Supporting Information

Decoration of Pd nanoparticles with N and S doped carbon quantum dots as the robust catalyst for the chemoselective hydrogenation reaction

Chunshan Lu*, Qianwen Zhu, Xuejie Zhang, Haoke Ji, Yebin Zhou, Hao Wang, Qiangqiang Liu, Juanjuan Nie, Wenfeng Han* and Xiaonian Li*

Industrial Catalysis Institute of Zhejiang University of Technology, State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, Hangzhou, 310032, People's Republic of China.

E-mail: lcszjcn@zjut.edu.cn; jackhanwf@hotmail.com; xnli@zjut.edu.cn

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Table S1. **The actual N,S-CQDs loadings of different catalysts.**

Catalyst	Pd@N,S-CQD-25	Pd@N,S-CQD-31.25	Pd@N,S-CQD-62.5	Pd@N,S-CQD-125
Loading (wt%)	0.43	0.54	1.07	2.15

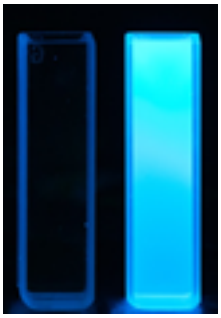

Figure S1. The photoluminescent photographs of the N,S-CQDs solution before (right) and after (left) impregnation under 365 nm UV light.

Table S2. Reusability test of Pd@N,S-CQDs-62.5 for the hydrogenation of ρ-CNB.

Runs	Reaction time(min)	Conversion (%)	Selectivity of production (%)		
			ρ-CAN	Aniline	other
1	240	100	100	0	0
2	240	100	100	0	0
3	240	100	100	0	0
4	240	100	100	0	0
5	240	100	100	0	0
6[a]	235	100	100	0	0
7	240	100	99.9	0.01	0
8	242	100	100	0	0
9	238	100	100	0	0
10	236	100	100	0	0
11[a]	238	100	99.98	0.02	0
12	240	100	99.99	0.01	0
13	242	100	100	0	0
14	245	100	100	0	0
15	243	100	100	0	0
16 [a]	230	100	99.9	0.01	0
17	232	100	100	0	0
18	235	100	100	0	0
19	234	100	100	0	0
20	236	100	100	0	0
21[a]	238	100	100	0	0
22	239	100	100	0	0
23	237	100	99.99	0.01	0
24	235	100	100	0	0
25	238	100	100	0	0

Reaction conditions: 0.02 g catalyst, 1 g ρ-CNB, 25 ml methanol, P = 1 MPa, T = 323 K. The used Pd/AC was washed with deionized water and methanol until pH 7.0.

[a]: About five percent of the initial fresh catalyst was added every five times because of loss during the catalyst filtration.

Table S3. The actual Pd content in the used Pd@N,S-CQDs-62.5 and reaction liquid of the hydrogenation of ρ-CNB over Pd@N,S-CQDs-62.5.

Element	Standard solution (μg ml^{-1})	Linear regression equation	Correlation coefficient	Pd loading amount (wt %)	Pd concentration in the reaction liquid (μg.ml^{-1})
Pd	0.5, 1.0, 1.5, 2.0, 3.0	[C]=28.8629[A]+0.1050	0.999	0.490	/

Note: The actual Pd content in the sample or reaction liquid was analyzed using the air-acetylene flame atomic absorption spectrophotometer on a Beijing Purkinje TAS-990 atomic absorption spectrophotometer. The wavelength, acetylene flow rate, burner height and lamp current were 244.79 nm, 1300 ml min^{-1}, 6 mm and 6.0 mA, respectively.

Table S4. The S content in the reaction liquid of the hydrogenation of ρ-CNB over Pd@N,S-CQDs-62.5.

Element	Standard solution (μg ml^{-1})	Oven temperature (℃)	S concentration in the reaction liquid (μg ml^{-1})
S	10	900	/

Note: The S content in the reaction liquid was measured on a JF-WK-2000 Microcoulomb comprehensive analyzer.

Table S5. **Pilot experiment for the hydrogenation of 2-chloro-4-nitrotoluene into 3-chloro-4-methylaniline.**

Runs	Raw material Kg	Catalyst Kg	Conversion %	Selectivity %		
				ρ-CAN	Aniline	other
1	1000	10	100	99.9	0.01	0
2	1000	10	100	100	0	0
3	1000	10	100	99.8	0.02	0
4	1000	10	100	100	0	0
5	1000	10	100	99.9	0.01	0
6	1000	10	100	100	0	0
7	1000	10	100	99.9	0.01	0
8	1000	10	100	100	0	0
9	1000	10	100	100	0	0
10	1000	10	100	100	0	0
11[a]	1000	10+0.5	100	99.98	0.02	0
12	1000	10	100	99.99	0.01	0
13	1000	10	100	100	0	0
14	1000	10	100	100	0	0
15	1000	10	100	100	0	0
16	1000	10	100	99.9	0.01	0
17	1000	10	100	100	0	0
18[a]	1000	10+0.2	100	99.9	0.01	0
19	1000	10	100	100	0	0
20	1000	10	100	100	0	0
21	1000	10	100	99.9	0.01	0
22	1000	10	100	100	0	0
23	1000	10	100	99.99	0.01	0
24	1000	10	100	100	0	0
25	1000	10	100	100	0	0

Reaction conditions: the mass ratio of raw material-methanol was 1:1.5, P = 0.5-0.8 MPa, T = 323-333 K, The Pd and N,S-CQDs loadings of the catalyst prepared by the same method as Pd@N,S-CQDs-62.5 are both 1 wt %. The hydrogenation reaction was carried out in 8000L tank reactor. The catalyst cycle in reaction system was carried out by closed and highly efficient filters.

[a]: 0.5 and 0.3 Kg of fresh catalyst were added on 11^{th} and 18^{th} cycle because of mass loss during the catalyst filtration.