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Supplementary

Rational design of sandwich-like MnO_2-Pd-CeO_2 hollow spheres with enhanced activity and stability for CO oxidation

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Synthesis of CeO_2-Pd hollow spheres.

Typically, 50 mg carbon sphere templates were dispersed in 30 mL ethyl alcohol under ultra-sonication to obtain homogenous slurry and subsequently, 15 mL homogeneous Pd colloidal solution was added. After 6 hours of stirring at room temperature, 30 ml mixed solution composed of 100mg $Ce(NO_3)_3.6H_2O$ and 100 mg HMT was poured into the CSs@Pd slurry, followed by reflux at 75°C for 4 h. Finally, the as-prepared CSs@Pd@CeO_2 precursor was separated by filtration and then calcinated at 450℃ in air for 2h to achieve CeO_2-Pd hollow spheres.

Synthesis of MnO_2-Pd hollow spheres

Firstly, 50mg carbon spheres and 15ml Pd colloidal solution were dispersed in 50ml deionized water by sonication treatment and then stirred at room temperature for 6 hours. In the next, 100mg $KMnO_4$ was add to the homogenous slurry and keep heating at 80℃ for 2h. Finally, the dark brown CSs@ MnO_2-Pd precursor was collected by filtration, then the MnO_2-Pd hollow spheres were obtained by annealing the precursor in air at 450℃ for 2h.

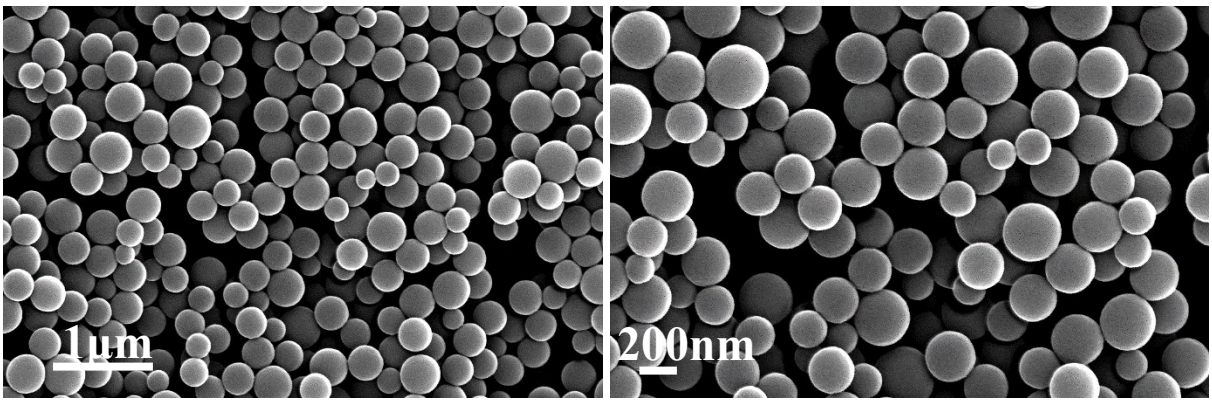


Figure S1 SEM images of carbon spheres

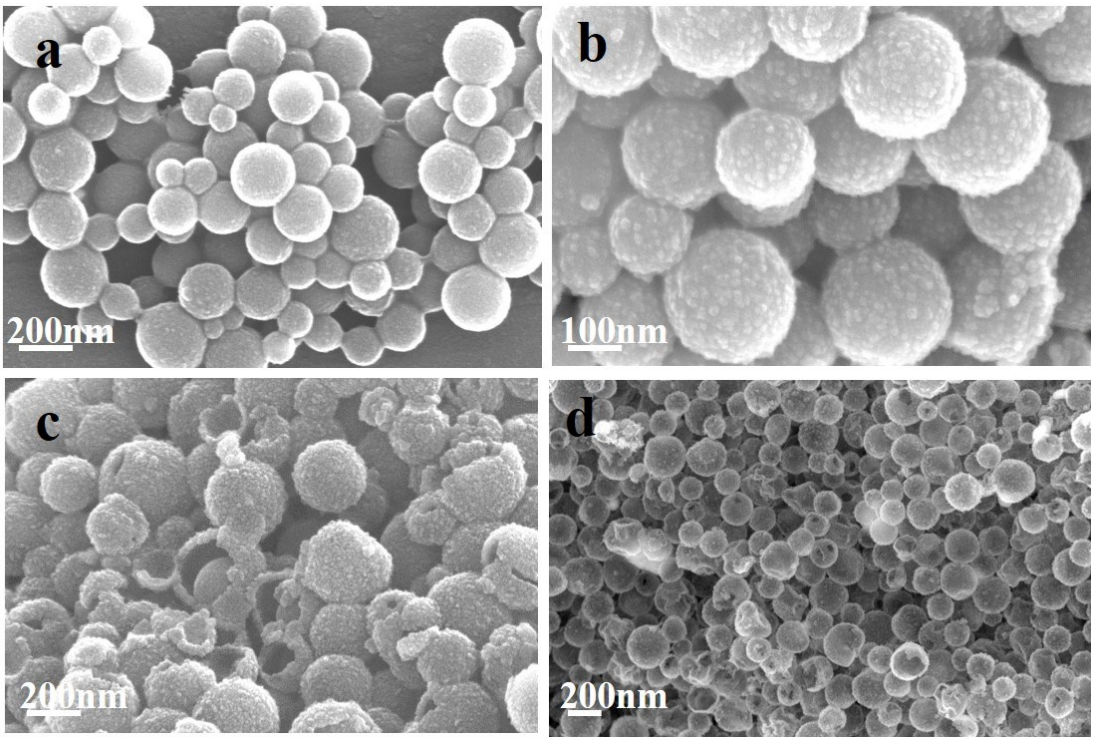


Figure S2 SEM images of CSs@Pd(a), CSs@Pd@CeO_2(b), CSs@ MnO_2@Pd@CeO_2(c) and MnO_2-Pd-CeO_2 particles.

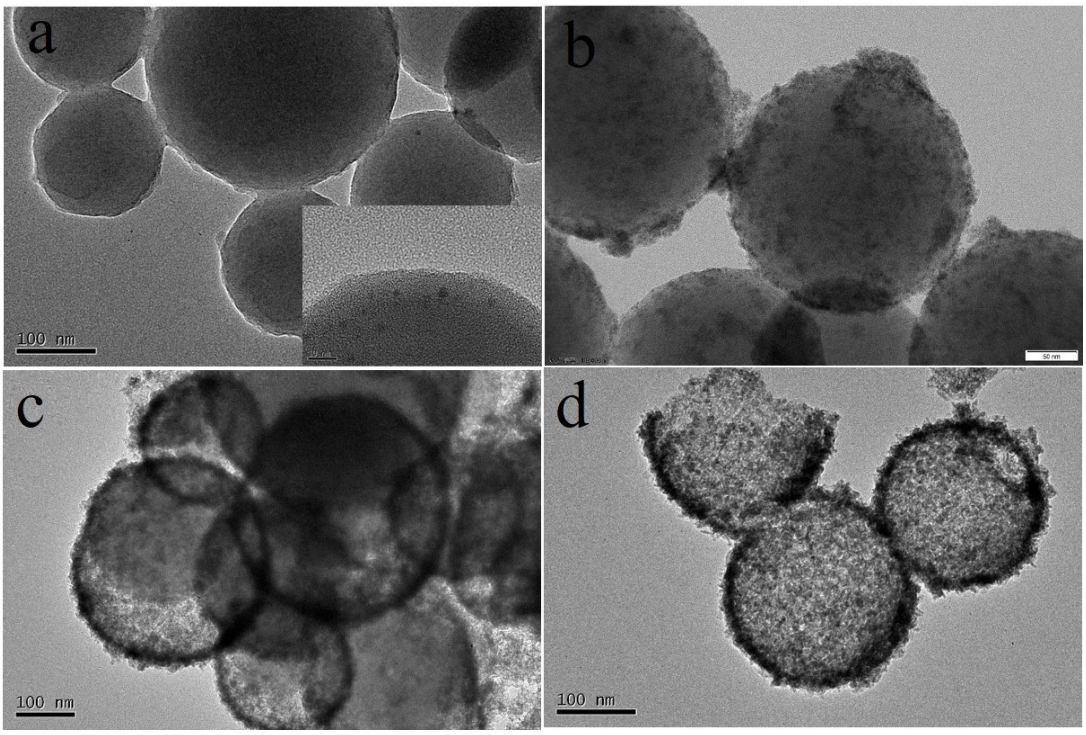


Figure S3 TEM images of CSs@Pd(a), CSs@Pd@CeO_2(b), CSs@ MnO_2@Pd@CeO_2(c) and MnO_2-Pd-CeO_2 particles.

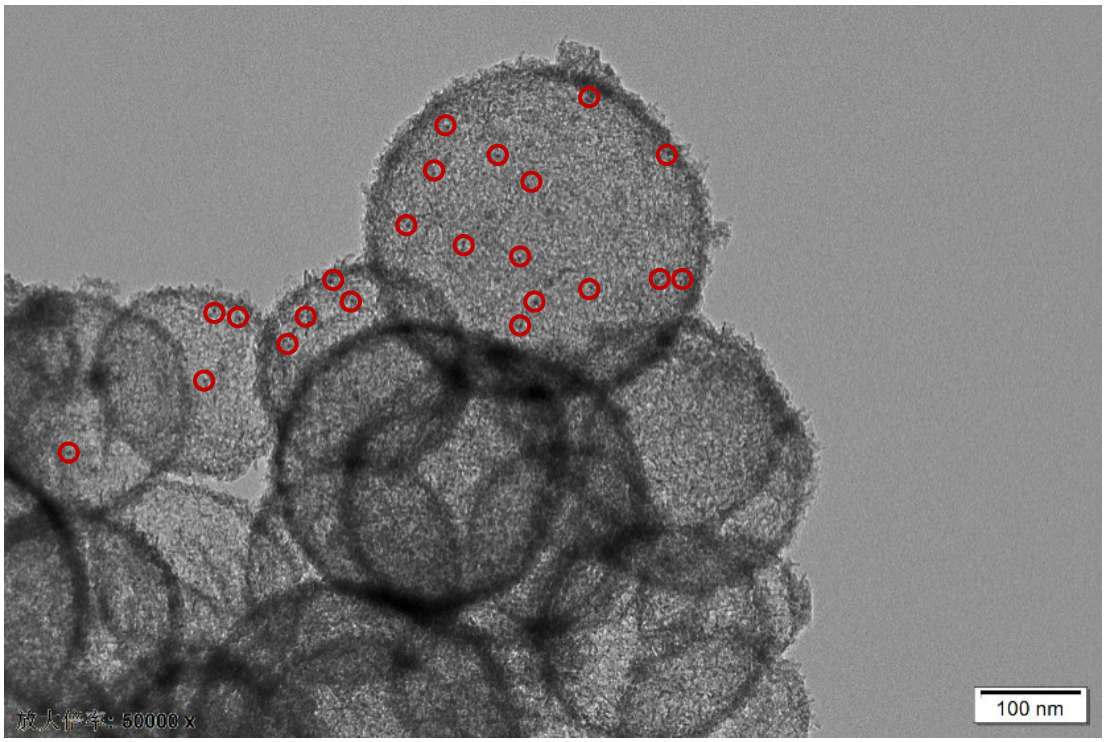
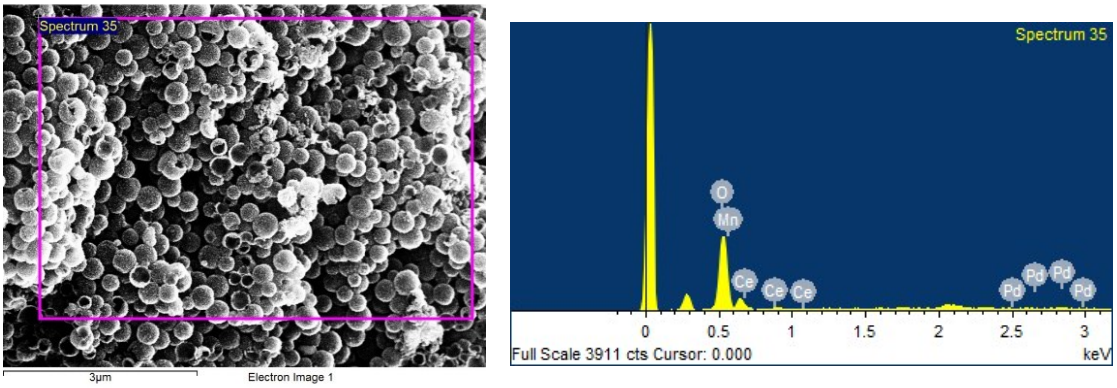
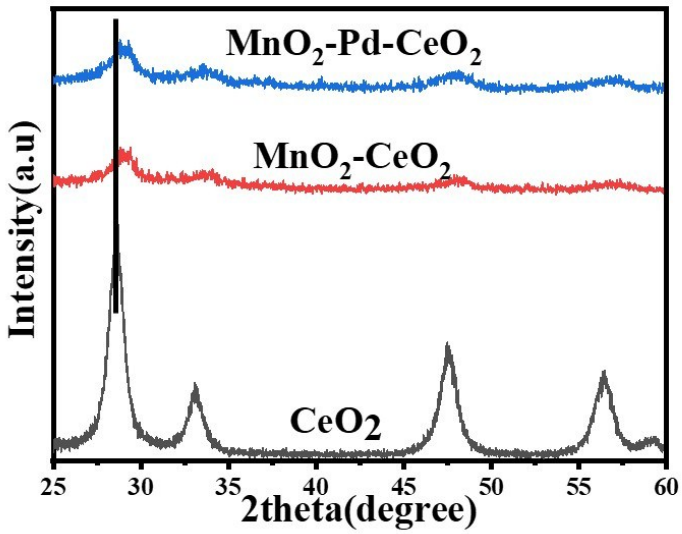


Figure S4 HR-TEM images of MnO_2-Pd-CeO_2 hollow spheres (In the red circle are Pd particles).



Element	Weight%	Atomic%
O K	23.30	58.34
Mn K	44.26	32.28
Pd L	1.18	0.44
Ce L	31.26	8.94
Totals	100.00	

FigureS5 SEM images and corresponding EDS spectrum of MnO_2-Pd-CeO_2 hollow spheres



FigureS6 XRD spectra of MnO_2-Pd-CeO_2, MnO_2-CeO_2 and CeO_2

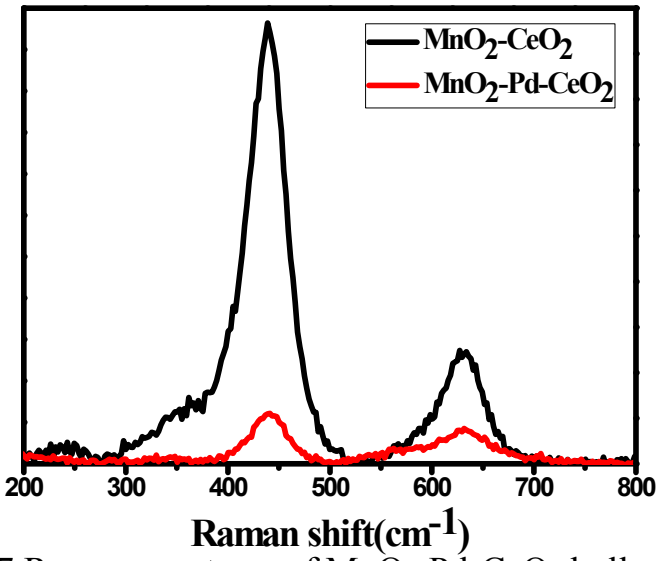


Figure S7 Raman spectrum of MnO_2-Pd-CeO_2 hollow spheres

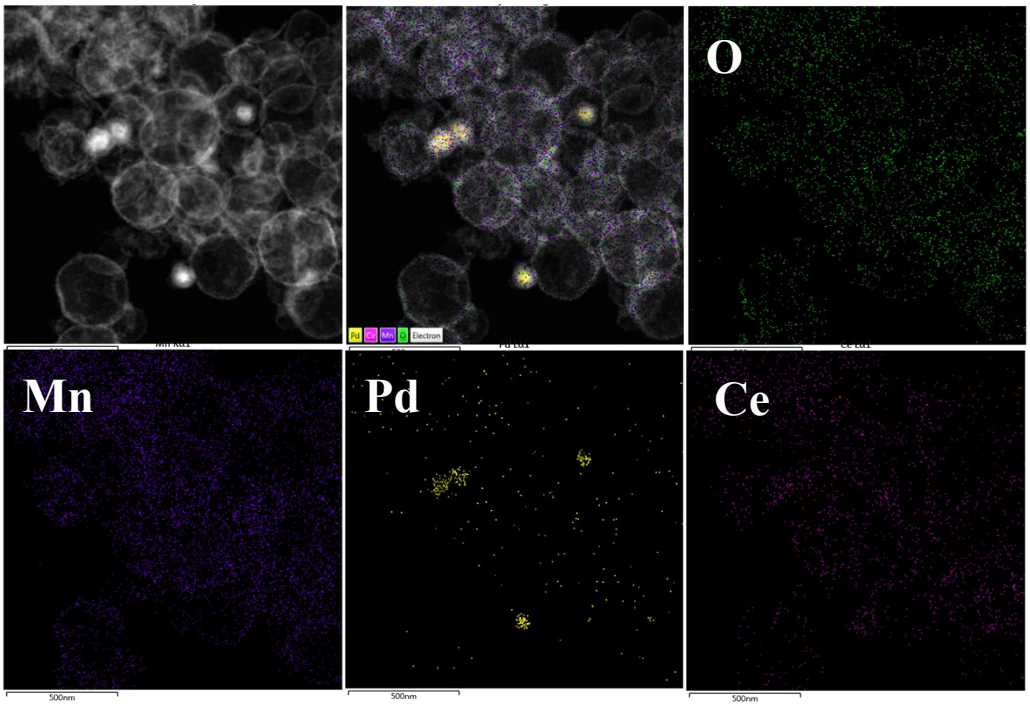


Figure S8 HAADF-STEM image of Pd/MnO_2 -CeO_2 hollow spheres and corresponding maps of O, Mn, Pd and Ce.

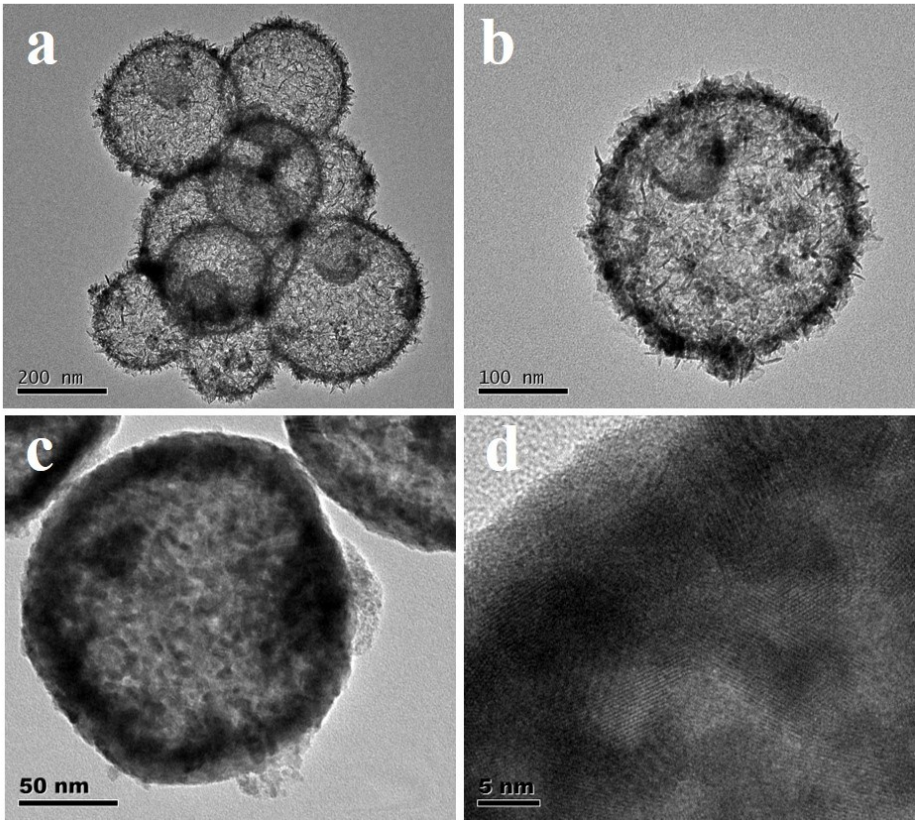


Figure S9 TEM images of MnO_2-Pd (a,b) and CeO_2-Pd hollow spheres.

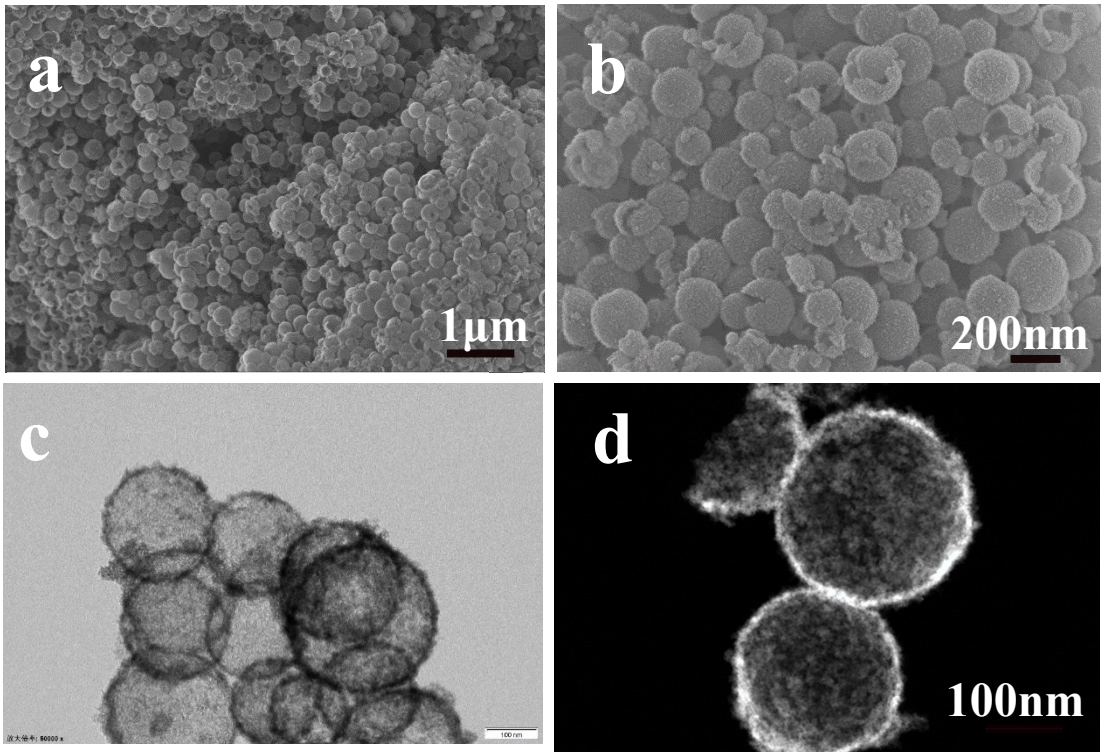


Figure S10 SEM, TEM and HAADF-STEM images of MnO_2-Pd-CeO_2 hollow spheres after catalytic reaction

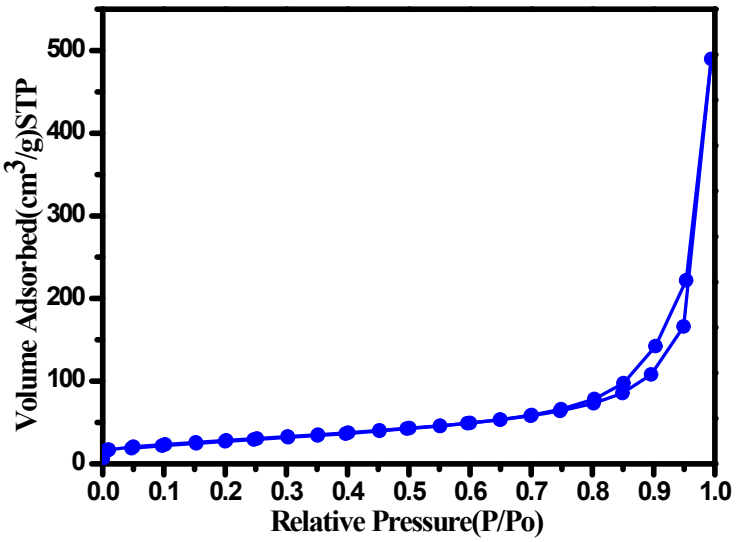


Figure S11 N_2 adsorption−desorption isotherms of MnO_2-Pd-CeO_2 hollow spheres

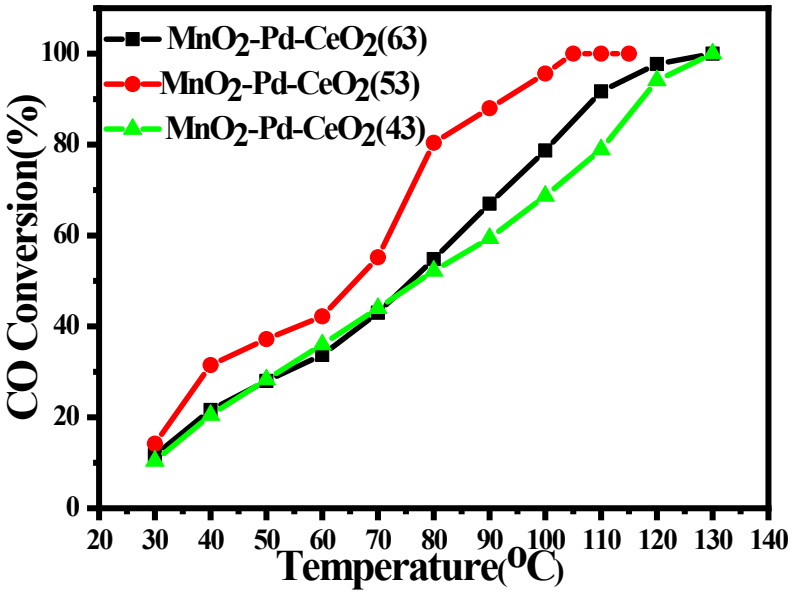
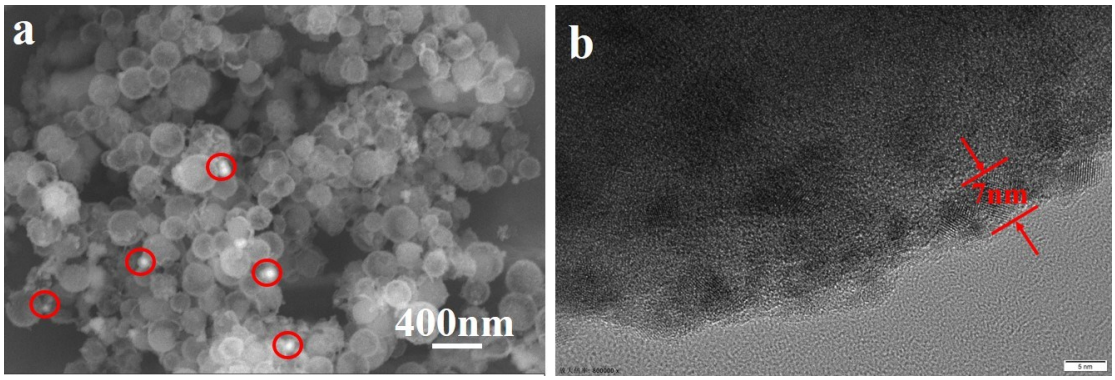


Figure S12 the influence of $Ce(NO_3)_3.6H_2O$(43,53 and 63mg) concentration on the catalytic performance of sandwich-like MnO_2-Pd-CeO_2 hollow spheres catalyst



FigureS13 (a) SEM images of CS@MnO_2-Pd-CeO_2(43mg) yolk-shell spheres; (b) TEM image of CS@Pd-CeO_2(53mg) spheres.

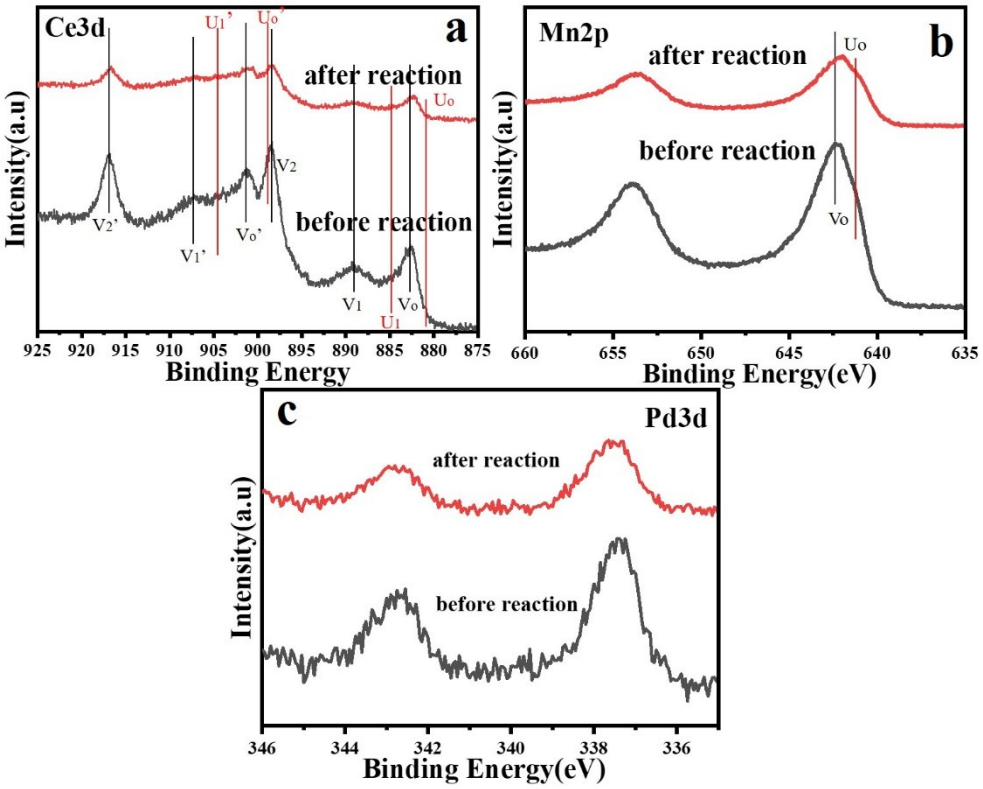


Figure S14 XPS spectra of catalyst after reaction

The XPS spectra of MnO_2-Pd-CeO_2 hollow spheres before and after catalytic reaction (after cycle and stability test) were demonstrated in figure S14. As shown in figureS14a, peaks denoted as V_0 V_1, V_2 (3d5/2), V_0', V_1', V_2' (3d3/2) were assigned to Ce(Ⅳ) species, while peaks labeled as U_0, U_1, U_0' and U_1' corresponded to Ce(III) species.[1-3] Before catalytic reaction, only Ce(Ⅳ) species existed in the samples as mentioned in manuscript. But after a long time reaction, the characteristic peaks of Ce(III) species appeared in the catalyst. A similar phenomenon was also found in Mn2p spectra, the Mn2p peaks shifted to lower binding energy and a distinct Mn(III) characteristic peak can be found after catalytic reaction, where peaks noted as Vo and Uo was assigned to Mn(Ⅳ) and Mn(III) respectively (figure S14 b).[4] However, no significant changes were found in Pd3d spectrum after reaction and Pd species still existed mainly in a Pd^{2+} ionic state (figure S14 C). Combining the above results, we can speculate that the lattice oxygen at the interface (Pd/MnO_2 and Pd/CeO_2 interface) other than the adsorbed active oxygen also participates in the catalytic reaction.[5] In brief, the extraction of lattice oxygen leads to the appearance of trivalent metal species. However, this result is difficult to reflect the whole catalytic reaction process.

Reference

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