_2/Ag was shown in and Fig.S10. As seen from the Figure, it is clear that the diffraction lines could be indexed to CeO_2 and Ag, and the core-shell structure will be further investigated by TEM.

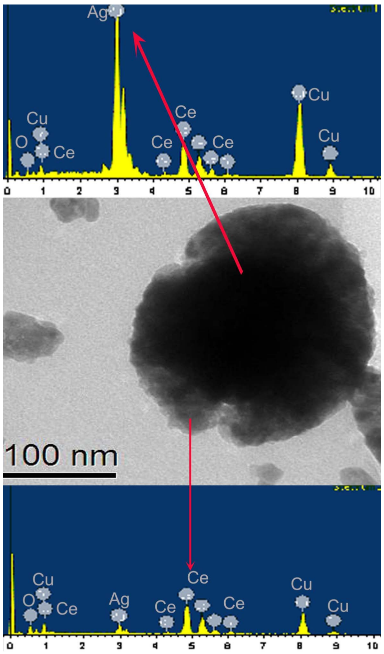

Fig.S11 (a) TEM, (b) and (c) EDX spectra of CeO_2/Ag. Microstructure of CeO_2/Ag is shown in Fig. S11. The formation of Ag core and CeO_2 shell could be well indicated from the figure.

References

1. E. Beche, G. Peraudeau, V. Flaud and D. Perarnau, *Surf. Interface Anal.*, 2012, **44**, 1045-1050. 2. X.-S. Huang, H. Sun, L.-C. Wang, Y.-M. Liu, K.-N. Fan and Y. Cao, *Appl. Catal.,B*, 2009, **90**, 224-232.

3. S. Hilaire, J. P. Delaroche and M. Girod, *European Physical Journal A*, 2001, **12**, 169-184.

4. M. Romeo, K. Bak, J. Elfallah, F. Lenormand and L. Hilaire, *Surf. Interface Anal.*, 1993, **20**, 508-512.

5. A. T. Kozakov, A. G. Kochur, K. A. Googlev, A. V. Nikolsky, I. P. Raevski, V. G. Smotrakov and V. V. Yeremkin, *J. Electron Spectrosc. Relat. Phenom.*, 2011, **184**, 16-23.