

## **Supplementary Information**

### **Sustainable and scalable synthesis of monodisperse carbon nanospheres and their derived superstructures**

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### **Experimental Section**

**Chemicals and Materials:** Glucose, fructose, sucrose and PSSMA were purchased from Aladdin. Sulfuric acid, hydrochloric acid, phosphoric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without any further purification.

**Synthesis of colloidal carbonaceous spheres:** In a typical experiment, 10.0 g glucose was added to 50.0 mL water, and then 70.0 mg PSSMA was introduced. After stirring for 2.0 h at room temperature, the solution was transferred into 100 mL autoclave and hydrothermally treated at 180 °C for 8.0 h. After the autoclave cooled to room temperature, the solid products were collected by centrifugation. After washed three times with water and ethanol, materials were dried at 70 °C overnight.

**Synthesis of CCSSs and CSSs:** Typically, 10.0 g glucose was added to 50.0 mL HCl solution, and then 70.0 or 800 mg PSSMA was introduced. After stirring for 2.0 h at room temperature, the solution was transferred into 100 mL autoclave and hydrothermally treated at 180 °C for 8.0 h. After the autoclave cooled to room temperature, the solid products were collected by centrifugation. After washed three times with water and ethanol, materials were dried at 70 °C overnight. CCSSs were calcined to 800 °C at a heating rate of 5 °C min<sup>-1</sup> and was held at that temperature for 2 h under N<sub>2</sub> atmosphere. After the sample was cooled, the black powder was obtained and named as CSSs.

**Catalysts Preparation:** Ru/CSSs and Ru/AC catalysts were prepared by an ultrasound-assisted coreduction method. CSSs or AC was dispersed in deionized water under ultrasound, and a desired amount RuCl<sub>3</sub> aqueous solution (0.01 g/mL) was added into the solution under treatment in ultrasound for 10 min. After that, 10 mL freshly NaBH<sub>4</sub> aqueous solution (2 mg/mL) was added to the solution under ultrasound treatment for another 30 min. The solid were separated by filtration and washed with water thoroughly. The obtained catalysts were dried at 70 °C overnight, then treated with a simple grinding and denoted as Ru/CSSs and Ru/AC.

Ru/AC-HCOOH catalysts was prepared by a HCOOH reduction method. Typically, AC was added to an aqueous solution of RuCl<sub>3</sub> (0.01 g/mL) and of Na<sub>2</sub>CO<sub>3</sub> (0.05 M). After that, the pH was adjust to ~10 by using

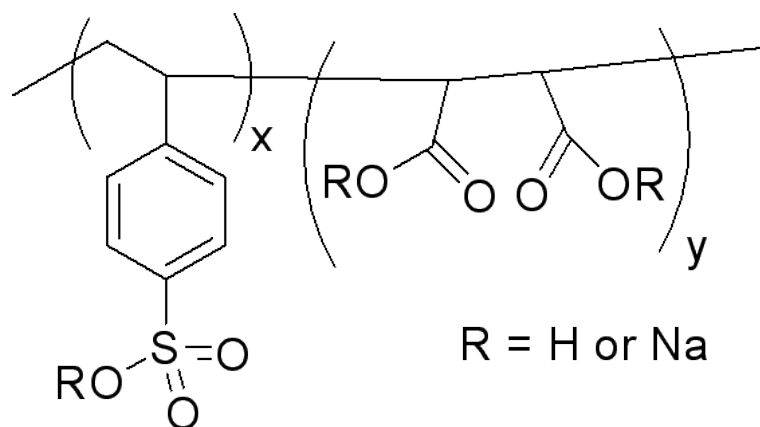
Na<sub>2</sub>CO<sub>3</sub> solution. The suspension was vigorously stirred for 2 h at 60 °C, and washed by deionized water to pH ~7.

The solid was dispersed in deionized water, and HCOOH (0.05 M) was added to reduce the Ru<sup>3+</sup>. After that, the Na<sub>2</sub>CO<sub>3</sub> solution was added to adjust the pH to 9~10. After the deposition-precipitation process, the sample was washed with water and then centrifuged, vacuum-dried overnight.

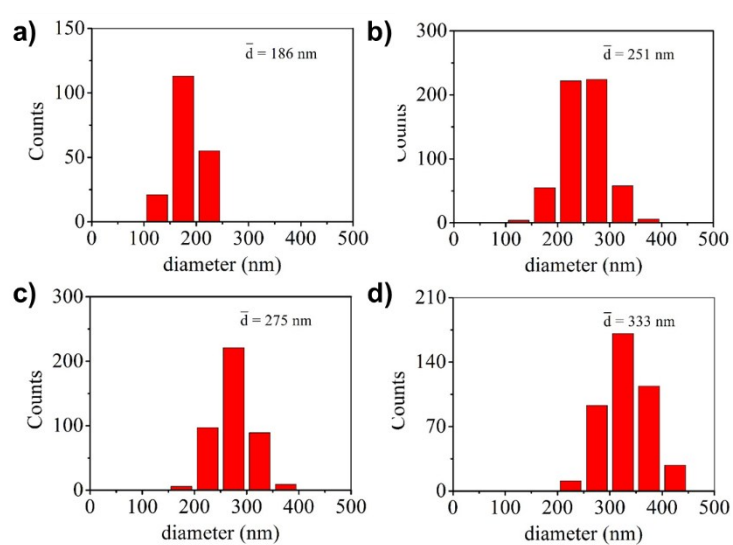
**Catalytic Evaluation:** Hydrogenation experiments were carried out using a 50 mL stainless steel autoclave equipped with a magnetic stirrer. In a typical process, a mixture of substrate, catalyst and solvent were introduced into the autoclave, then the autoclave was sealed tight. After being purged by low H<sub>2</sub> pressure three times to remove air, the reactor was pressurized with hydrogen at a desired pressure, after which the reactor was heated to the reaction temperature. After the reaction, the content of products and substrates were determined by gas chromatography flame ionization detection (GC-FID).

**Characterization:** SEM images were obtained using a Hitachi SU-8010. TEM was carried out with a Hitachi HT-7700 microscope. The N<sub>2</sub> adsorption–desorption isothermal analysis was performed using a Micromeritics ASAP 2020 HD88, and the surface area was calculated using the BET equation. X-ray photoelectron spectroscopy (XPS) was operated on an ESCALAB 250Xi spherical analyzer using an aluminum node (Al 1486.6 eV) X-ray source.

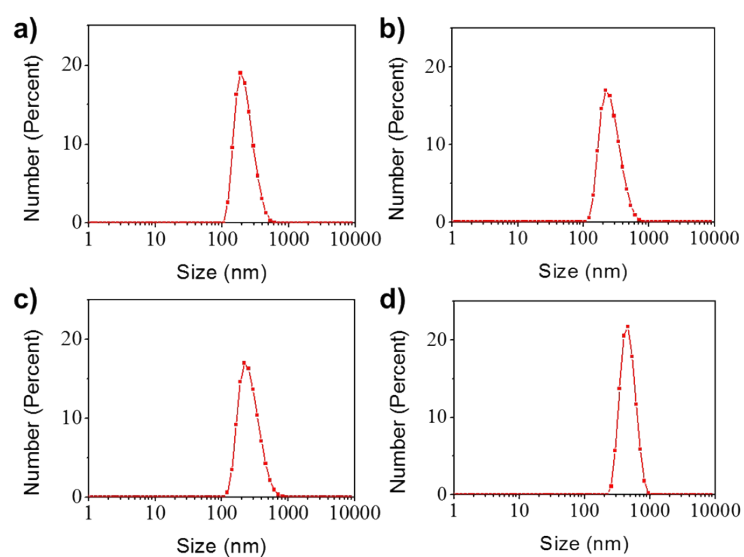
The Raman spectra were collected on a Raman spectrometer (JY, HR 800) using a 514 nm laser. The FT-IR spectrum was collected on a Nicolet Nexus 470. XRD data were collected using a D/tex-Ultima TV wide-angle X-ray diffractometer equipped with Cu K $\alpha$  radiation. Thermogravimetric analysis was performed using Mettler Toledo TGA/DSC 1100SF. The element analysis was carried out on the Flash EA 1112, ThermoFinnigan.



**Fig. S1.** Chemical structural formula of PSSMA (molar ratio,  $x : y = 1 : 1$ ).

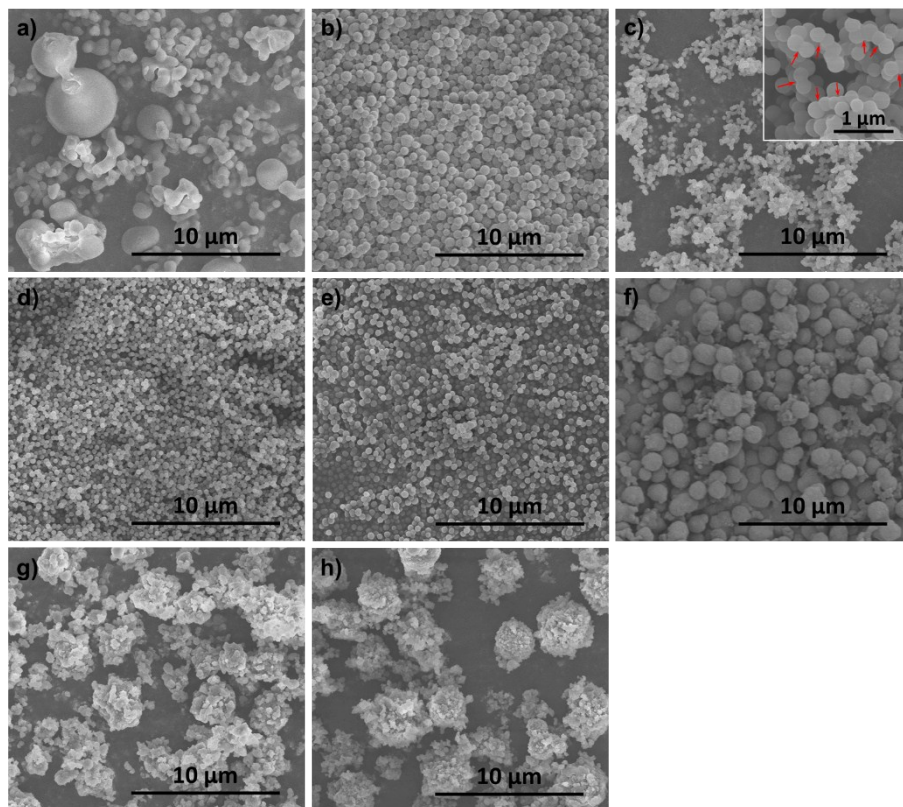


**Fig. S2.** Distribution histograms of the diameters of nanoparticles at different times (inset d is the average diameter). (a) 4 h. (b) 6 h. (c) 8 h. (d) 24 h.



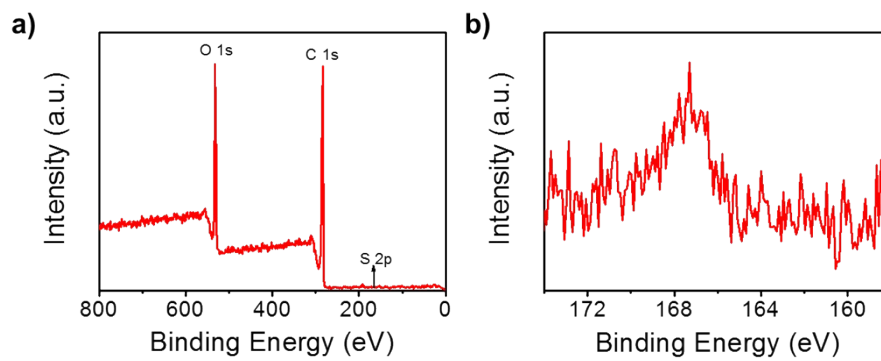
**Fig. S3.** DLS curves of the diameters of nanoparticles at different times. (a) 4 h. (b) 6 h. (c) 8 h. (d) 24 h.

The variation trend of the sizes measured by DLS is consistent with the results from SEM images, while the average size is larger than that from SEM. Three reasons are attributed to this difference: (1) the diameter measured by DLS is the hydrodynamic radius, which is larger than the actual size; (2) the swelling of the carbonaceous nanoparticles after absorbing water; (3) there may be slight aggregation of the carbonaceous spheres in aqueous dispersion.

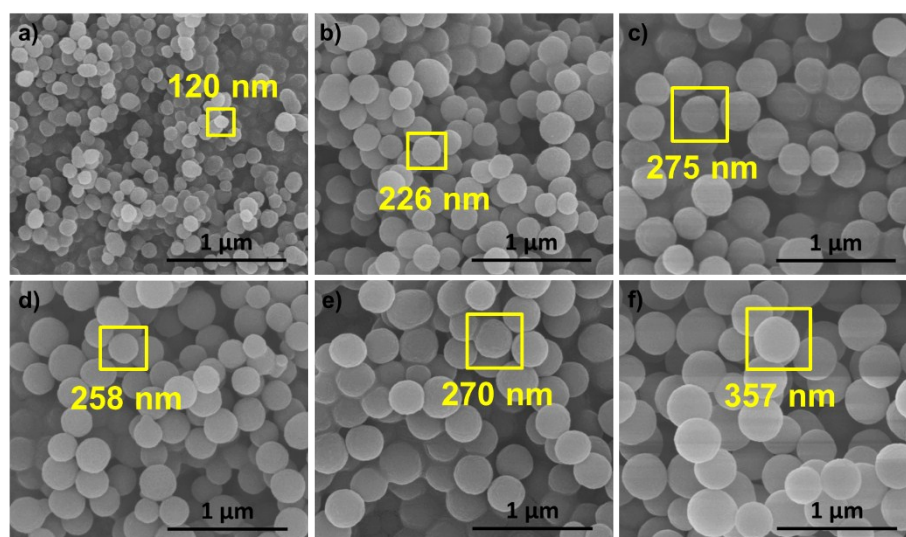


**Fig. S4.** SEM images of products from HTC of glucose and different amount of PSSMA. (a) 0 mg. (b) 20 mg. (c) 50 mg. (d) 70 mg. (e) 100 mg. (f) 200 mg. (g) 400 mg. (h) 800 mg.

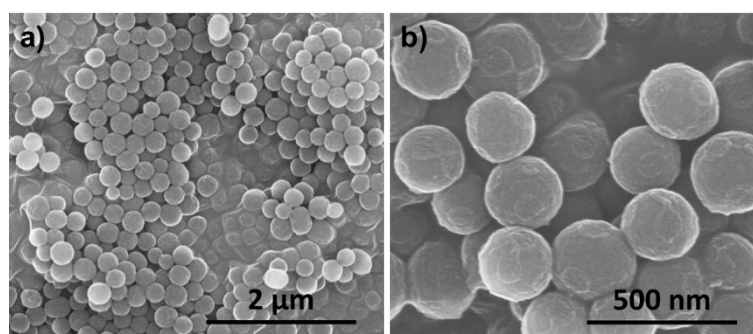
Compared to the nanospheres with 70 mg PSSMA added, nanospheres with a similar size were achieved with 100 mg PSSMA. However, two types of spheres formed (one  $> 1 \mu\text{m}$ , and another  $< 300 \text{ nm}$ ) when 200 mg PSSMA reached, which is similar to our previous report<sup>22</sup>. Because more PSSMA adsorbed on carbonaceous seeds, while the increased adsorbed layers and thickness fully blocked the surface and arrest growth ( $< 300 \text{ nm}$  particles), so that new nucleation occurs. These new particles are likely to grow into bigger spheres ( $> 1 \mu\text{m}$ ) because the free PSSMA concentration in solution is much lower than that at the beginning (as most is adsorbed on the initially nucleated particles). A further increase of the PSSMA to 400 and 800 mg lead to irregular structure from the aggregation of small particles. These results may result from the stability of so many small nanoparticles.



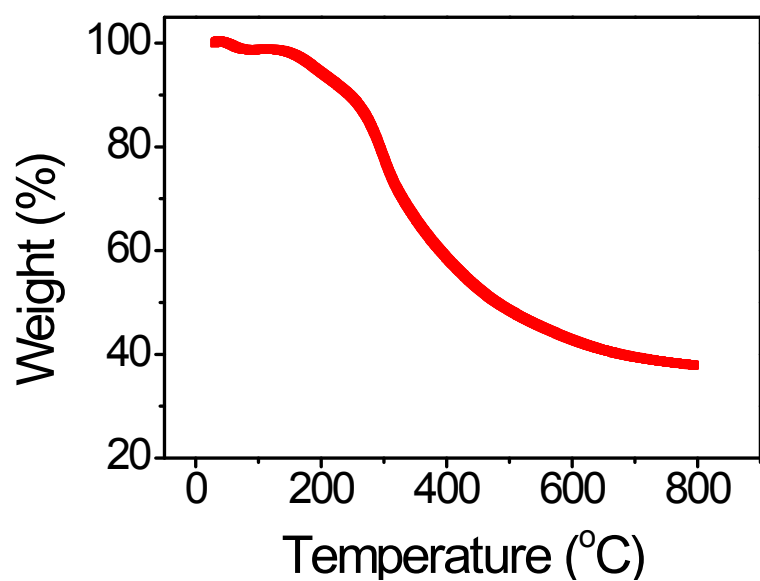
**Fig. S5.** (a) Survey spectra and (b) high-resolution S2p XPS spectra of material at 8 h.



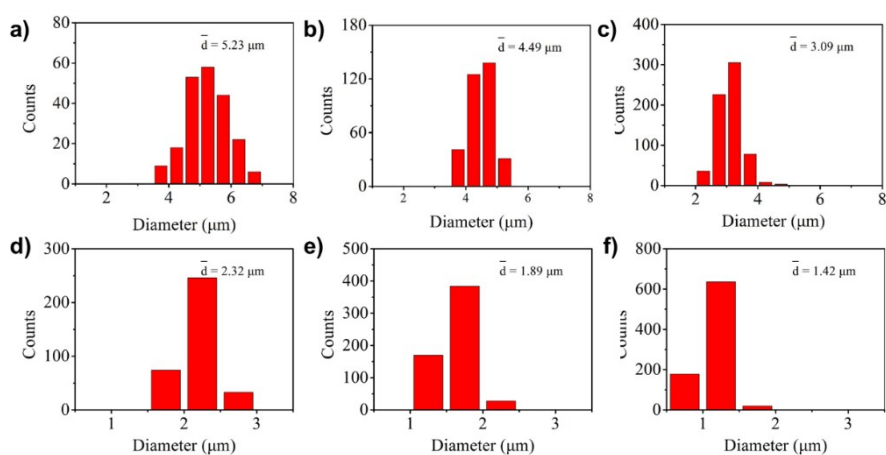
**Fig. S6.** SEM images of products from HTC of glucose and PSSMA. (a) 160 °C. (b) 170 °C. (c) 180 °C. (d) 6 g glucose. (e) 8 g glucose. (f) 16 g glucose.



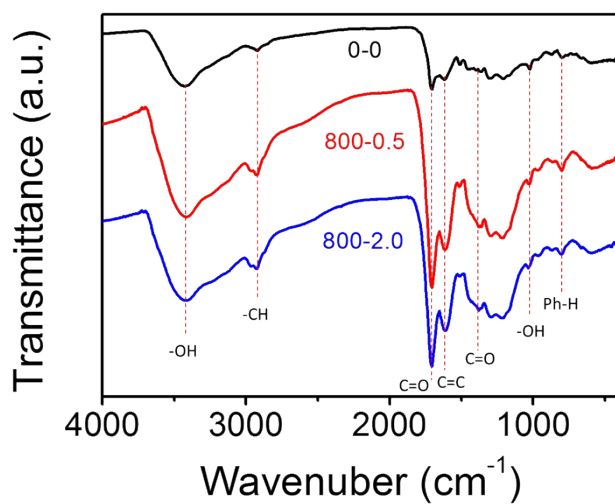
**Fig. S7.** SEM images of products from scale-up experiment.



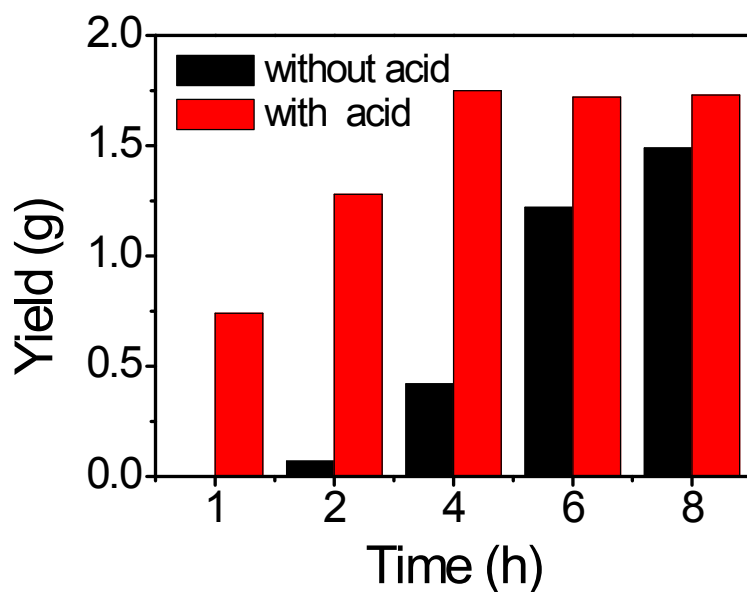
**Fig. S8.** Thermogravimetric analysis of carbonaceous nanospheres.



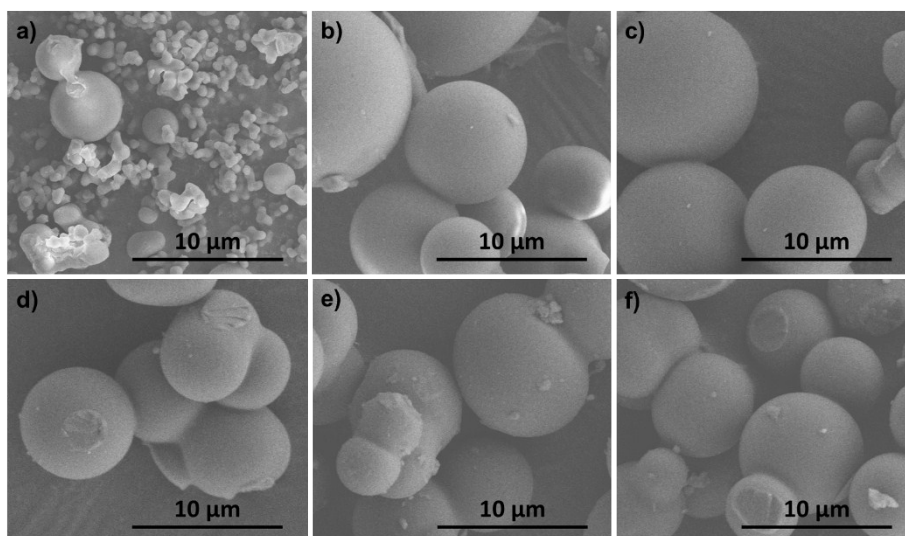
**Fig. S9.** Distribution histograms of the diameters of CCSSs (inset  $\bar{d}$  is the average diameter). (a) CCSSs-70-0.2. (b) CCSSs-70-0.5. (c) CCSSs-70-1.0. (d) CCSSs-800-0.5. (e) CCSSs-800-1.0. (f) CCSSs-800-2.0.



**Fig. S10.** FT-IR spectrum of product from HTC of glucose without PSSMA or acid, CCSSs-800-0.5 and CCSSs-800-2.0. The increased or appeared bonds in the region between 1700 to 1600  $\text{cm}^{-1}$  (C=O and C=C stretching vibrations) and between 875 to 750  $\text{cm}^{-1}$  (Ph-H out-of-plane bending vibrations) indicate the increase of  $\text{sp}^2$  carbon.

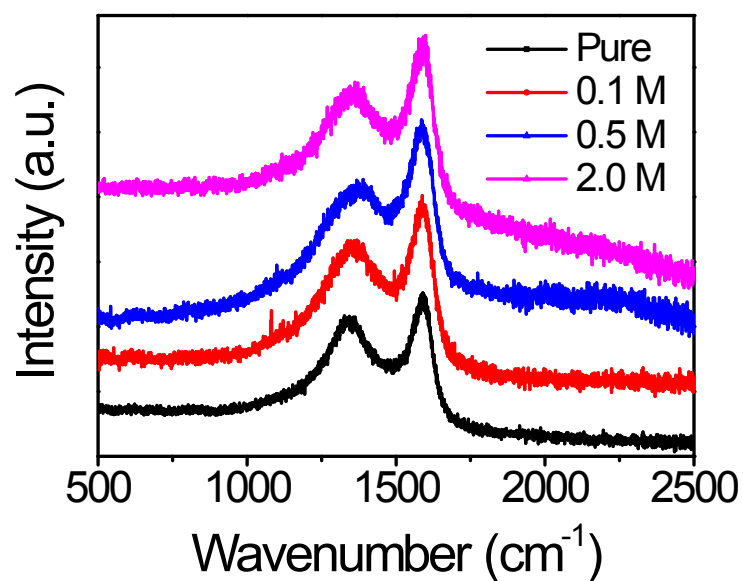


**Fig. S11.** Yields of products from HTC of glucose with and without 0.5M acid.

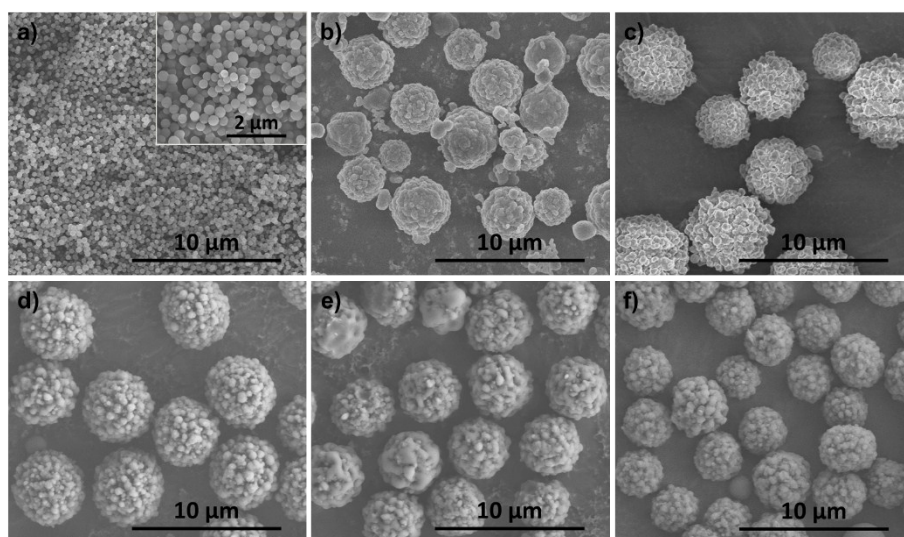


**Fig. S12.** SEM images of products from HTC of glucose at different acid concentrations. (a) 0 M. (b) 0.1 M. (c) 0.2 M. (d) 0.5 M. (e) 1.0 M. (f) 2.0 M.

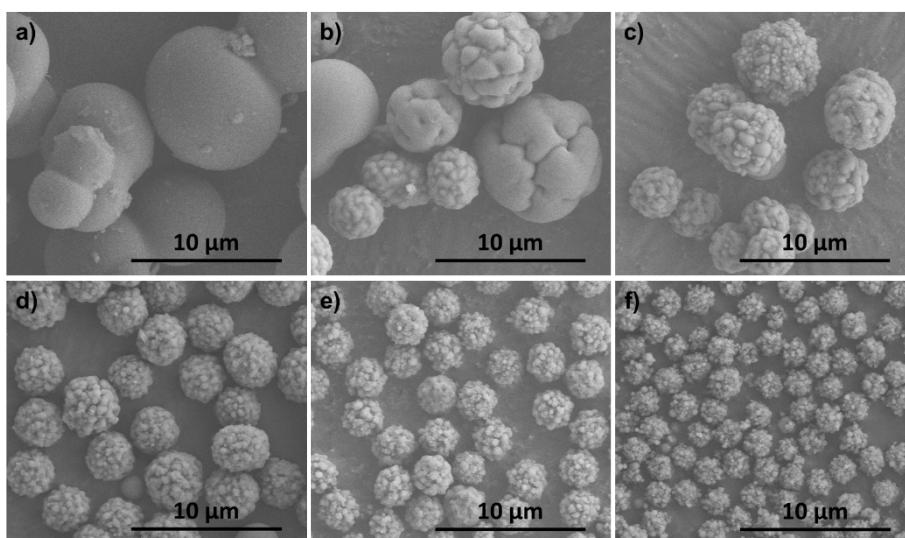




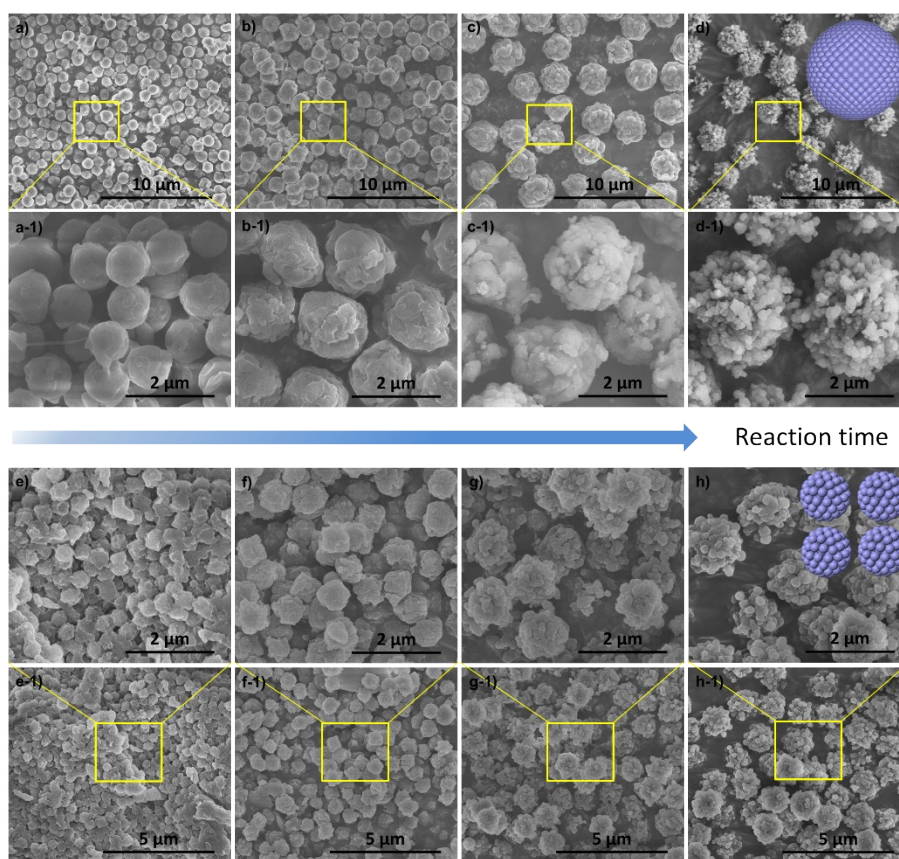
**Fig. S13.** Raman spectra of samples with different acid concentration.



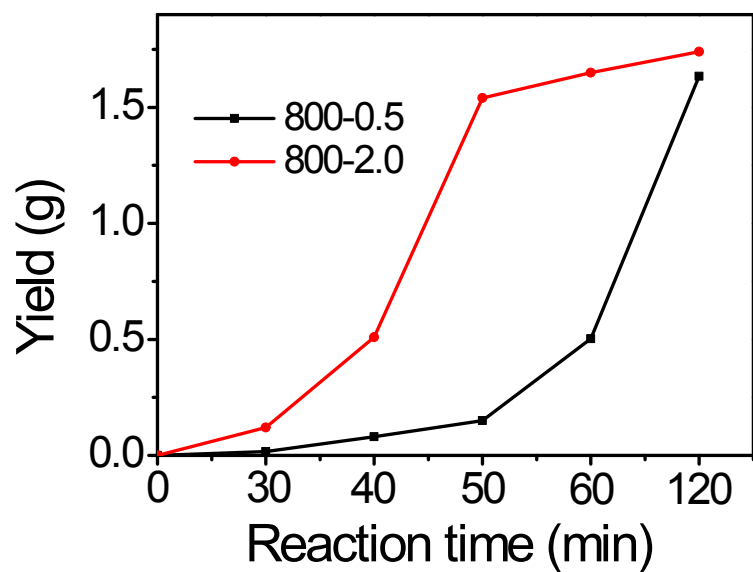
**Fig. S14.** SEM images of samples from HTC of glucose at the presence of 70 mg PSSMA and various concentration of acid. (a) 0 M. (b) 0.05 M. (c) 0.1 M. (d) 0.2 M. (e) 0.5 M. (f) 1.0 M.



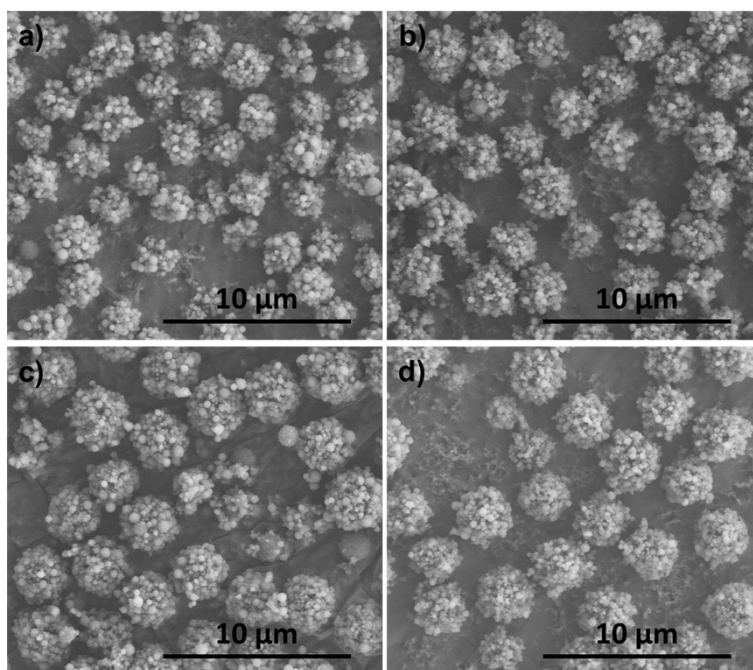
**Fig. S15.** SEM images of samples from HTC of glucose at the presence of 1.0 M acid and various amount of PSSMA. (a) 0 mg. (b) 10 mg. (c) 40 mg. (d) 70 mg. (e) 200 mg. (f) 800 mg.



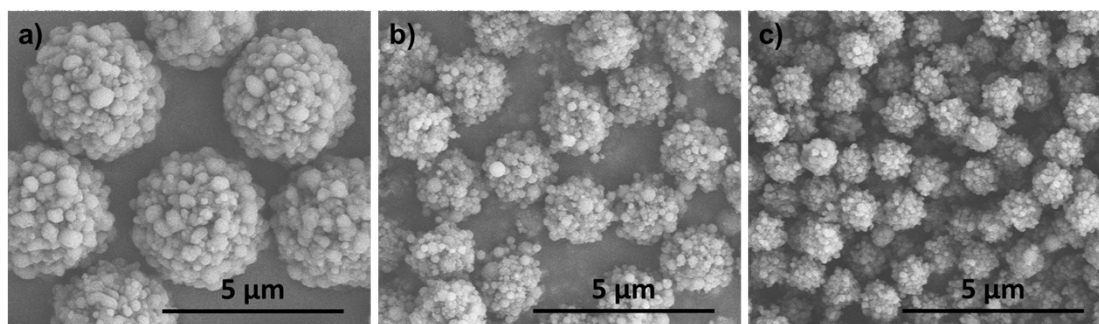
**Fig. S16.** SEM images of CCSSs-800-0.5 (a-d) and CCSSs-800-2.0 (e-h) at different reaction times. (a, e) 30 min. (b, f) 40 min. (c, g) 1.0 h. (d, h) 2.0 h.



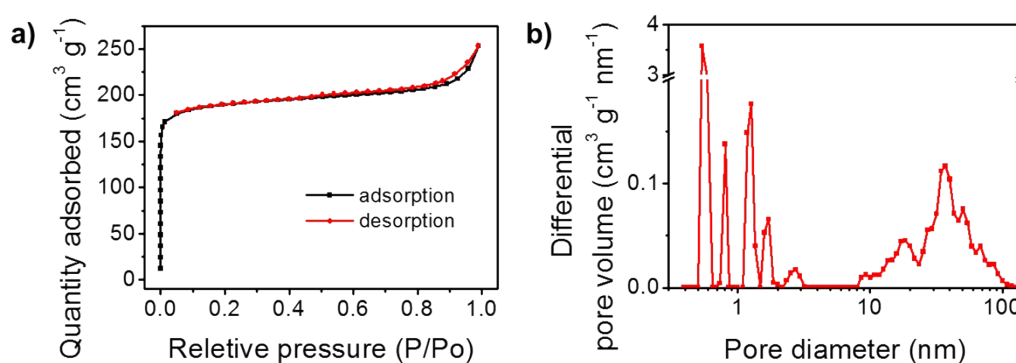
**Fig. S17.** Yields of CCSSs-800-0.5 and CCSSs-800-2.0 at different reaction times.



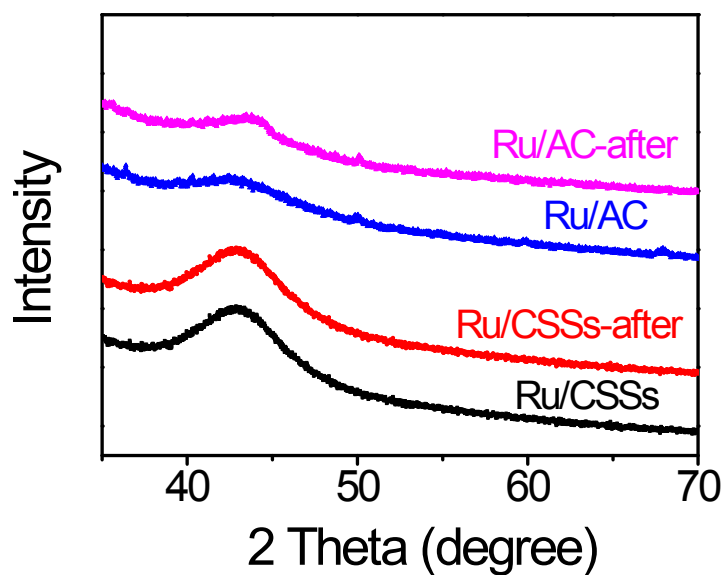
**Fig. S18.** SEM images of products from HTC of saccharides and 800 mg PSSMA at 0.5M acid concentrations. (a) Fructose. (b) Sucrose. (c) Sulfuric acid. (e) Scale-up experiment.



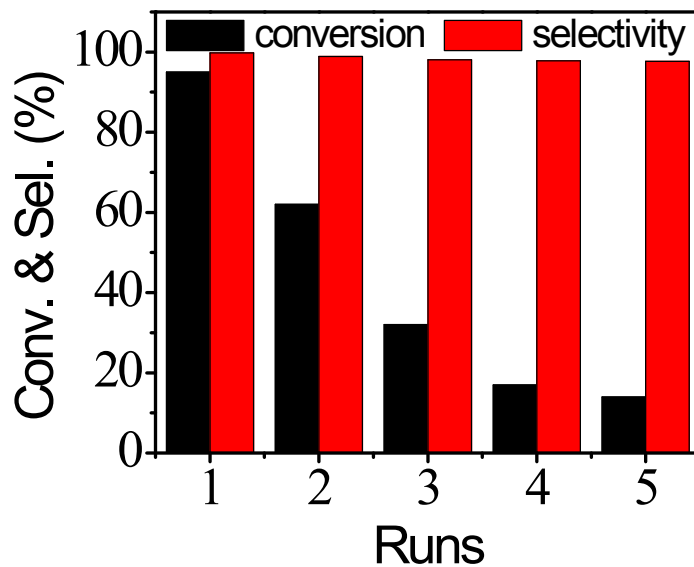
**Fig. S19.** SEM images of (a) CSSs-70-0.5, (b) CSSs-800-0.5 and (c) CSSs-800-2.0.



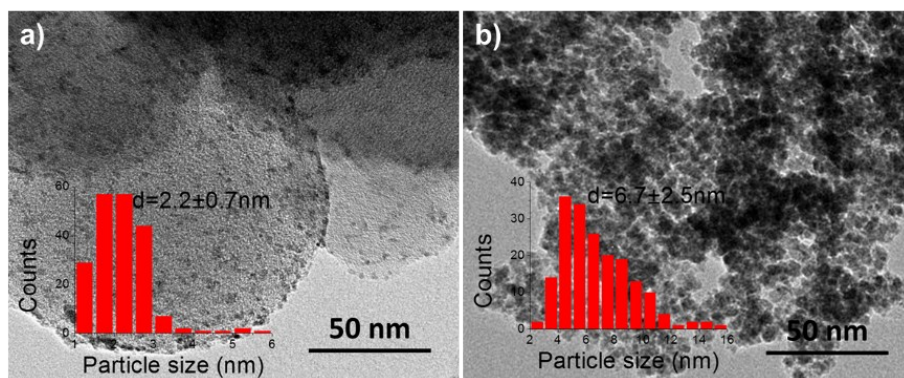
**Fig. S20.** N<sub>2</sub> adsorption-desorption isotherms and pore size distribution of CCSs. (a) N<sub>2</sub> adsorption-desorption isotherms. (b) Pore size distribution, which was derived from the desorption branches of the isotherms using the DFT method.



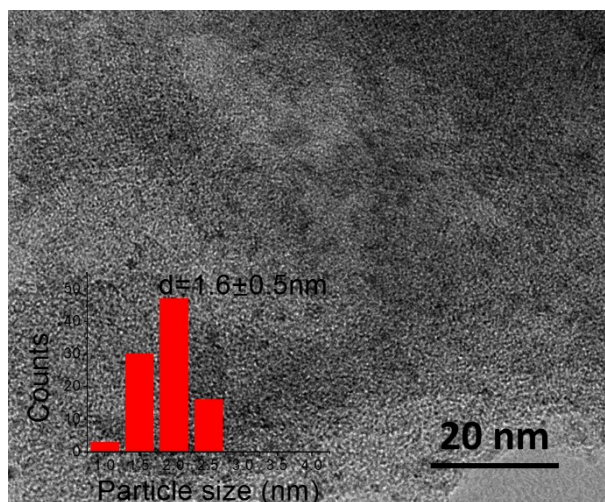
**Fig. S21.** XRD patterns of Ru/CSSs and Ru/AC before and after multiple runs.



**Fig. S22.** Performance of Ru/AC catalyst in multiple runs. Reaction condition: cat. 25 mg, toluene 94.4 mmol, 100 °C, 1.4 MPa H<sub>2</sub> pressure.



**Fig. S23.** HRTEM images and particle size distribution of (a) Ru/CSSs and (b) Ru/AC after multiple runs.



**Fig. S24.** HRTEM images and particle size distribution of Ru/AC-HCOOH.

**Table S1.** Reaction conditions to prepare carbonaceous nanospheres.

Entry	Glucose (g)	PSSMA (mg)	Temperature (°C)	Time (h)	Size (nm)	Yield (g)
1	10	70	180	4	186	0.5
2	10	70	180	6	251	1.1
3	10	70	180	8	275	1.6
4	10	70	180	24	333	3.2
5	10	70	160	8	120	0.2
6	10	70	170	8	226	0.6
7	10	70	190	8	523	3.2
8	10	70	200	8	634	3.9
7	6	70	180	8	258	1.0
8	8	70	180	8	285	1.2
9	16	70	180	8	357	2.9

All experiments were carried out in 50 mL deionized water.

**Table S2.** Reaction conditions to prepare CCSSs.

Name	PSSMA (mg)	Hydrochloric acid (M)	Size (µm)	Yield (g)
CCSSs-70-0.2	70	0.2	5.23	1.9
CCSSs-70-0.5	70	0.5	4.49	1.7
CCSSs-70-1.0	70	1	3.09	1.5
CCSSs-800-0.5	800	0.5	2.32	1.7
CCSSs-800-1.0	800	1	1.89	1.5
CCSSs-800-2.0	800	2	1.42	1.5

All experiments were carried out with 10 g glucose in 50 mL deionized water, and at 180 °C for 8 h.

**Table S3.** Hydrogenation of toluene over various catalysts.

Entry	Catalyst	Conversion (%)	Selectivity (%)
1	Ru/CSS-70-0.5	70	97
2	Ru/CSS-800-0.5	78	97
3	Ru/CSS-800-2.0	84	99
4	Ru/AC	32	90
5	Ru/AC-HCOOH	43	95

Reaction condition: cat. 25 mg, toluene 94.4 mmol, 100 °C, 1.4 MPa H<sub>2</sub> pressure, 1h.