Supplementary Information for

Superhydrophobic Ru catalyst for highly efficient hydrogenation of phenol under mild aqueous conditions

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1. Properties of catalysts

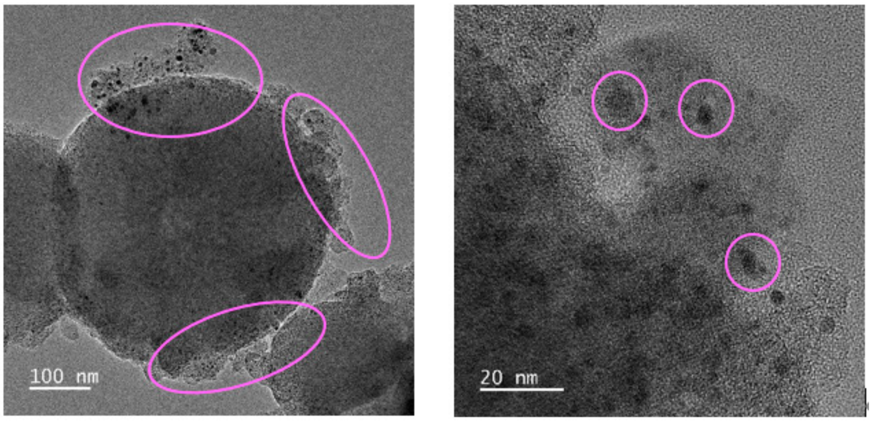

Figure S1. HRTEM image of Ru/N-CS

HRTEM image shows that the Ru nanoparticles in the Ru/N-CS were only detected on the external surface of the carbon spheres. The particles sizes were 3-6 nm. ICP reveals that the content of Ru in the catalyst was 0.16 wt%.

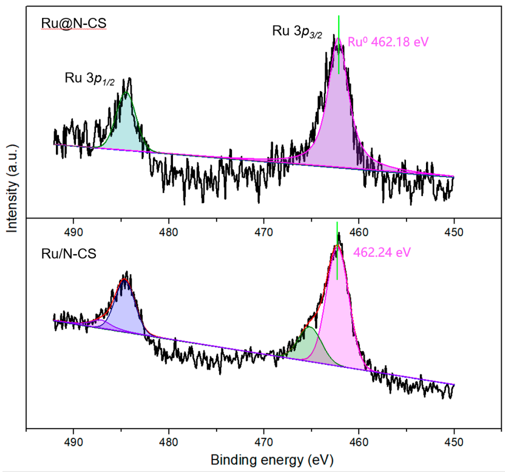

Figure S2. XPS spectra for Ru 3$p_{3/2}$ and Ru 3$p_{1/2}$ of Ru@N-CS and Ru/N-CS.

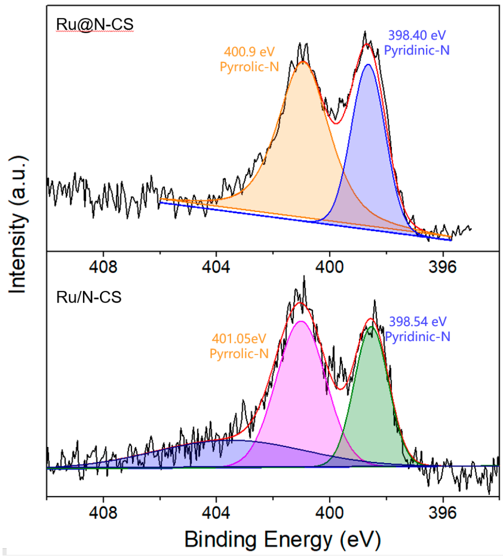

Figure S3. XPS spectra for N 1*s* of Ru@N-CS and Ru/N-CS.

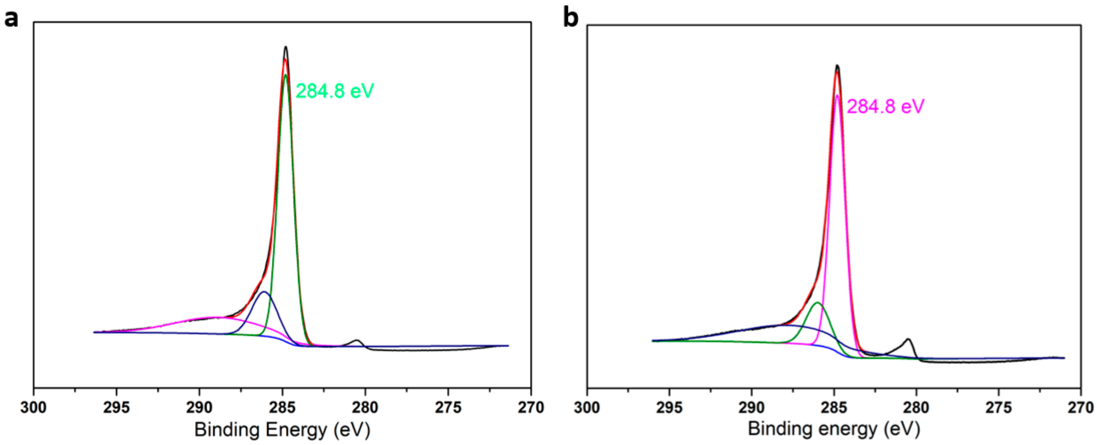

Figure S4. XPS spectra for C 1*s* of **a**, Ru@N-CS and **b**, Ru/N-CS

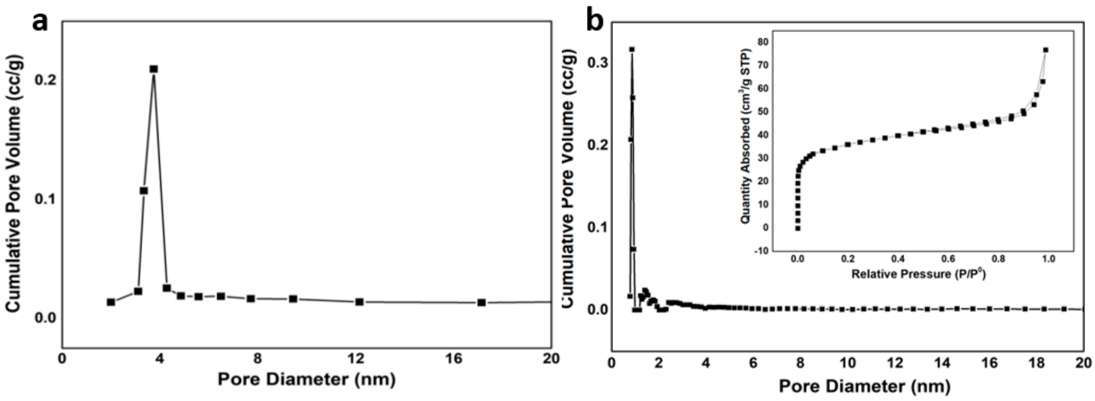

Figure S5. The pore size distribution by using the Barrett-Joyner-Halenda (BJH) method. **a**, for Ru@N-CS, **b**, for Ru/N-CS, the inset is nitrogen adsorption–desorption isotherms of Ru/N-CS.

2. Catalytic performance of phenol hydrogenation

The N-doped carbon spheres without Ru failed to catalyze the reaction. The peak that appeared at 2.2 minutes was dichloromethane extractant, and the peak that appeared at 9.4 minutes was phenol.

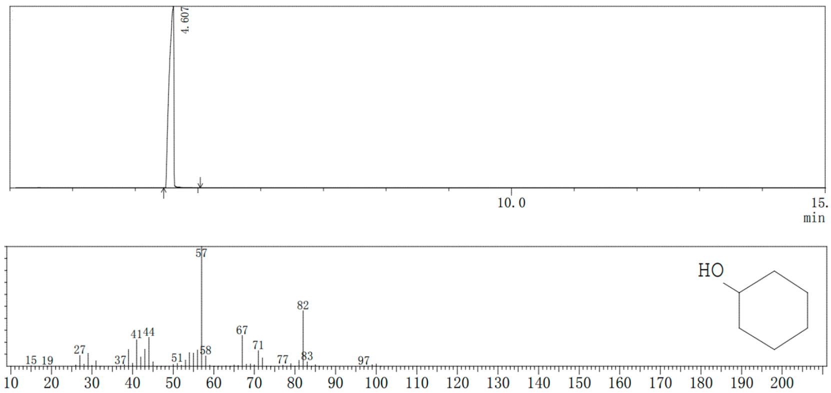

Figure S6. GC-MS for hydrogenation of phenol over Ru@N-CS. Experimental conditions: 0.11M of phenol, mass ratio of phenol and Ru was 13000:1, 80 °C, 0.5 MPa H_2, 30 min, 800r.

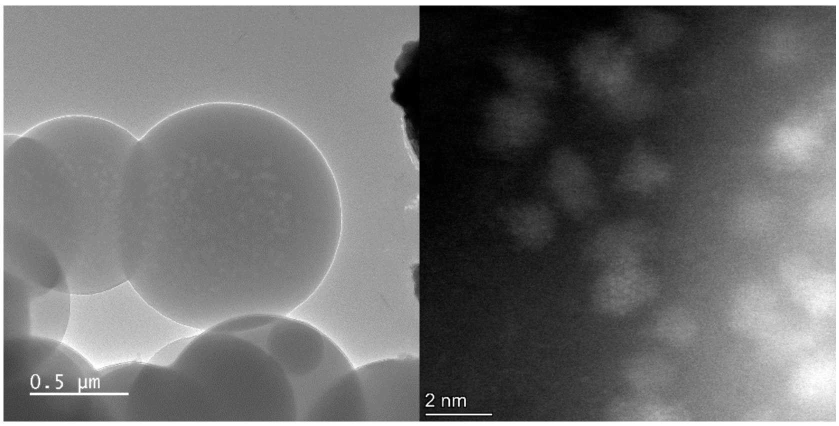

Figure S7. HRTEM and STEM image of Ru@N-CS after 8 cycles.

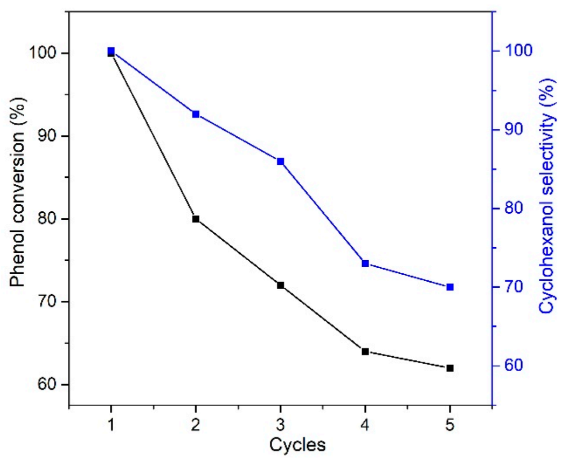

Figure S8. Reusability tests of phenol hydrogenation over Ru/N-CS catalyst under the following conditions: 0.11M of phenol, mass ratio of phenol and Ru was 1250:1, 80 °C, 0.5 MPa H_2, 3h, 800 rpm.

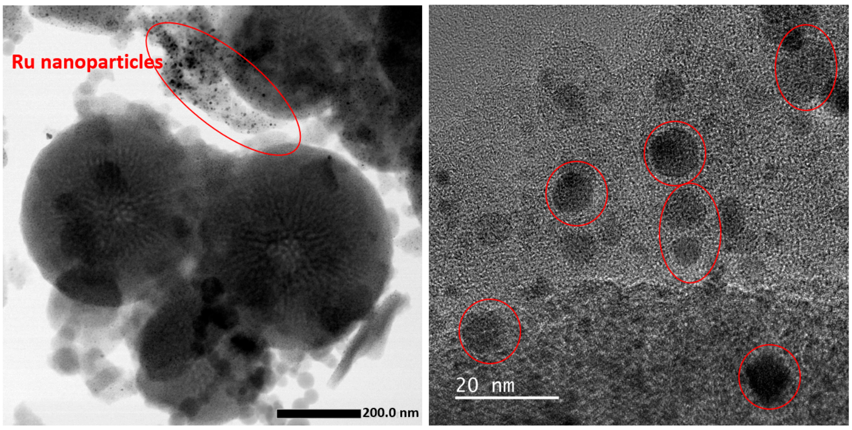

Figure S9. The HRTEM image of spend Ru/N-CS catalyst (5 cycles)

The HRTEM image (Figure S10) of spend catalyst (5 cycles) shows the structure of carbon spheres did not change, but Ru nanoparticles appeared agglomeration.

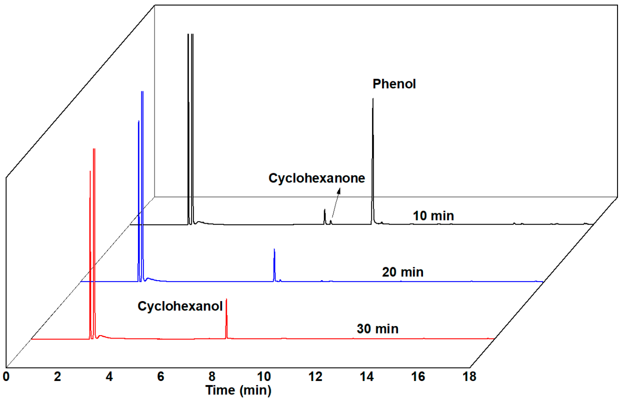

Figure S10. GC-MS for hydrogenation of phenol over Ru@N-CS at different times. Experimental conditions: 0.11M of phenol, mass ratio of phenol and Ru was 13000:1, 80 °C, 0.5 MPa H_2, 10 mL H_2O, 800 rpm.

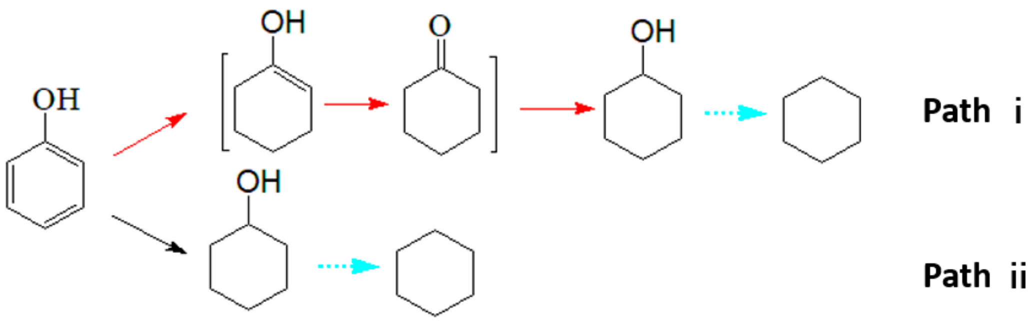

Figure S11. Possible reaction paths for phenol hydrogenation.

Table S1. Phenol conversion and cyclohexanol selectivity under different parameters over Ru@N-HC catalyst

	Mass ratio (phenol:Ru)	*T* (°C)	H_2 pressure (MPa)	Time (min)	Conversion (%)	Selectivity (%)
1	6500:1				100	100
2	9750:1	80	0.5	30	100	100
3	13000:				100	100

4	19500:1				48	
5			-		0	0
6			0.3		90	95
7	13000	80	0.5	30	100	100
8			1.0		100	100
9			2.0		100	100
10				10	11	90
11	13000	80	0.5	20	90	95
13				40	100	100
14				120	100	100
15	13000	60	0.5	30	96	98
16		70			99	99

Table S2. TOF and cyclic comparison over various catalysts for phenol conversion into cyclohexanol in an aqueous solution

	T (°C)	H_2 pressure (MPa)	Time (h)	phenol conv. (%); cyclohexanol selec. (%)	TOF (h^{-1})	Cycles	Ref.
Carbon sphere	80	0.5	0.5	0; 0	-	-	This work
Ru@N-CS	80	0.5	0.5	100; 100	9880[a]	7	This work
Ru/N-CS	80	0.5	0.5	10; 90	689[b]	5	This work
Ru/N-doped carbon	40	0.5	2	95; 99	40	5	Nat. Commun. 7 11326 2016
Ru/G-CS	20	1	1	100; 100	20[c]	10	J. Mater. Chem. A 4 5842 2016
Ru/SiCN	50	0.3	24	100; 99	165 [d]	3	Nat. Commun. 9 1751, 2018
Ru@NHC ligands	r.t.	0.5	20	100; 100	1[e]	4	Chem. Commun., 54, 7070, 2018
Ru/Nb_2O_5-100C18PA	80	1.2	4	100; 93	27 [f]	5	Green Chem., 24, 1152, 2022
Rh/N-doped carbon	30	0.5	6	100; 100	49 [g]	5	Green Chem. 22 3069, 2020
Rh/hollow mesoporous silica	45	0.5	3	90.6; 96.6	946 [h]	-	Chem. Eng. J. 397, 125484, 2020
Pt/CeO_2	100	3	1.5	100; 94.6	650 [i]	5	J. Mater. Chem. A 2 18398, 2014

TOF was calculated on the basis of molar amount of Ru active metal on the catalyst surface with

[a] conversion of 10% in 10 min.
[b] conversion of 11% in 30 min.

$$\text{TOF} = \frac{\text{Mole of phenol conversion}}{\text{Mole number of active metal on the surface} \times \text{reaction time [h]}}$$

TOF was calculated on the basis of molar amount of Ru with
[c] conversion of 100% in 1.0 h.
[d] conversion of 80% in 5 h.
[e] conversion of 100% in 20 h, THF medium.
[f] conversion of 100% in 4 h decalin/water mixture medium.
[g] conversion of 100% in 6 h.
[h] conversion of 100% in 3 h.
i conversion of 100% in 1.5 h.

TOF was calculated using the following equation.

$$\text{TOF} = \frac{\text{Mole of phenol conversion}}{\text{Mole number of tatol Ru active metal} \times \text{reaction time [h]}}$$

Table S3. Table S3 The content of different types of nitrogen and Ru in two catalysts

Samples	Relative elemental percentage (%)					Binding energy (eV)				
	Pyri-N	Pyrr-N	Oxid-N	Ru^0	Ru^{4+}	Pyri-N	Pyrr-N	Oxid-N	Ru^0	Ru^{4+}
Ru@N-CS	39.7%	60.3%	-	~100	0	398.40	400.9	-	462.18	-
Ru/N-CS	28.6%	45.1%	26%	72	28	398.54	401.05	403.6	462.24	464.02

Note: Pyri-N, Pyrr-N, and Oxid-N represented pyridinic N, pyrrolic N, and Oxidic N, respectively.

Table S4. Reaction apparent activation energies (E_a) for phebol conversion into cyclohexanol over various catalysts

Catalysts	E_a (kJ mol^{-1})	Refs.
Ru@N-CS	33.8	This work
Ru/C-SBA-15	42.09	28
Ni_3Co_1@C/ZrO_2	44.31	31
Ni/HZSM-5	48	29
Ni/Al_2O_3-HZSM-5	56	29
1% Pd/ZrO_2	81	30
1% PdAg/ZrO_2	57	30

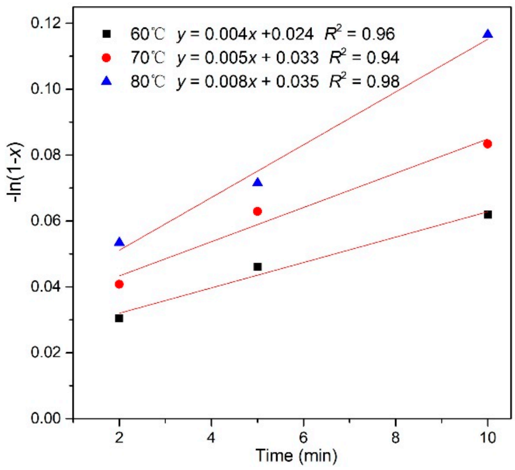

Figure S12. Kinetics study for plots of $-\ln(1-x)$ vs. reaction time.

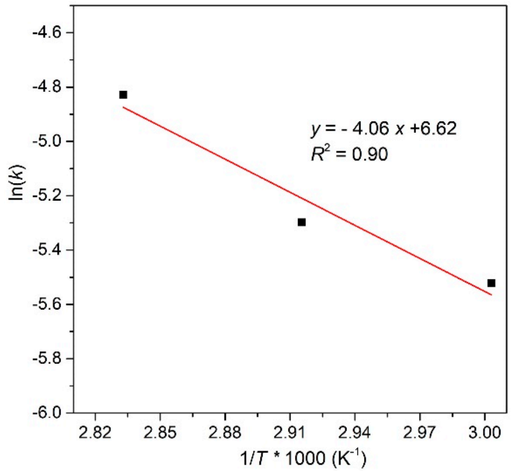

Figure S13. Arrhenius plots for the hydrogenation reaction of phenol.

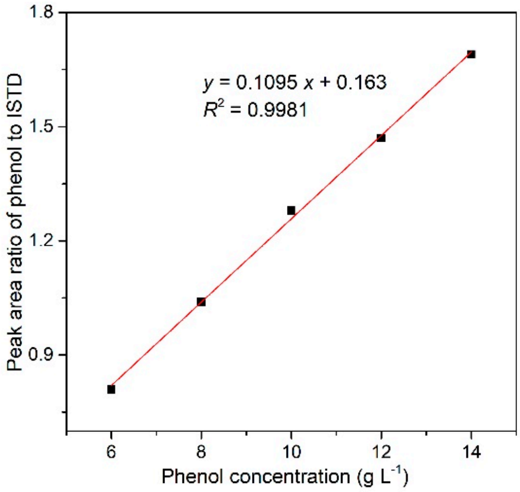

Figure S14. The standard curve for phenol conversion rate of 5–15%.

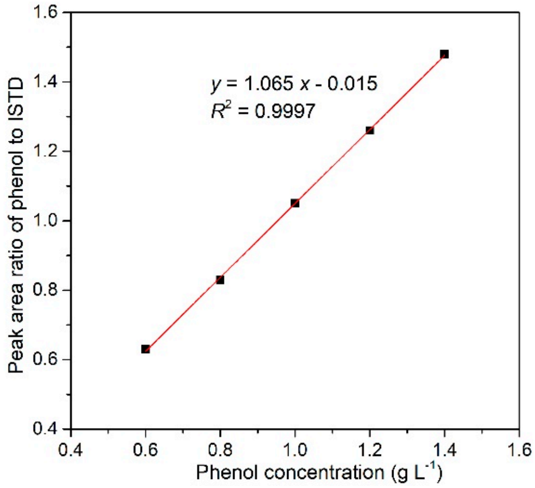

Figure S15. The standard curve for phenol conversion rate of 85–95%.