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Supporting Information

A liquid marble method for synthesizing large-sized carbon microspheres with controlled interior structures

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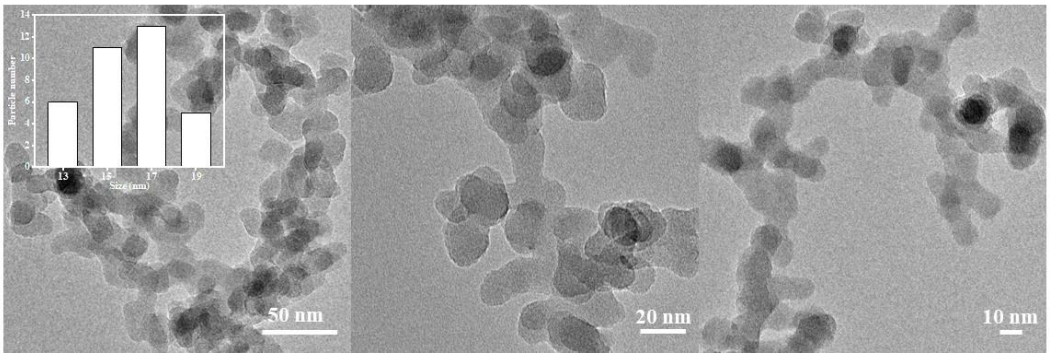


Figure S1. Three TEM images showing morphology of H-18 particle (inset is H-18 nanoparticle size distribution).

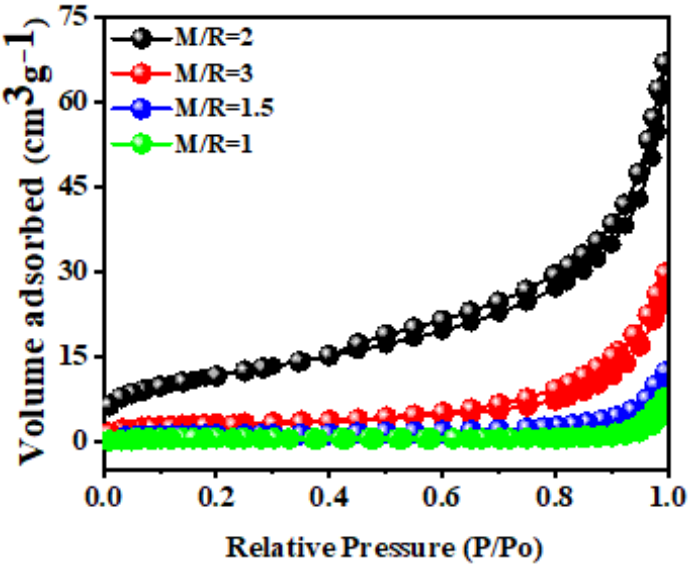


Figure S2. N_2 adsorption-desorption isotherm of MRF resin microspheres.

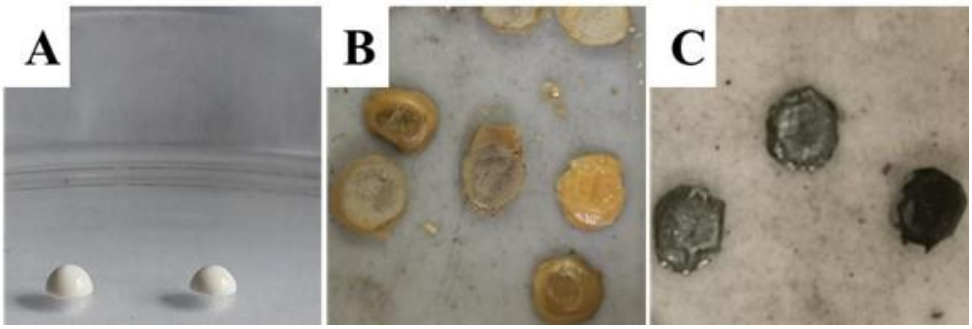
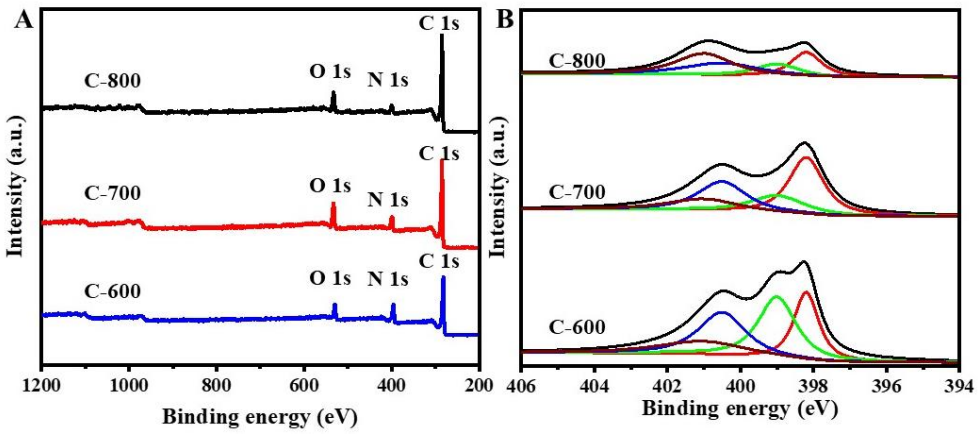


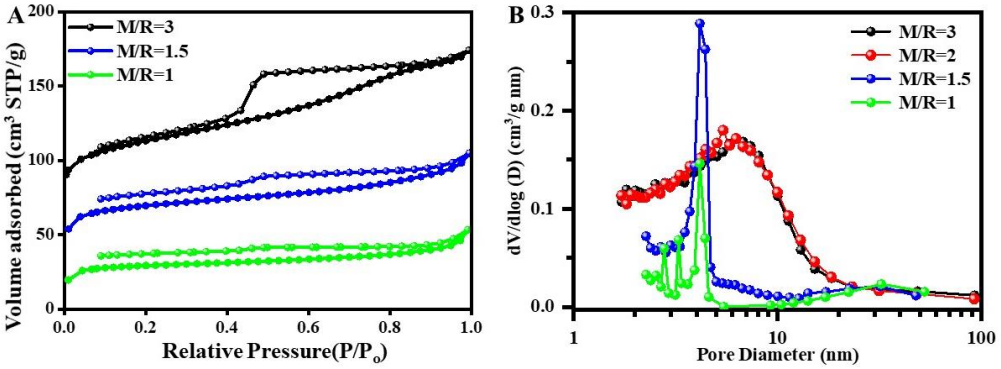
Figure S3. Appearances of the bare droplet, MRF resin and carbonized MRF resin. (A) Appearance of the bare droplet of a hydrochloric acid solution containing resorcinol (R) and melamine (M). (B) Appearance of the MRF resin prepared with the bare droplet. (C) Appearance of the MRF resin prepared with the bare droplet, after carbonization at 600 ^{o}C.



C Results of elemental analysis

Samples	N (wt%)	C (wt%)	H (wt%)
600 ºC	14.73	73.44	3.23
700 ºC	11.02	79.24	2.66
800 ºC	9.86	73.08	2.06

Figure S4. Characterization of MPCS at different carbonization temperatures. (A) XPS spectra of the honeycombed MPCS synthesized at different carbonization temperatures. (B) XPS N1s spectra of honeycombed MPCS synthesized at different carbonization temperatures. (C) Results of elemental analysis of honeycombed MPCS synthesized at different carbonization temperatures.



C Textural parameters of MPCS

Samples	S_{BET} (m^2 g^{-1})	V (cm^3 g^{-1})	Pore Size (nm)
M/R=3	396	0.269	6.7
M/R=1.5	347	0.208	4.1
M/R=1	206	0.129	4.0

Figure S5. Results of N_2 sorption analysis of MPCS synthesized with different molar ratios of M/R. (A) N_2 adsorption-desorption isotherms. (B) Pore size distribution plots. (C) Data of specific surface area, pore volume and pore size.

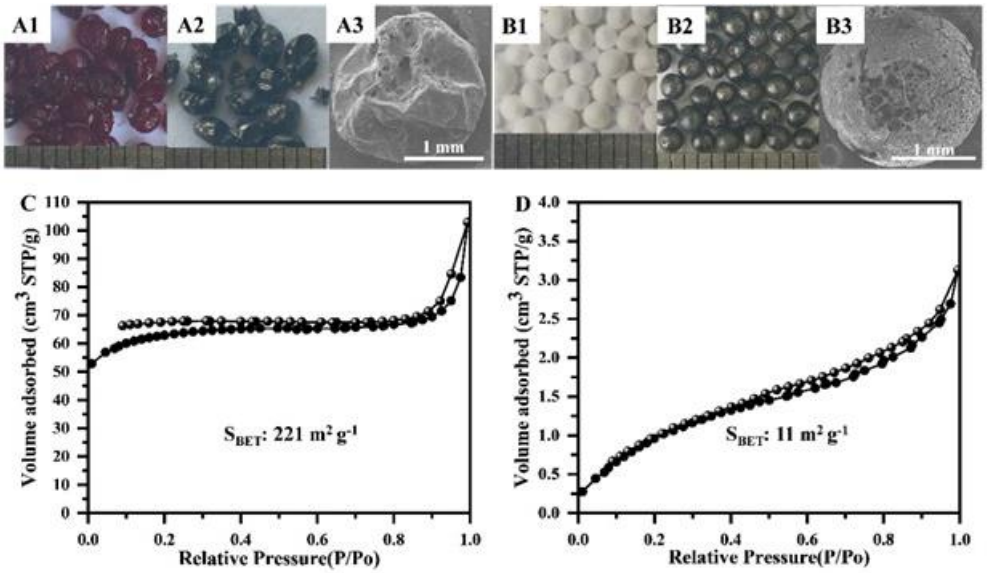


Figure S6. Characterization of RF resin, MF resin and the corresponding carbon materials. (A1) Appearances of RF resin before carbonization. (A2) Appearances of RF resin after carbonization. (A3) SEM image of RF resin after carbonization. (B1) Appearances of MF resin before carbonization. (B2) Appearances of MF resin after carbonization. (B3) SEM image of MF resin after carbonization. (C) N_2 adsorption-desorption isotherm of RF resin after carbonization. (D) N_2 adsorption-desorption isotherm of MF after carbonization.

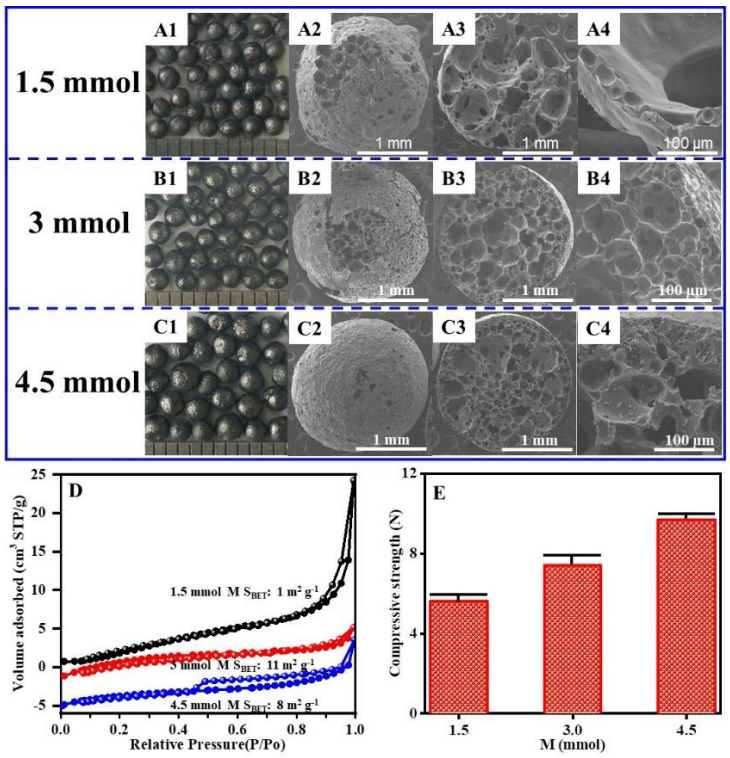
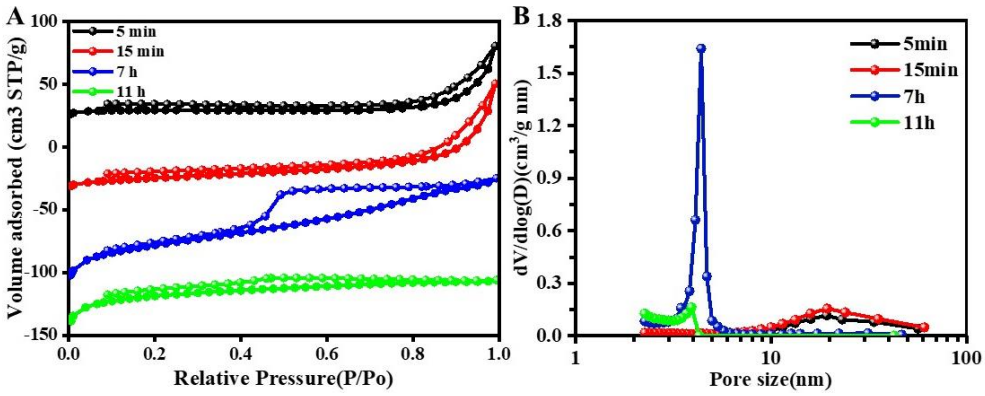


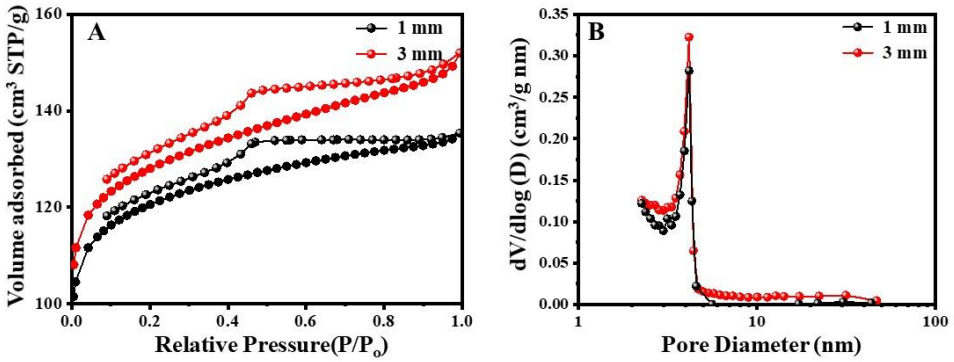
Figure S7. Characterization of carbon materials prepared with different amounts of M (without R). (A1) Appearance of carbon materials prepared with 1.5 mol melamine-formaldehyde (MF). (A2-A4) SEM images for a single microsphere and the interior structure of carbon materials prepared with 1.5 mol melamine-formaldehyde (MF). (B1) Appearance of carbon materials prepared with 3 mol melamine-formaldehyde (MF). (B2-B4) SEM images for a single microsphere and the interior structure of MPCS prepared with 3 mol melamine-formaldehyde (MF). (C1) Appearance of carbon materials prepared with 4.5 mol melamine-formaldehyde (MF). (C2-C4) SEM images for a single microsphere and the interior structure of MPCS prepared with 4.5 mol melamine-formaldehyde (MF). (D) N_2 adsorption-desorption isotherms of carbon materials prepared with different amounts of M. (E) Compressive strength of carbon materials prepared with different amounts of M.



C Textural parameters of MPCS

Samples	S_{BET} (m^2 g^{-1})	V (cm^3 g^{-1})	Pore Size (nm)
5 min	101	0.12	19.6
15 min	122	0.17	19.4
7 h	425	0.19	4.4
11 h	458	0.22	4.0

Figure S8. Results of N_2 sorption analysis of the honeycombed MPCS synthesized with the different times of formaldehyde vapour treatment. (A) N_2 adsorption-desorption isotherms. (B) Pore size distribution plots. (C) Data of specific surface area, pore volume and pore size.



C Textural parameters of the honeycombed MPCS

Samples	S_{BET} (m^2 g^{-1})	V (cm^3 g^{-1})	Pore Size (nm)
1 mm	420	0.209	4.16
3 mm	446	0.235	4.20

Figure S9. Results of N_2 sorption analysis of honeycombed MPCS of different sizes. (A) N_2 adsorption-desorption isotherms. (B) Pore size distribution plots. (C) Data of specific surface area, pore volume and pore size.

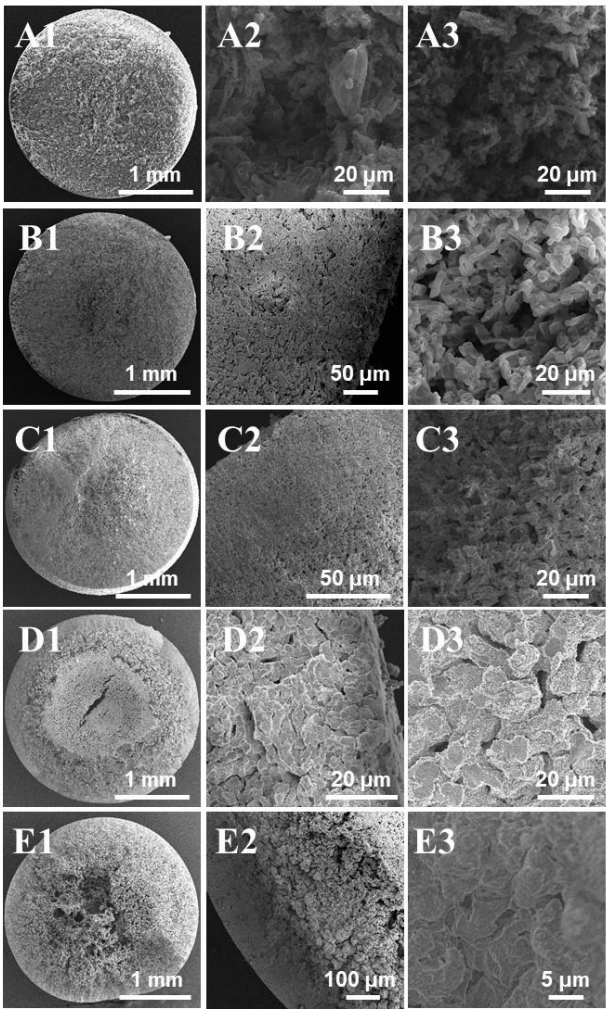


Figure S10. SEM images showing the interior structure of MF resin and MRF resin with different molar ratios of M to R. (A1-A3) SEM images for the interior structure (cut deliberately) and its interior structure of MF resin. (B1-B3) SEM images for the interior structure and its interior structure of MF resin prepared with the molar ratio of M/R =3. (C1-C3) SEM images for the interior structure and its interior structure of MF resin prepared with the molar ratio of M/R =2. (D1-D3) SEM images for the interior structure and its interior structure of MF resin prepared with the molar ratio of M/R =1.5. (E1-E3) SEM images for the interior structure and its interior structure of MF resin prepared with the molar ratio of M/R =1.

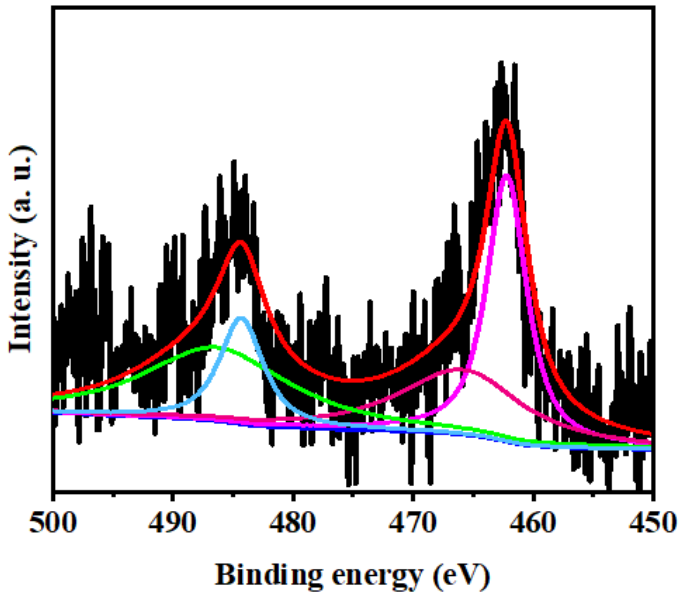


Figure S11. Ru 3p XPS spectrum of the Ru/MPCS catalyst.

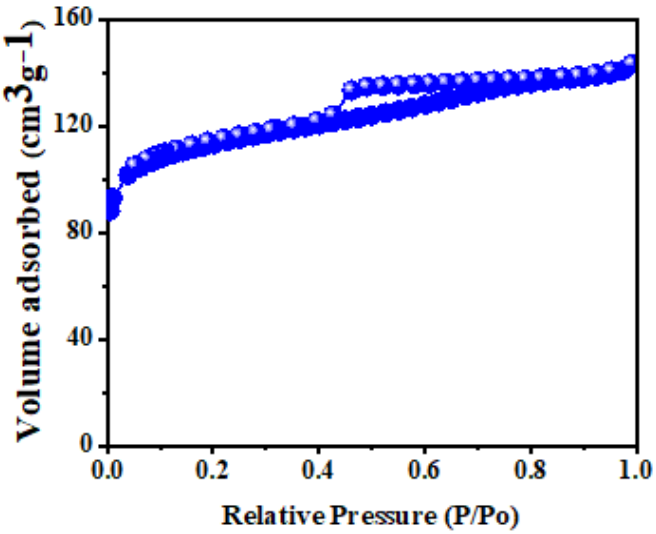


Figure S12. N_2 adsorption-desorption isotherm of the Ru/MPCS catalyst.

Figure S13. Appearances of image of the Ru/MPCS after recycling experiments.

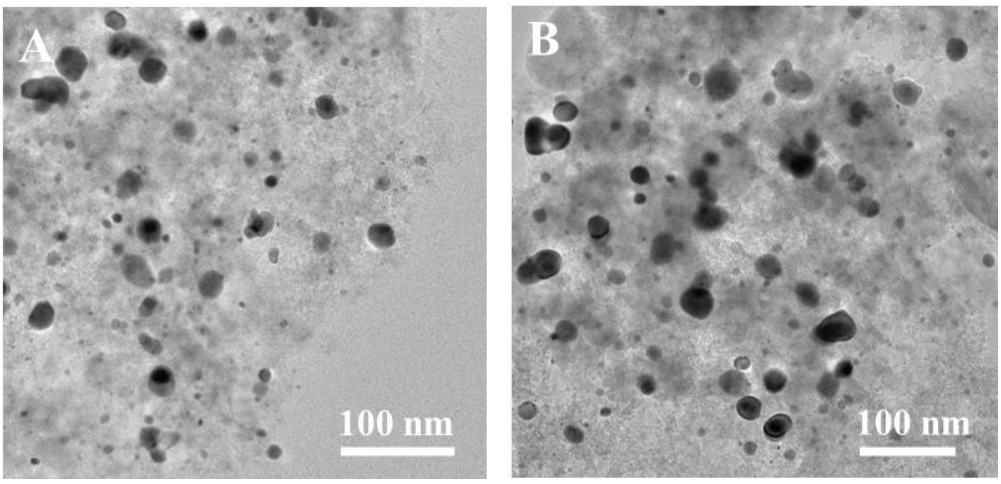


Figure S14. TEM images of Ru nanoparticles supported on the honeycombed MPCS. (A) fresh Ru/MPCS. (B) Ru/MPCS after twenty reaction cycles.

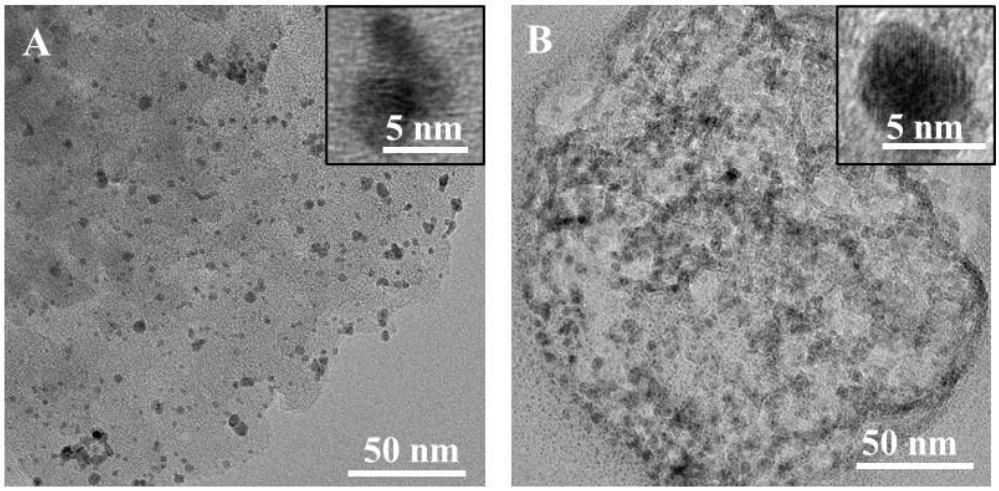


Figure S15. TEM images of Ru nanoparticles supported on the AC-based catalysts from Sinopharm Chemical Reagent Co., Ltd. (A) fresh Ru/AC. (B) TEM image of Ru/AC after eight reaction cycles.

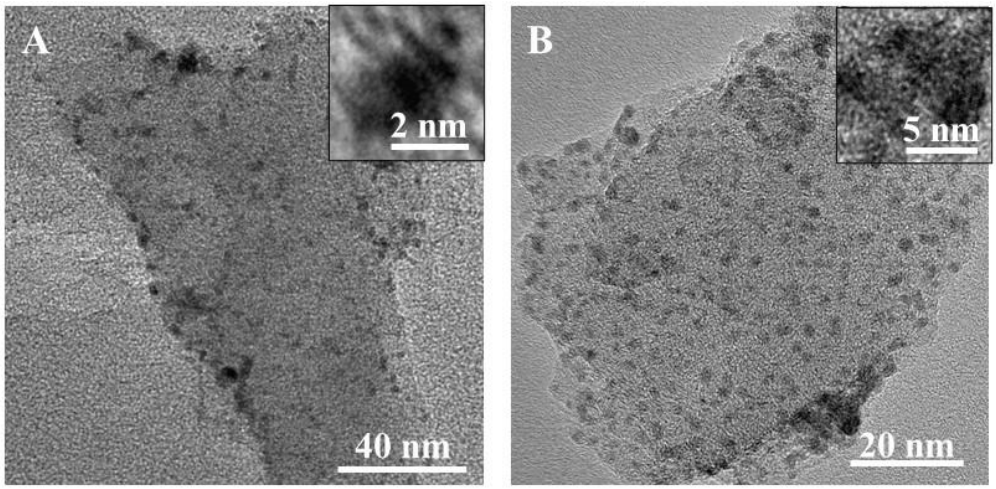


Figure S16. TEM images of Ru nanoparticles supported on the AC-based catalysts from QiXian Hui Hong Yuan Chemical Co. Ltd Company. (A) fresh Ru/AC. (B) TEM image of Ru/AC after five reaction cycles.

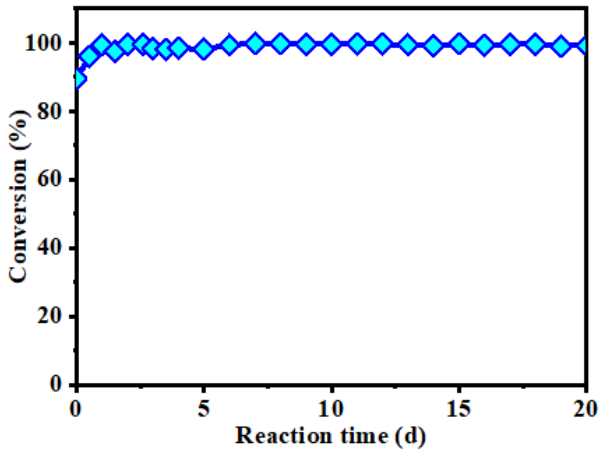


Figure S17. Continuous flow benzene hydrogenation over Ru/MPCS. Reaction conditions: benzene 0.017 mL/h, 0.519 g catalyst (with 0.88 wt% Ru), H_2 4 MPa, 110°C.

Table S1. Results of ICP-MS analysis of Ru/MPCS before and after reaction cycle.

Catalyst	Ru loading (wt%)
Ru/MPCS	0.88
Ru/MPCS after twenty reaction cycles	0.77

Table S2. Results of LA hydrogenation over the Ru/MPCS catalysts prepared at different carbonization temperatures.

T/ºC	S/C	Conversion (%)
600 ºC	3000:1	99.48
	6000:1	84.84
700 ºC	3000:1	99.99
	6000:1	42.88
800 ºC	3000:1	66.28
	6000:1	45.40

Reaction conditions: 110 ºC, 3 MPa H_2 and 2 h.

Table S3. Results of benzene hydrogenation over the Ru/MPCS catalysts prepared at different carbonization temperatures.

T/ºC	Conversion (%)	TOF /h^{-1}
600 ºC	64.2	5831
700 ºC	59.0	5358
800 ºC	24.7	2243

Reaction conditions: 0.2 g catalyst (with 0.88 wt% Ru), 12 ml benzene, 80 ºC, 4 MPa H_2, 30 min and the molar ratio of benzene to Ru (S/C) = 7733:1.

Mass Spectrometry Spectra