Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Sustainable and scalable production of monodisperse and highly uniform colloidal carbonaceous spheres using sodium polyacrylate as dispersant

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Experimental Section

The synthesis of MDCSs

The MDCSs were prepared by a sodium polyacrylate (PAANa) assisted hydrothermal carbonization of glucose. In a typical process, 12 g of glucose was firstly dissolved in 50 mL of water. Then 15 mg of PAANa was added in the solution and dissolved by magnetic stir. The solution was transferred into a Teflon-lined autoclave, sealed and treated under desired temperatures for 8 hours. The obtained brown carbonaceous materials were washed several times with water and ethanol. Lastly, the materials were dried in the air at 80 °C. Scanning electron microscope (SEM, LEO 1550) was applied to characterize the morphology of the carbon materials. Transmission electron microscope (TEM) images were obtained from a Hitachi H7700 transmission electron microscope with CCD imaging system on an acceleration voltage of 100 kV. The size distribution of the MDCSs in water was assessed by Nano-ZS ZEN 3600 (MALVERN Instrument) at 25 °C.

The synthesis of macro-mesoporous silica

The hierarchically macro-mesoporous silica was fabricated by a dual-templating approach using the MDCSs as the hard-template and P123 as the soft template. The precursor of silica was prepared based on an early report.[1] Firstly, 2 g the monodisperse carbon spheres were redispersed in 40 mL of ethanol and rest for 5 days to form a close packed monolith. After careful removal of the ethanol, the monolith was dried at 70 °C in the air. Secondly, the silica precursor was prepared by mixing TEOS (2.08 g), H_2O (0.9 g), HCl (0.8 g), P123 (1.0 g) and ethanol (15 g) with 2 hours of stirring. 0.6 g of the carbon monolith was immersed into 5 g of the silica precursor. After the evaporation under 40 °C for 48 h, the composite was calcined in air at 550 °C for 4 h with a ramping rate of 2 °C/min to remove the carbonaceous spheres and P123. The resulting white powder was collected and characterized.

The synthesis of hollow metal oxides

The hollow metal spheres was synthesized according to a previous report.[2] In a typical synthetic process, 0.5 g of $Ni(NO_3)_2 \cdot 6H_2O$ or $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in 40 ml ethanol. 0.2 g of the MDCSs were added and ultrasonically treated for 15 minutes. Then, 0.5 g of hexamethylenetetramine (HMT) was introduced and stirred for 30 minutes. The precursors were hydrothermally treated for 24 hours at 100 °C. Then the resulting suspensions were filtrated, washed with water and ethanol, and dried in 70 ^{o}C for 8 hours. The powders were lastly calcined at 450 ^{o}C with a ramping temperature of 3^{o} C/min. The resulting grey (NiO) and yellow (CeO_2) powders were collected and characterized.

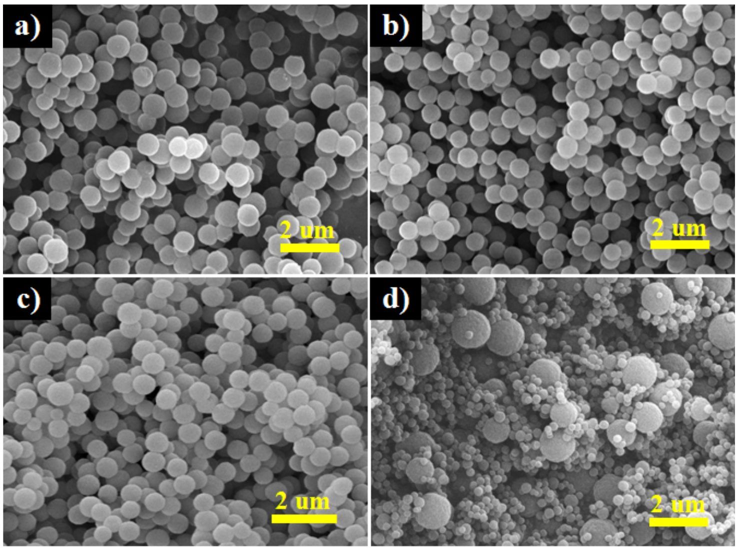


Fig. S1 SEM images of MDCSs prepared with 10 mg (a), 15 mg (b), 20 mg (c) and 40 mg (d) of PAANa at 190 ^{o}C over 8 hours.

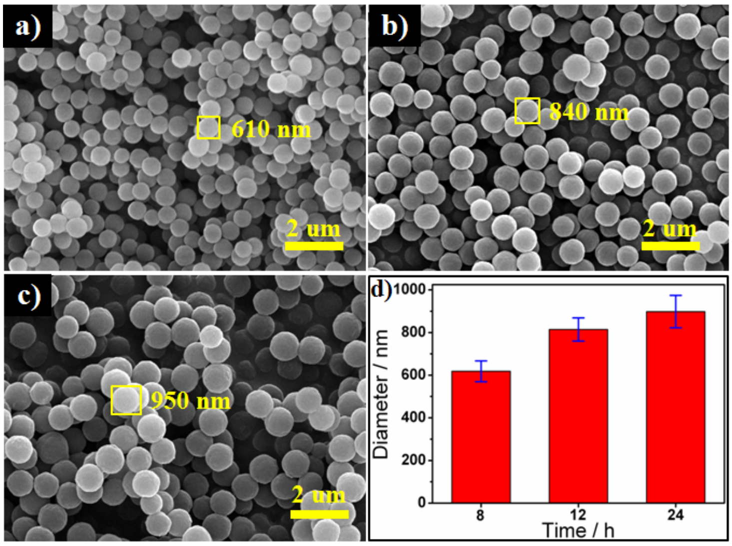


Fig. S2 SEM images of MDCSs prepared with 15mg PAANa at 190 ^{o}C over 8 hours (a), 12 hours (b), 24 hours (c) and corresponding average sizes (d).

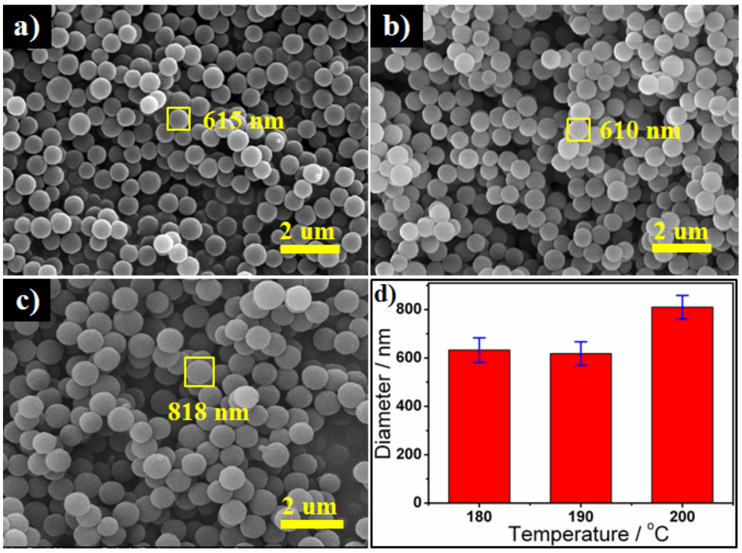


Fig. S3 SEM images of MDCSs prepared with 15 mg of PAANa at 180 °C (a), 190 °C (b), and 200 °C (c) over 8 hours and corresponding average sizes (d).

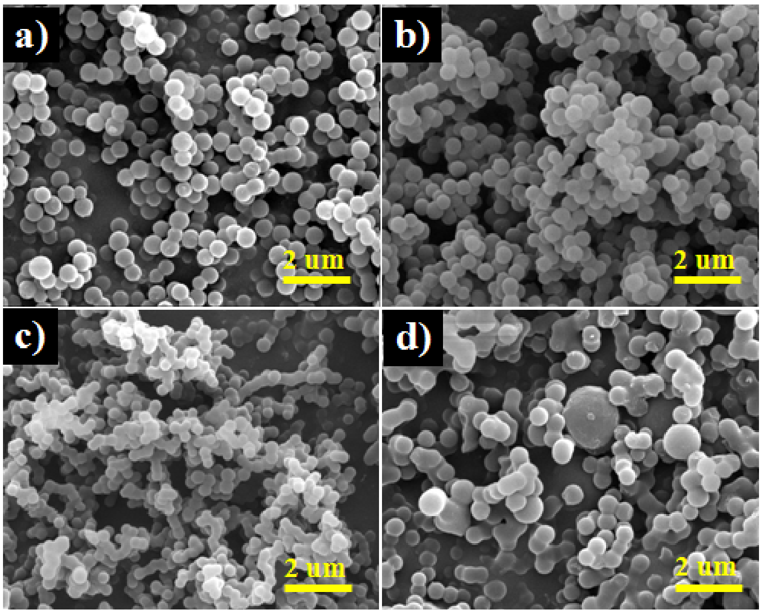
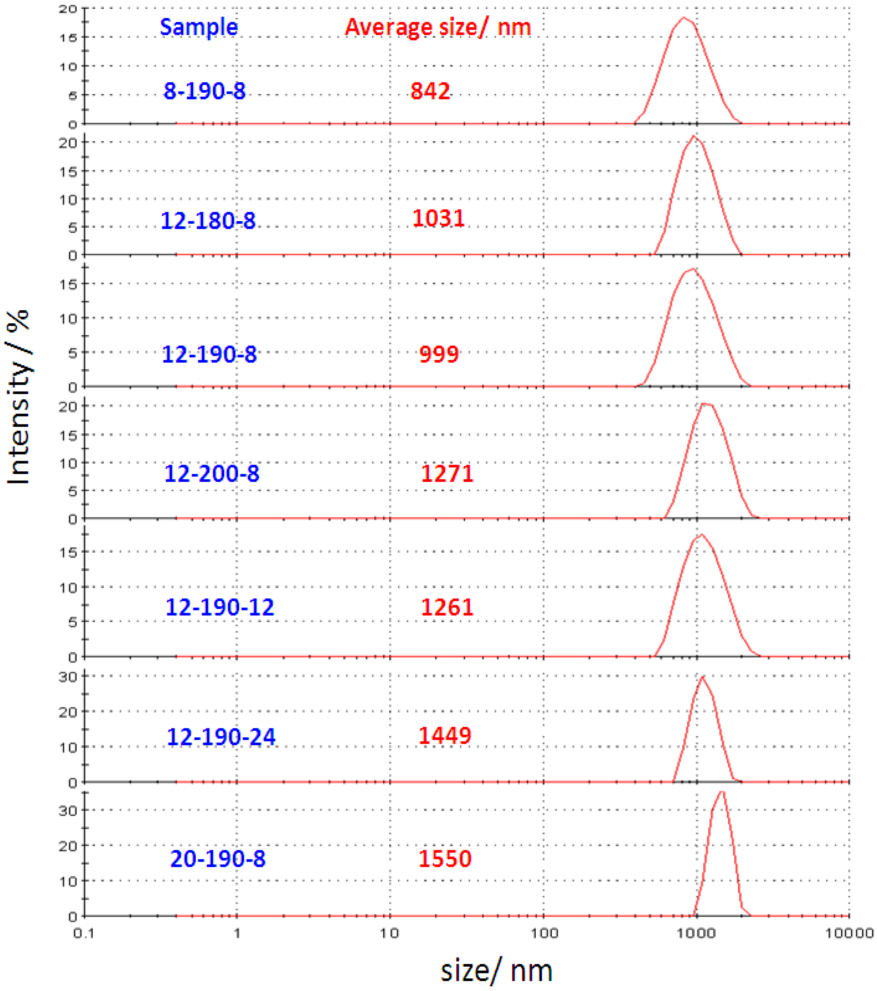


Fig. S4 Four batches of colloidal carbonaceous spheres prepared at glucose concentration of 4 g/40 ml water under 180 °C over 4 hours without PAANa.



The size distribution was measured by DLS. The variation trend of the spheres size is consistent with the SEM results while the average size is larger than that summarized from SEM. There are mainly three reasons leading to the difference: 1, the swelling of the MDCSs after absorbing water; 2, the diameter from DLS is the hydrodynamic radius which is larger than the actual size, 3, there is slight aggregation of the carbonaceous spheres in aqueous dispersion.

Fig. S5 DLS curves of the MDCSs. (X-Y-Z, X is the glucose mass, Y is the reaction temperature, Z is the reaction time, Polydispersity index (PDI) of the samples from top to down: 0.144, 0.198, 0.145, 0.171, 0.232, 0.335, 0.348)

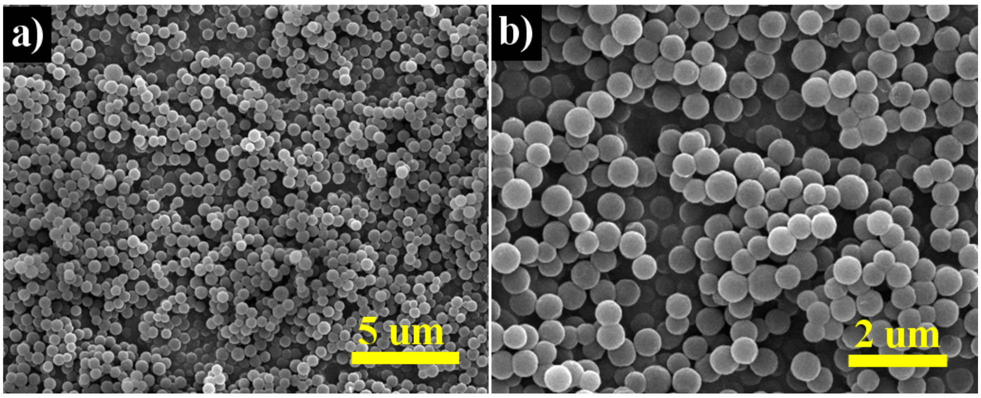


Fig. S6 SEM image of the product synthesized with 120 g glucose, 150 mg PAANa at 190 °C over 12 hours.

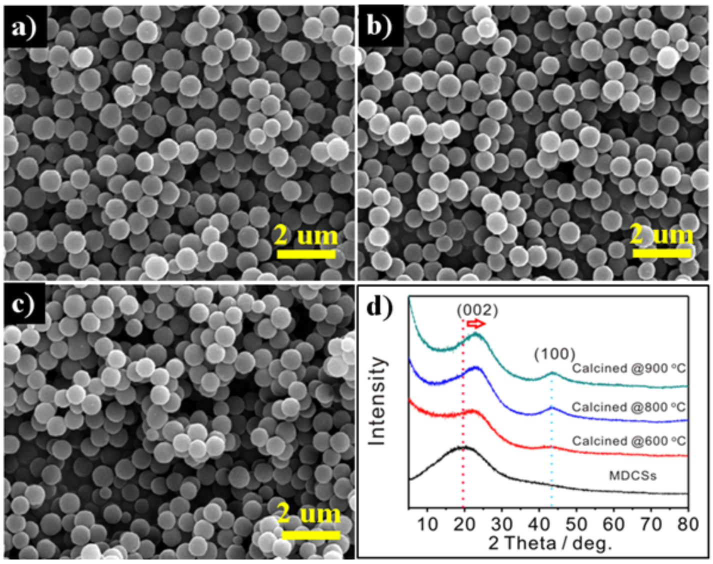


Fig. S7 SEM images of MDCSs carbonized at 600 °C, 800 °C, 900 °C and corresponding XRD analysis.

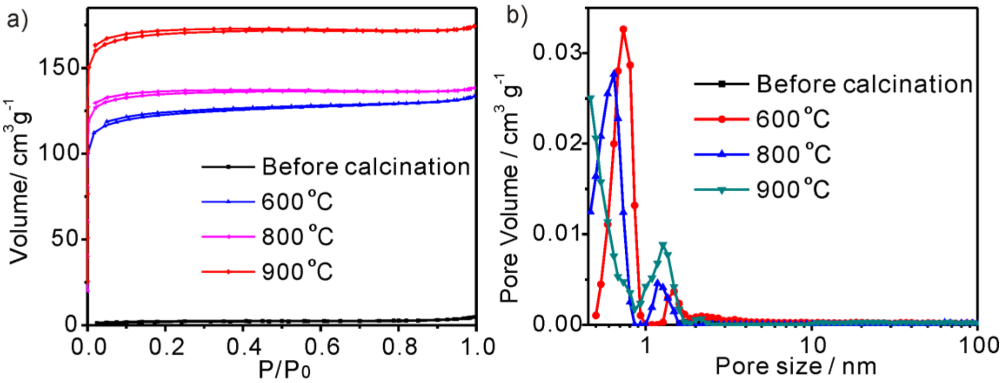


Fig. S8 N_2 sorption isotherms of the MDCSs before and after calcination at different temperatures (a) and corresponding DFT pore size distributions (b).

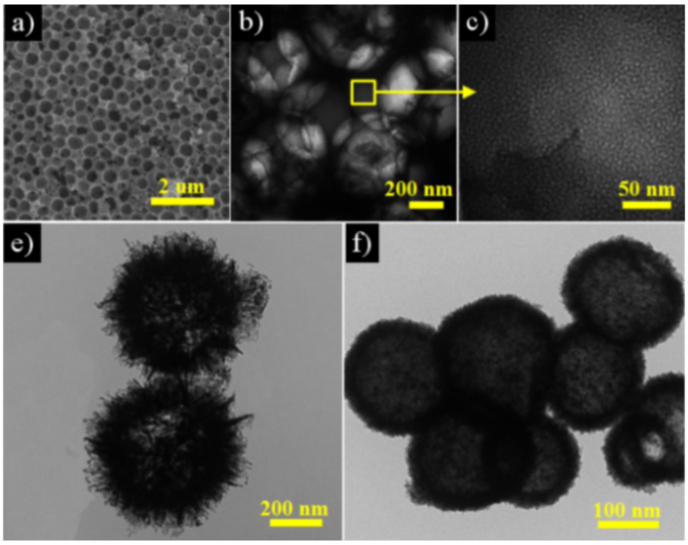


Fig. S9 SEM image of macro-mesoporous silica (a), corresponding TEM images (b, c), and TEM images of the hollow NiO (e) and CeO_2 (f).

Table S1. Product yield of different HTC process

Concentration (g/50ml water)	Yield by traditional HTC method / g	Yield by PAANa assisted HTC method /g
8	1.97	2.47
12	3.58	4.3
20	5.85	8.12

Reaction conditions: 50 ml water, 190 ^{o}C, 8 h

Table S2. Product yield of carbonization process

Carbonization temperature/ ^{o}C	Carbonization time / h	Yield / %
600	4	59
800	1	56
900	1	50

Reaction conditions: 1g of the MDCSs, under N_2 atmosphere

Table S3. Elemental analysis and textual properities

Carbonization temperature/ ^{o}C	C/ wt%	H / wt%	O / wt% ^{a}	S_{BET} / m^2g^{-1}	Pore volume / cm^3g^{-1}
Without calcination	67.2	4.95	27.85	7	0.007
600	85.2	2.41	12.39	420	0.19
800	86.8	1.76	11.44	463	0.21
900	87.0	1.74	11.26	587	0.27

Reaction conditions: 1g of the PAANa-assisted HTC carbon, under N_2 atmosphere

a: calculated.

1 Z. Sun, Y. Deng, J. Wei, D. Gu, B. Tu and D. Zhao, *Chem. Mater.*, 2011, **23**, 2176.

2 Y. J. Wu, M. T. Zheng, C. L. Xie, Q. Jin, G. G. Yi and Y. L. Liu, *Chin. J. Inorg. Chem*, 2011, **27**, 2447.