Electronic Supplementary Information

Upgrading of aromatic compounds in bio-oil over ultrathin graphene encapsulated Ru nanoparticles

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1. Experimental Section

1.1 Catalyst synthesis

The synthesis of Ru@G-CS composites involved self-assembly of glucose, melamine and RuCl$_3$. In a typical experiment, melamine (3.0 g) was mixed with a certain weighted RuCl$_3$, glucose (1.5 g), and 15.0 mL water, and then the homogenous mixture was heated at 80 °C until completely drying to form a brown powder (denoted as S80). Then S80 was transformed into a furnace and heated at suitable temperature (500−800 °C) for 4.0 h (with a heating rate of 2.5 °C/min) under argon flow of 20 mL/min. After that, the sample was treated in 50 mL aqua regia solution under stirring for 6.0 h to remove the soluble species. The acid-treated solid sample was filtered and washed with water until free of Cl$^-$, and further washed with 50 mL acetone. Finally, the sample was dried at 70 °C in a vacuum oven for 4.0 h to obtain the final material. N-doped CS was prepared from glucose (1.5 g) and melamine (3.0 g) *via*

pyrolysis reaction at 700 °C for 4.0 h. Ru/AC catalysts were prepared *via* microwave-assisted green synthesis method [1].

Ru NPs loaded on other different supports (such as SiO_2, Al_2O_3, Fe_3O_4 and MgO) were prepared according to the same procedure as reported in previous work [2]. The metal contents in the prepared catalysts were checked *via* inductively coupled plasma-atomic emission spectroscopy (ICP, Plasma-Spec-II spectrometer), which were listed in Table S1.

Ru contents in prepared Ru@G-CS catalysts were measured in the following procedures, sample (0.1 g) was first pretreated in air from 25 to 900 °C (with a heating rate of 5 °C/min), and then the residual solids were dissolved with 50 mL aqua regia solution. Metal ion (Ru^{4+}) in above solution was detected *via* inductively coupled plasma-atomic emission spectroscopy (ICP, Plasma-Spec-II spectrometer), and the results were also listed in Table S1.

1.2 Characterization

X-ray diffraction (XRD) patterns were recorded on a diffractometer (RIGAKUD/MAX 2550/PC) at 40 kV and 100 mA with Cu Kα radiation (λ=1.5406 Å). Raman spectra were collected on a Rhenishaw 2000 Confocal Raman Microprobe (Rhenishaw, Instruments, England) using a 514.5 nm argon laser. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer PHI ESCA System. X-ray source was Mg standard anode (1253.6 eV) at 12 kV and 300 W. The scanning electron microscope (SEM) images were obtained with Zeiss Sigma field emission SEM (Model 8100). Scanning transmission electron microscopy (STEM) and high angle annular dark field (HAADF) imaging were utilized to observe the image of individual particle at atomic resolution with an aberration corrected JEOL 2200FS (S)TEM

operating at 200 kV, in addition with the capability of taking X-ray energy dispersive spectrometer (EDS) spectra from individual particles larger than 1−2 nm. The Brunauer-Emmett-Teller (BET) surface areas and porous structure of the samples were measured by using micromeritics ASAP 2020 HD88.

1.3 Catalytic reactions

The hydrogenation reaction was carried out in a 20 mL custom designed stainless autoclave with a Teflon inner layer. In a typical procedure, catalyst was dispersed in 5.0 mL water, and then put into a certain amount of substrate. The autoclave was sealed, purged with H_2, pressurized to 1.0 MPa, and subsequently stirred with a magnetic stirrer (MAG-NEO, RV-06M, Japan) at a rate of 1000 rpm at the desired temperature. After reaction, solid catalyst was separated by centrifugation and products were analyzed by gas chromatograph (HP 5890, USA) with a 30 m capillary column (HP-5) using a flame ionization detector. And all products were confirmed by GC-MS (Agilent 6890-5973N). For each successive use, the catalyst was washed with water three times to remove the products, followed by drying at 80 °C for 6.0 h.
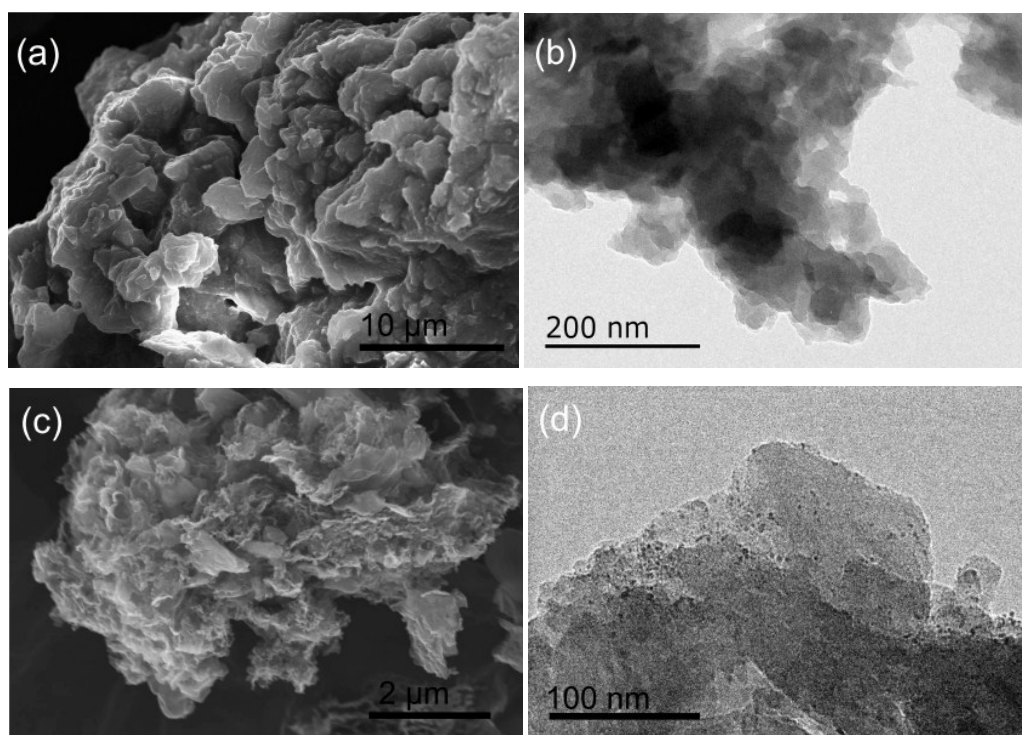
2. Results and disscussion

Fig. S1 (a) SEM and (b) TEM images of S80, (c) SEM and (d) TEM images of S80 at 500 °C point.

Table S1 Ru loading and particle size of different catalysts.

Entry	Sample	Ru loading (wt%) [a]	Particle size of Ru (nm) [b]	Raman analysis	
				I_D/I_G	I_{2D}/I_G
1	Ru NPs	-	7.2	-	-
2	Ru@G-CS-500	9.4	18.5	1.37	0.11
3	Ru@G-CS-600	10.8	13.1	1.19	0.24
4	Ru@G-CS-700	11.9	2.5	1.03	0.38
5	Ru@G-CS-800	13.5	8.4	1.12	0.19
6	Ru/AC	8.9	5.4	-	-
7	Ru/SiO$_2$	8.4	4.2	-	-
8	Ru/Al$_2$O$_3$	9.2	5.9	-	-
9	Ru/Fe$_3$O$_4$	9.0	3.7	-	-
10	Ru/MgO	8.5	6.8	-	-

[a] Ru contents were estimated by ICP-AES. The controlled Ru loading amounts were 10.0 mass percent with respect to the mass of supports.

[b] Particle size of Ru was calculated from the broadening of Ru (101) plane using Scherrer's equation from XRD ananlysis.
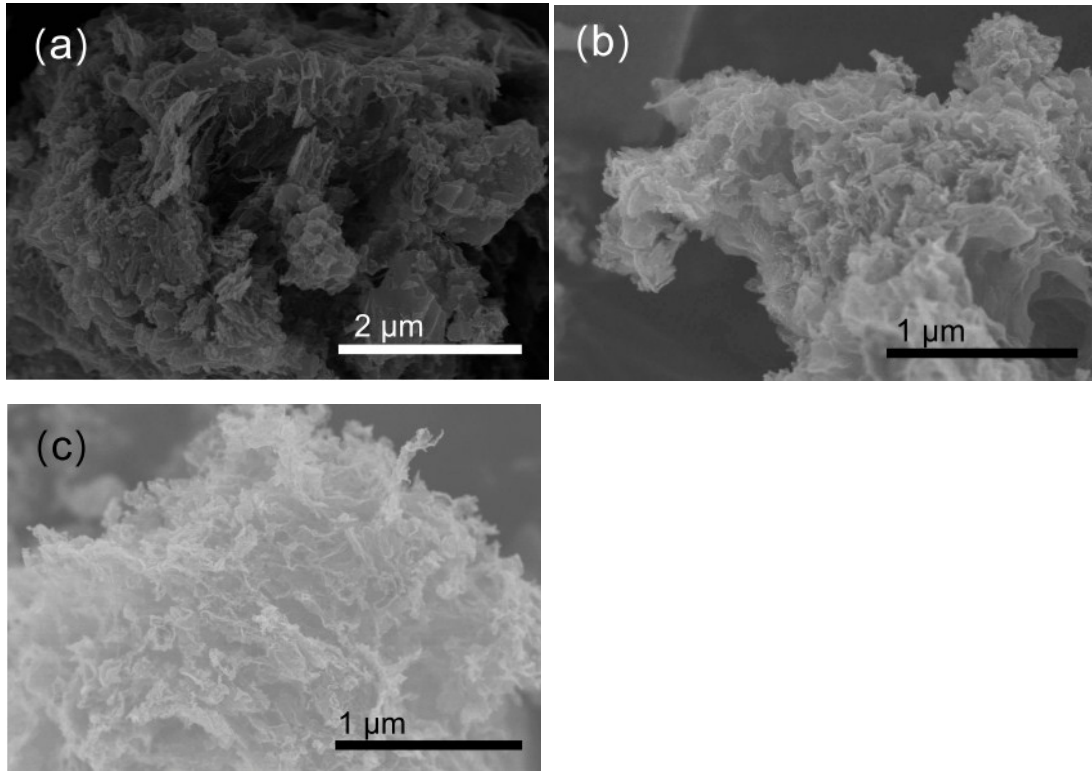
Fig. S2 SEM images of (a) Ru@G-CS-500, (b) Ru@G-CS-600 and (c) Ru@G-CS-800.

Table S2 Structure of Ru@G-CS hybrids.

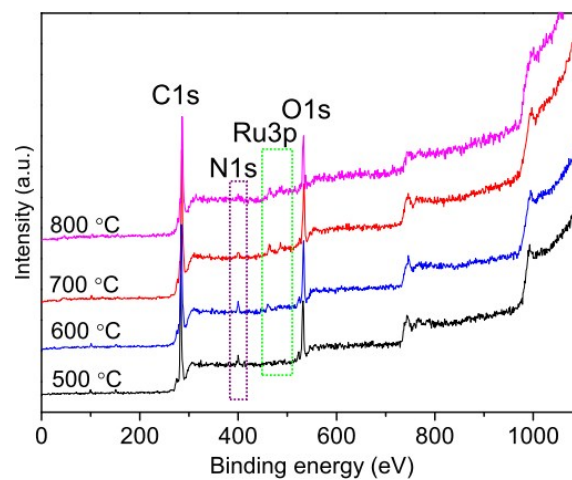| Sample	Particle size (nm)		Pore volume (cm^3/g)		Pore size (nm)		S_{BET} (m^2/g)
	XRD	TEM	Micro-	Meso-	Micro-	Meso-	
Ru@G-CS-500	18.5	19.4	0.079	0.105	1.78	3.59	171.6
Ru@G-CS-600	13.1	14.7	-	0.118	-	3.96	266.5
Ru@G-CS-700	2.5	2.6	-	0.144	-	3.92	311.8
Ru@G-CS-800	8.4	9.3	-	0.124	-	3.94	286.7

Fig. S3 XPS of survey spectra of Ru@G-CS composites prepared at varied pyrolysis

temperature.

Table S3 Surface composition of the synthesized Ru@G-CS composites.[a]

Sample	Relative atomic percentage (%)				Relative elemental percentage (%)				
	C	O	N	Ru	pyridinic N	pyrrolic N	graphitic N	Ru(0)	Ru(IV)
Ru@G-CS-500	77.57	19.83	2.17	0.43	39.1	34.5	26.4	43.7	56.3
Ru@G-CS-600	79.97	17.04	1.87	1.12	33.0	37.8	29.2	62.5	37.5
Ru@G-CS-700	82.45	14.32	1.74	1.49	31.3	35.6	33.1	71.4	28.6
Ru@G-CS-800	84.72	12.26	1.19	1.83	28.4	34.1	37.5	41.5	58.5

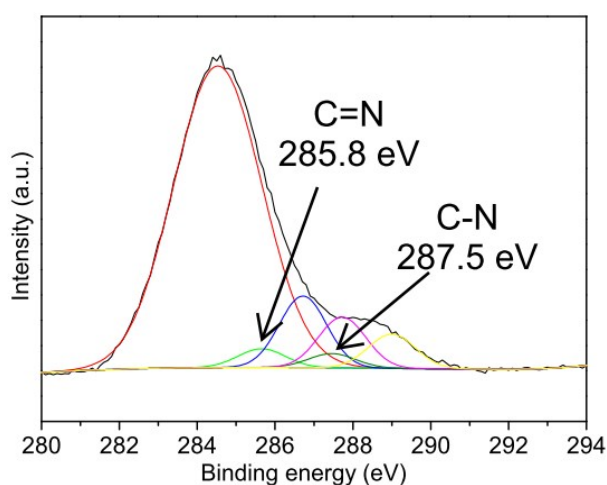[a] derived from XPS analysis.

Fig. S4 C1s spectra of Ru@G-CS-700.

Fig. S4 shows C1s XPS spectra of Fe_3C@G-CNT-700. Four kinds of carbon species in the main frame (C-C, sp^2) at 284.5 eV, carbon with dangling OH groups or an epoxy linkages (C-OH/epoxy) at 286.7 eV, carbonyls (C=O) at 287.7 eV and carboxylates (O-C=O) at 289.0 eV were detected in these samples [3]. C-N bonds were also detected at 285.8 and 287.5 eV, which were attributed to sp^2 and sp^3 bonded C-N, respectively [Ref. 32,39].
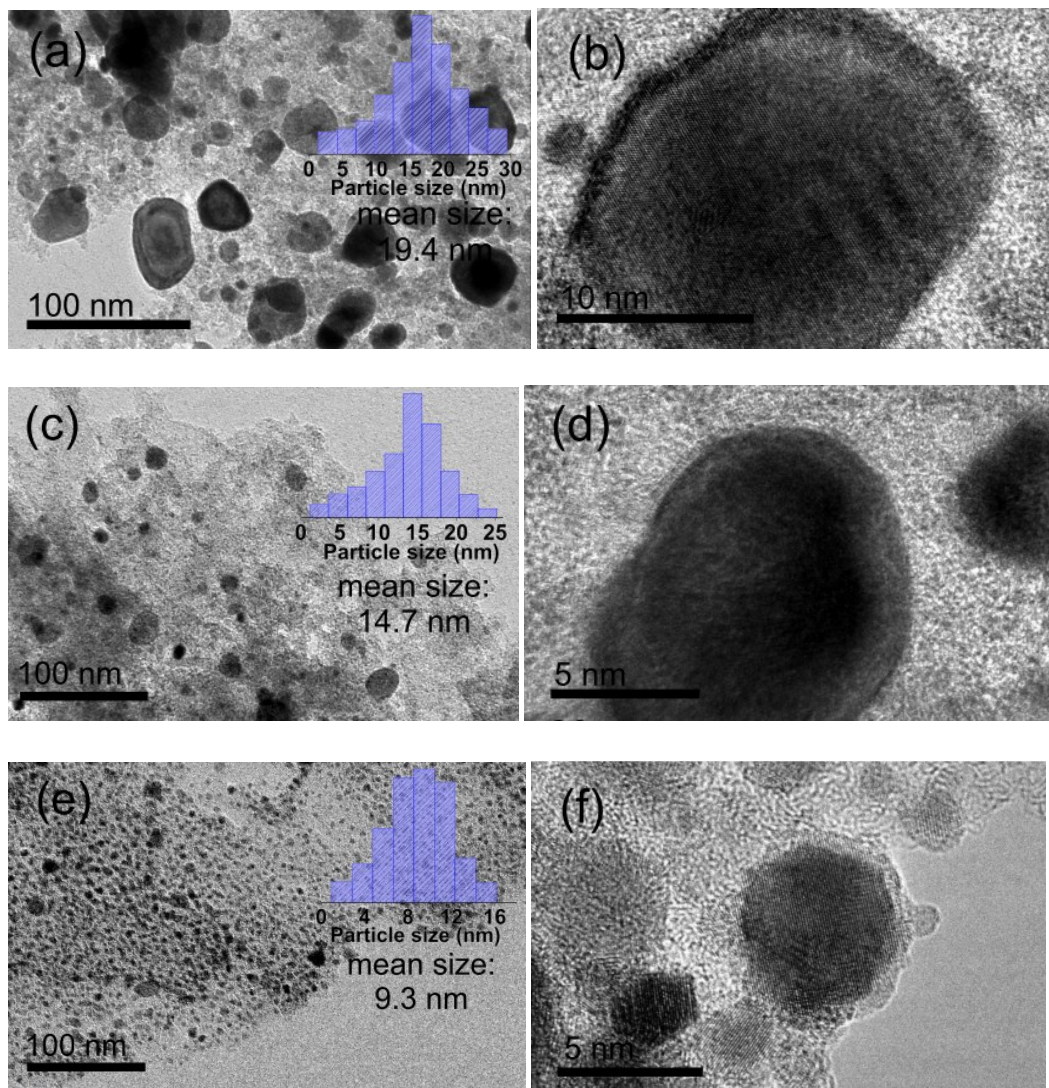
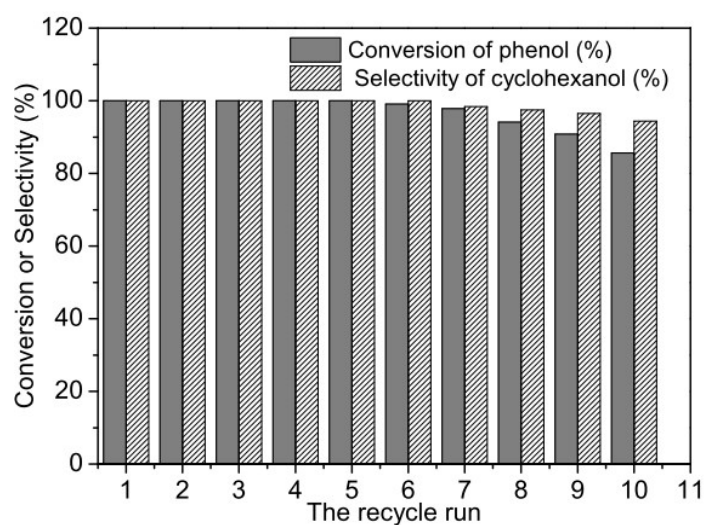Fig. S5 TEM and HRTEM images of (a,b) Ru@G-CS-500, (c,d) Ru@G-CS-600 and (e,f) Ru@G-CS-800.

Fig. S6 Reusability of the Ru@G-CS-700 catalyst. Reaction condition: Phenol, 0.2 mmol; Ru, 50 mol%; H_2O, 5.0 mL; H_2, 1.0 MPa; 20 °C; 1.0 h.

References

1 J.-J. Shi, M.-Y. Zhang, W.-C. Du, W.-S. Ning and Z.-Y. Hou, *Catal. Sci. Technol.*, 2015, **5**, 3108–3112.

2 W.-C. Du, S.-X. Xia, R.-F. Nie and Z.-Y. Hou, *Ind. Eng. Chem. Res.*, 2014, **53**, 4589−4594.

3 S.-J. Guo, S.-J. Dong and E.-K. Wang, *ACS Nano*, 2010, **4**, 547–555.