Supplementary Information

Pd-In bimetallic nanoparticles supported on chelating resin for nitrate removal in water: high efficiency and low NH_4^+ selectivity

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Abstract:

Nitrate pollution in ground water and surface water is a worldwide challenge. Reduction of nitrate to nitrogen gas according to electrocatalysis or hydrogenation catalysis is a prospective way to remove nitrate in water. Pd/In bimetallic catalyst supported on chelating resin was prepared by chemical reduction method in aqueous solution. SEM-EDS, TEM, XRD and XPS analysis revealed the Pd/In nanoparticles with a particle size range from 10 nm to 200 nm showed a uniform distribution in the prepared M-Pd/In composites. The prepared M-Pd/In composites showed high nitrate removal efficiency (96%) and low NH_4^+ selectivity (<2%) when the initial concentration of NO_3^--N was 100 mg N/L. The coexisting anion, organic matter and initial pH value showed little influence on the nitrate removal ability of the prepared M-Pd/In composites. H_{ads} and $NaBH_4$ could be stored during the preparing process of the Pd/In bimetallic composites, which acted as reducing reagent in the nitrate removal process. The prepared M-Pd/In composites showed good nitrate removal ability after recycling 5 times. When it was used to treat actual wastewater, nearly all of the nitrate, nitrite and ammonium was removed from municipal WWTP effluent.

Keywords: Palladium; Indium; Bimetallic nanoparticle; Catalysis; Nitrate

Table S1. Metal precursor solution for preparing Pd/In bimetallic nanoparticles on M4195 resin

Sample mark	Solution bulk (mL)	$PdCl_2$ (g)	$InCl_3$•$4H_2O$ (g)	Pd/In mole ratio
M-Pd	50	0.2226		
M-In	50		0.3665	
M-Pd/In(1/1)	50	0.2226	0.3665	1/1
M-Pd/In(1/0.5)	50	0.2226	0.1832	1/0.5
M-Pd/In(0.5/1)	50	0.1113	0.3665	0.5/1

Table S2 Pd/In mass loaded on 0.5 g DOW M4195 Resin in the prepared bimetallic composites

	Pd (mg)	In (mg)	Pd/In mass ratio	Pd + In (mg)
M-Pd/In(1/1)	64.8	23.9	2.7/1	88.7
M-Pd/In(1/0.5)	63.9	12.7	5.0/1	76.6
M-Pd/In(0.5/1)	45.2	28.6	1.6/1	73.8

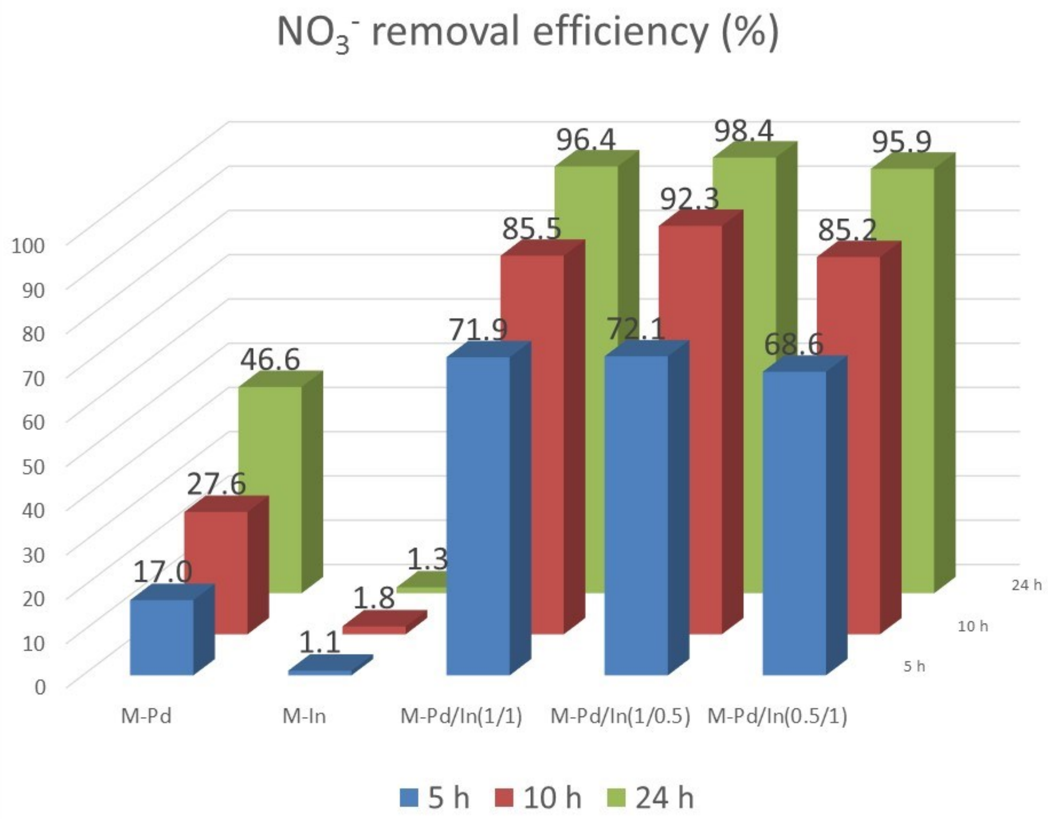

Fig. S1 The NO_3^- removal efficiency of the prepared Pd/In bimetallic composites after 5h, 10h and 24h of reaction

Table S3. Fitting results of the pseudo-first-order kinetic model for the three Pd/In bimetallic composites

	M-Pd/In(1/1)	M-Pd/In(1/0.5)	M-Pd/In(0.5/1)
k_{obs}	0.230	0.232	0.214
R^2	0.907	0.900	0.901

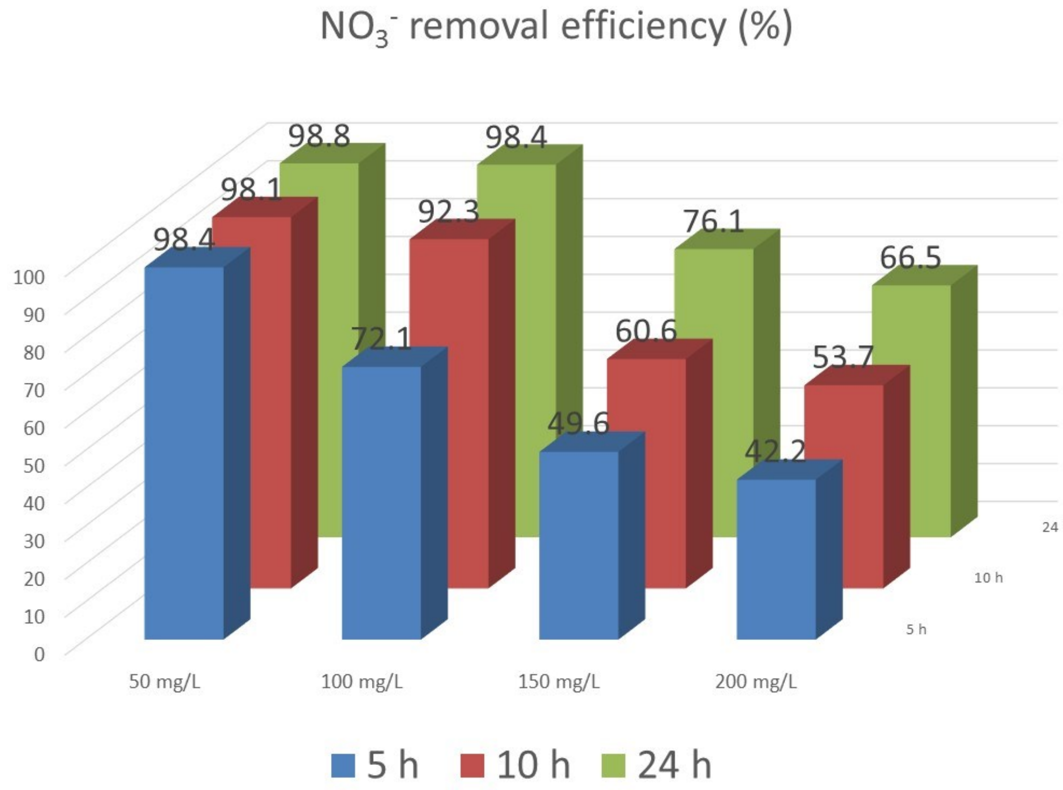

Fig. S2 The NO_3^- removal efficiency of M-Pd/In(1/0.5) at the 5th hour, the 10th hour and the 24th hour at the condition of different initial NO_3^--N concentration

Table S4. Fitting results of the pseudo-first-order kinetic model for nitrate removal process at different initial NO_3^--N concentration

	50 mg/L	100 mg/L	150 mg/L	200 mg/L
k_{obs}	0.807	0.232	0.125	0.095
R^2	0.987	0.900	0.797	0.786

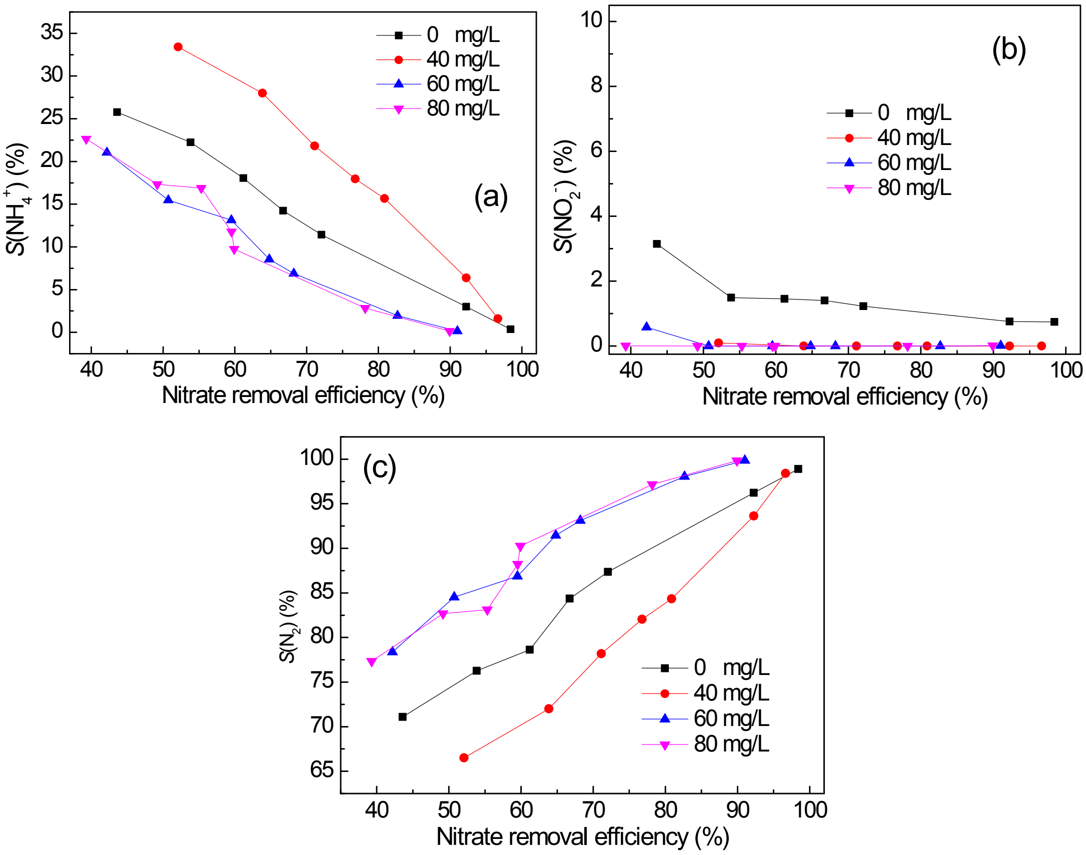

Fig. S3 Product selectivity as a function of nitrate removal efficiency at different concentration of HCO_3^-: (a) NH_4^+-N; (b) NO_2^--N; (c) N_2

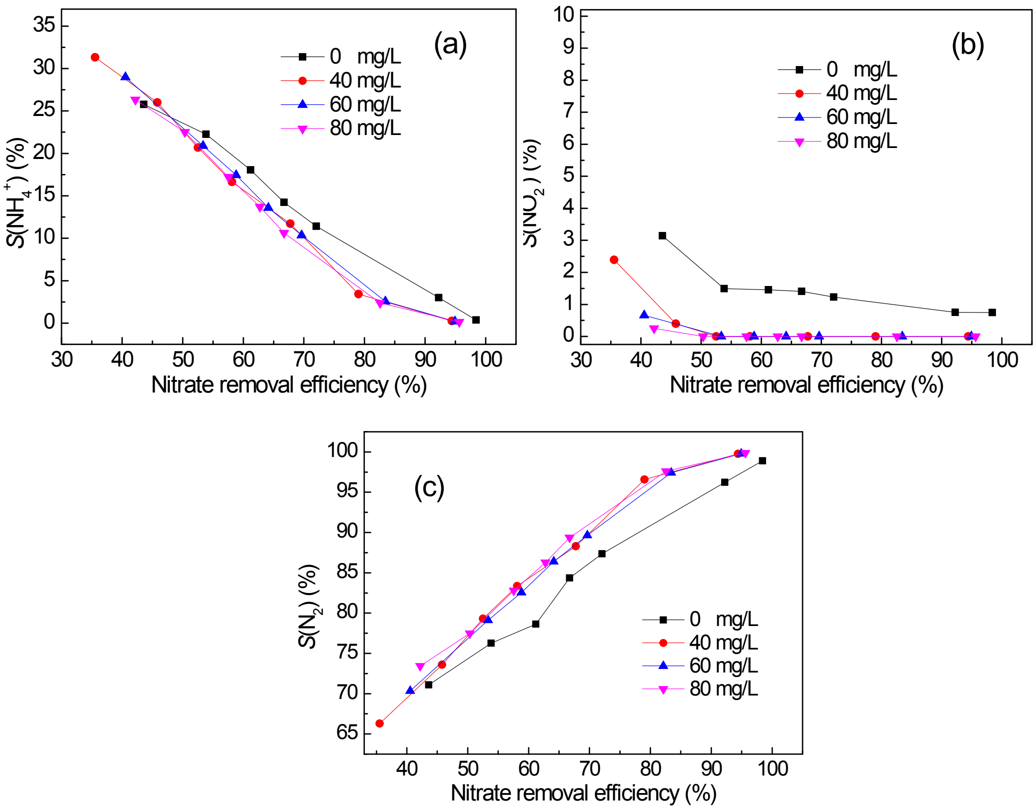

Fig. S4 Product selectivity as a function of nitrate removal efficiency at different concentration of Cl^-: (a) NH_4^+-N; (b) NO_2^--N; (c) N_2

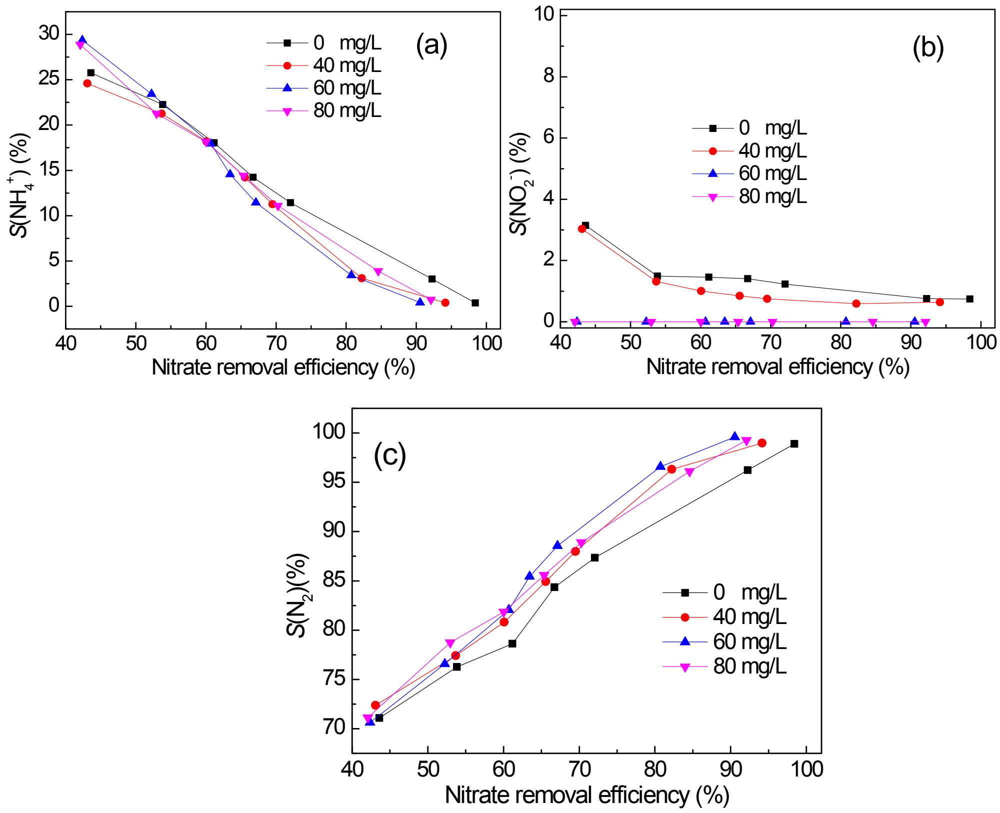

Fig. S5 Product selectivity as a function of nitrate removal efficiency at different concentration of SO_4^{2-}: (a) NH_4^+-N; (b) NO_2^--N; (c) N_2

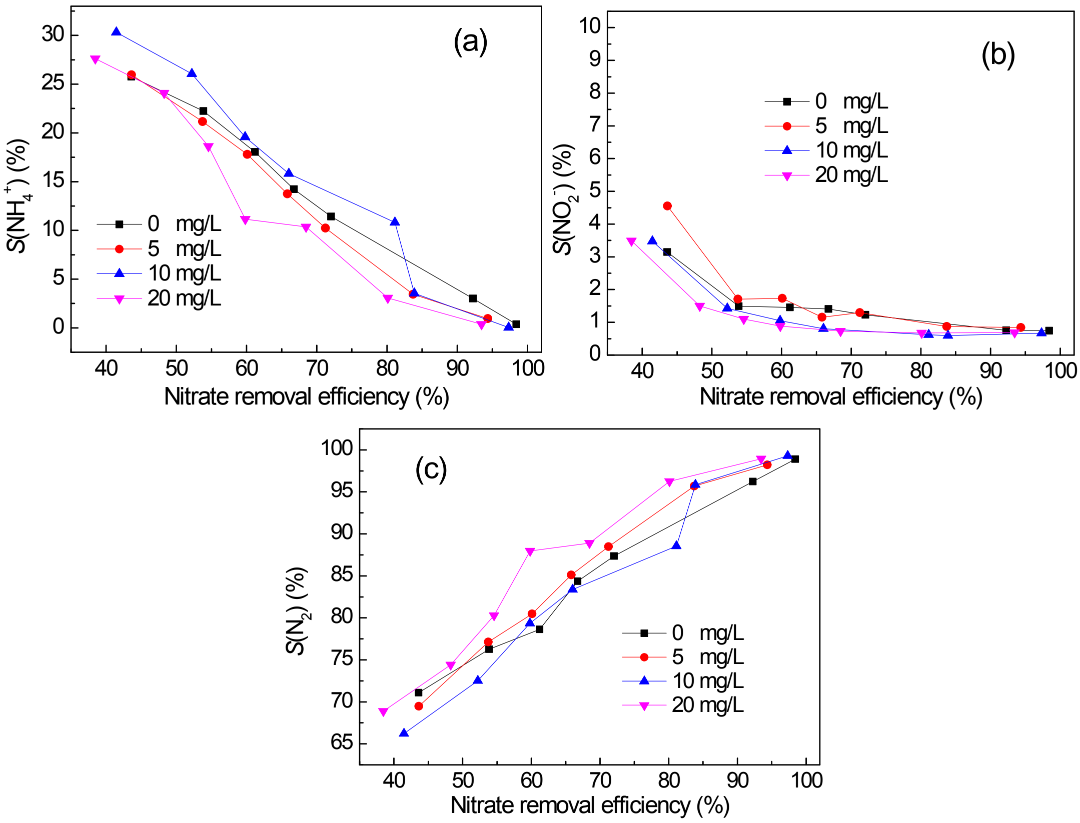

Fig. S6 Product selectivity as a function of nitrate removal efficiency at different concentration of humic acid: (a) NH_4^+-N; (b) NO_2^--N; (c) N_2

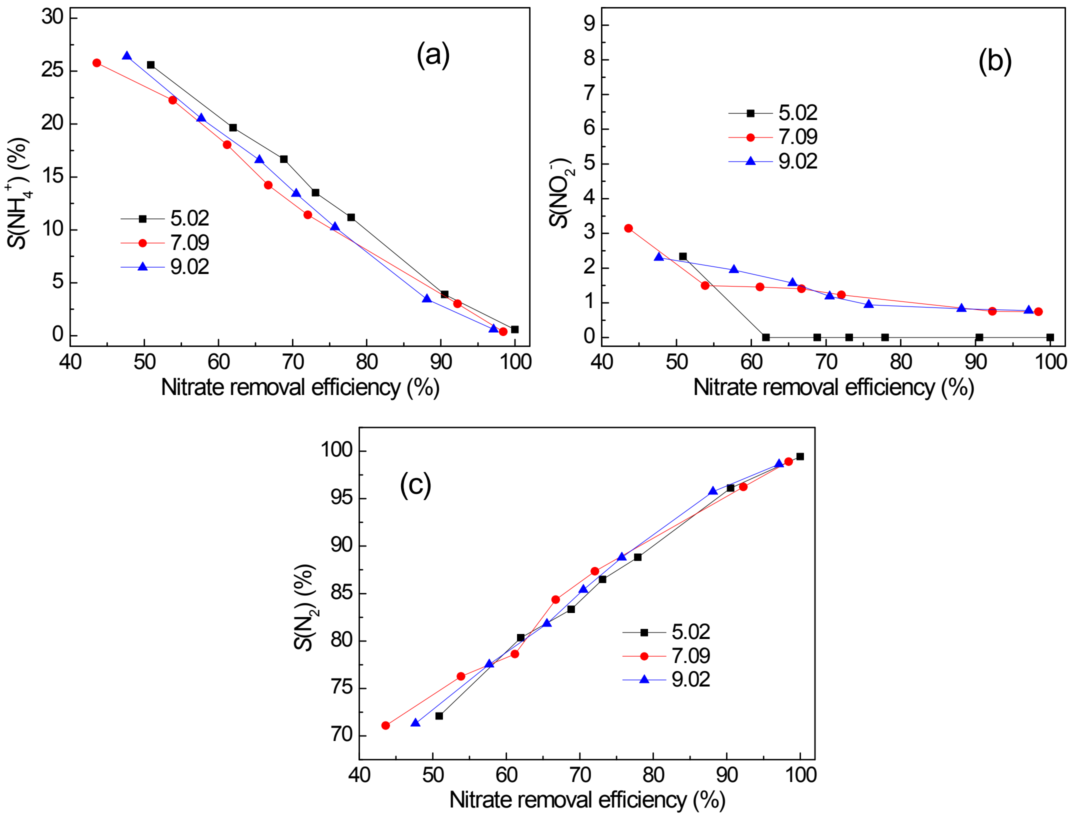

Fig. S7 Product selectivity as a function of nitrate removal efficiency at different initial pH: (a) NH_4^+-N; (b) NO_2^--N; (c) N_2

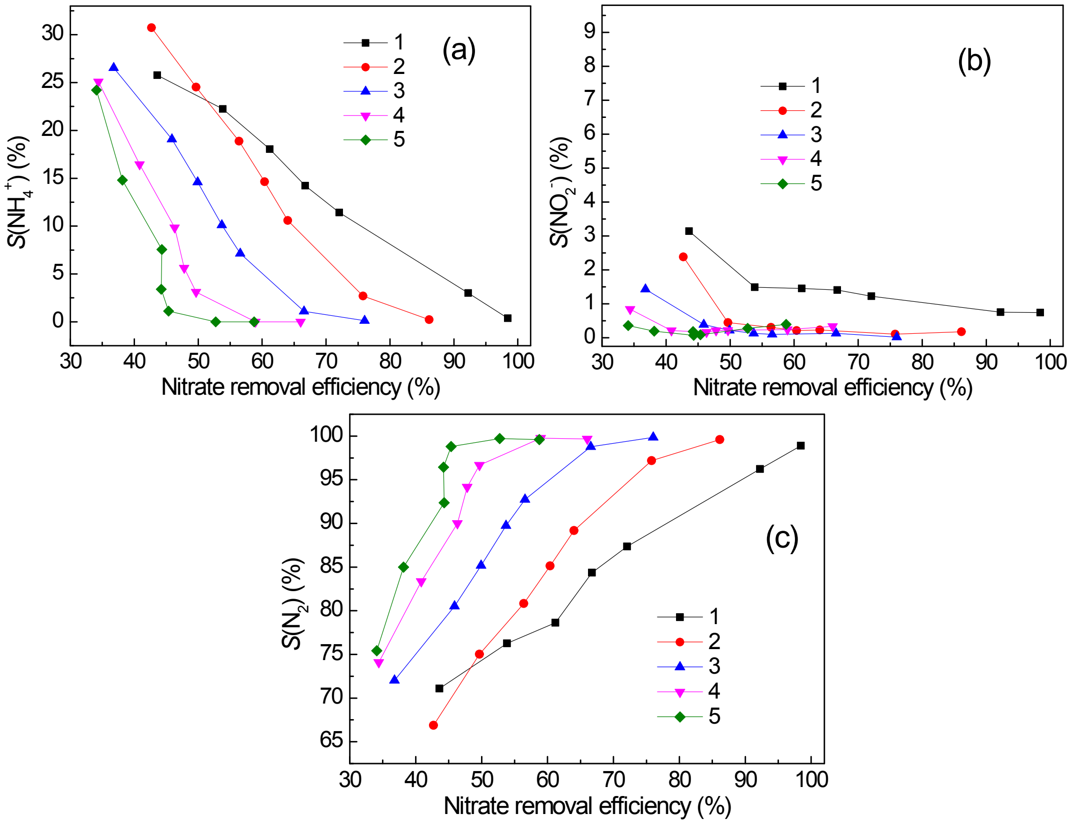

Fig. S8 Product selectivity as a function of nitrate removal efficiency at different recycling nitrate removal reaction (1 to 5): (a) NH_4^+-N; (b) NO_2^--N; (c) N_2

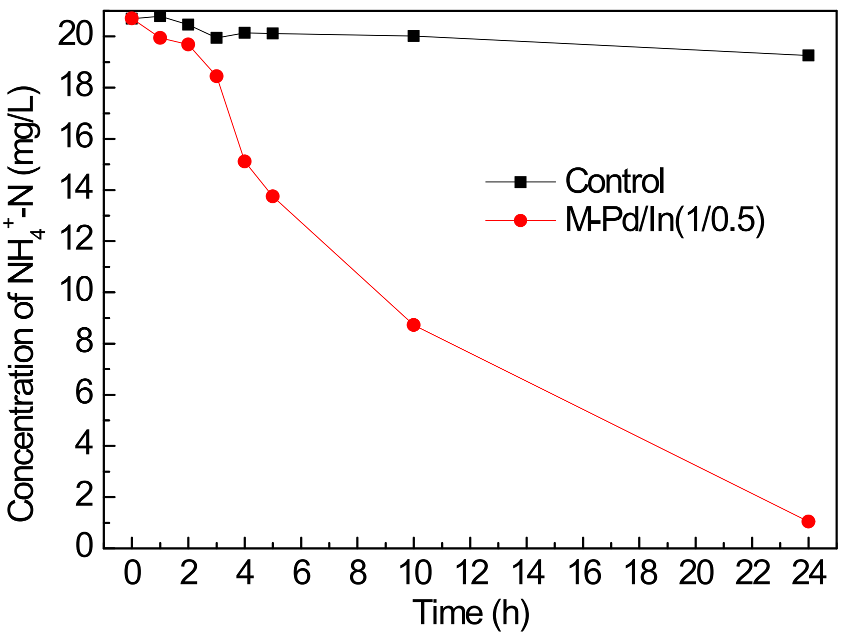

Fig. S9 The concentration of NH_4^+-N in the presence of M-Pd/In(1/0.5) and the control at the initial pH of 9.50

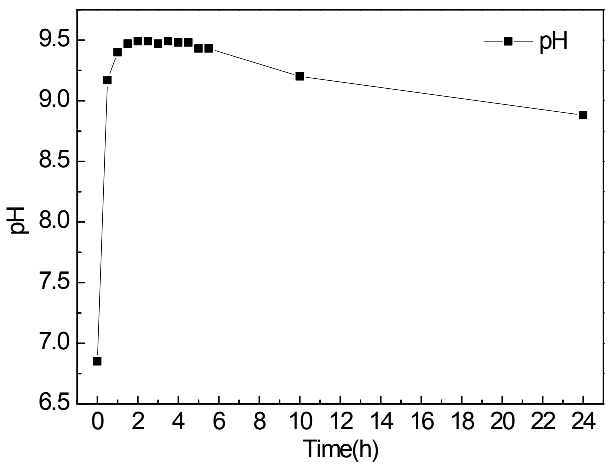

Fig. S10 The pH value during the nitrate removal reaction by M-Pd/In(1/0.5)

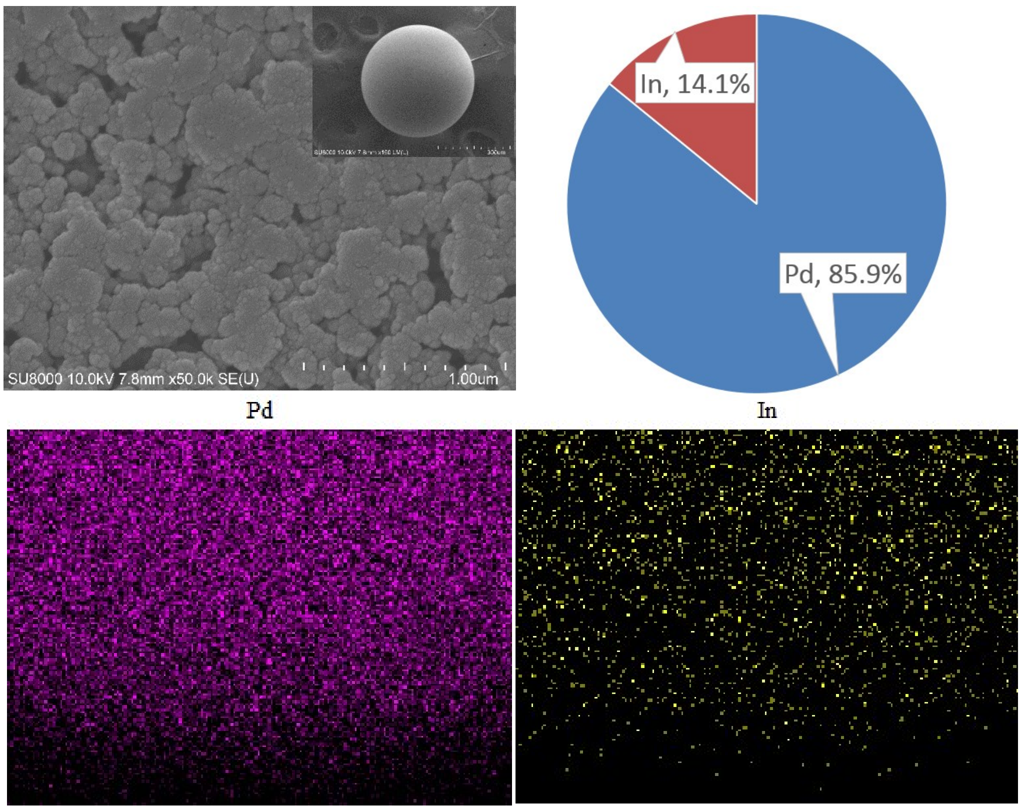

Fig. S11 FESEM-EDS results of M-Pd/In(1/0.5) after 5 cycles of reuse

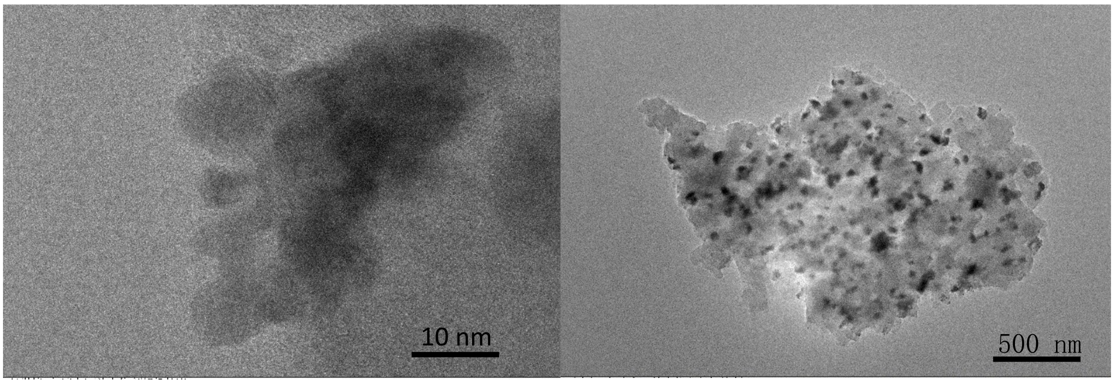

Fig. S12 TEM images of M-Pd/In(1/0.5) after 5 cycles of reuse

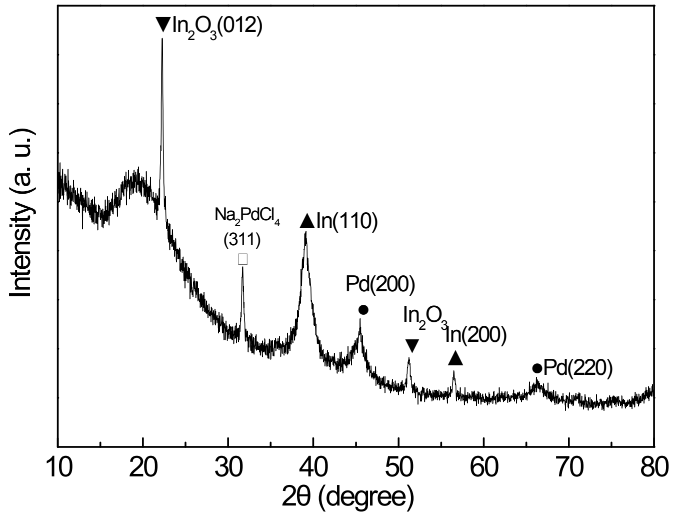

Fig. S13 XRD spectrum of M-Pd/In(1/0.5) after 5 cycles of reuse

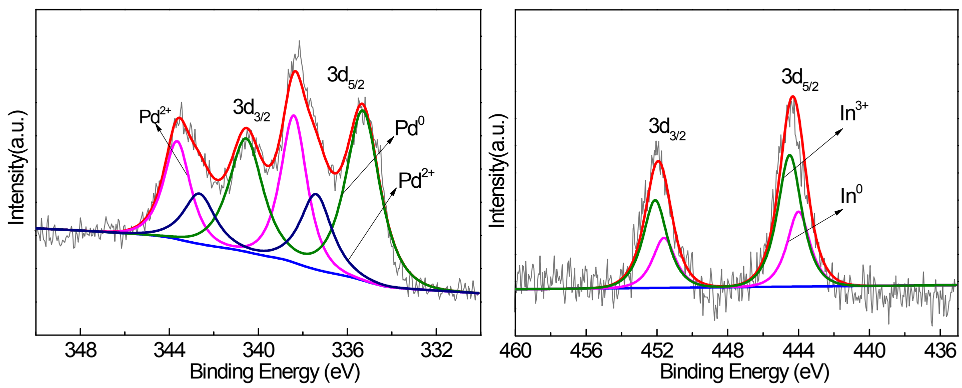

Fig. S14 XPS results of the prepared M-Pd/In composite after 5 cycles of reuse: (a) Pd and (b) In

Table S5. Characteristic of Influent and Effluent of Xiaoshangzhuang Municipal Wastewater Treatment Plant

	Influent	Effluent	Limits	Units
pH	7.7	7.42	6-9	1
BOD	181	5.6	10	mg/L
TP	1.9	0.29	0.5	mg/L
COD	489	23	50	mg/L
Volatile phenol	0.0067	0.0023	0.5	mg/L
Chromaticity	32	8	30	multiple
Hg	<0.00004	<0.00004	0.001	mg/L
Cd	0.071	<0.004	0.01	mg/L
Cr	0.404	<0.004	0.1	mg/L
Cr (Ⅵ)	<0.004	<0.004	0.05	mg/L
As	0.0047	0.0029	0.1	mg/L
Pb	0.024	<0.02	0.1	mg/L
SS	394	10	10	mg/L
LAS	1.19	0.129	0.5	mg/L
Fecal coliform	24000	3500	1000	1/L
NH_4^+-N	24.6	0.092	5	mg/L
TN	29.9	5.75	15	mg/L

The Effluent meets the limits of one-class A of Municipal Wastewater Treatment Plant Pollutant Discharge Standard (GB 18918-2002).

Table S6. Characteristic of Influent and Effluent of Luotuowan Municipal Wastewater Treatment Plant

	Influent	Effluent	Limits	Units
pH	7.72	7.41	6-9	1
BOD	65.5	3.3	10	mg/L
TP	2.34	0.38	0.5	mg/L
COD	177	18	50	mg/L
Volatile phenol	0.0076	0.0023	0.5	mg/L
Chromaticity	32	8	30	multiple
Hg	<0.00004	<0.00004	0.001	mg/L
Cd	0.071	<0.004	0.01	mg/L
Cr	0.404	<0.004	0.1	mg/L
Cr (Ⅵ)	<0.004	<0.004	0.05	mg/L
As	0.0032	0.0022	0.1	mg/L
Pb	<0.02	<0.02	0.1	mg/L
SS	135	7	10	mg/L
LAS	0.724	0.334	0.5	mg/L
Fecal coliform	24000	3500	1000	1/L
NH_4^+-N	28.8	0.293	5	mg/L
TN	35.1	14.7	15	mg/L

The Effluent meets the limits of one-class A of Municipal Wastewater Treatment Plant Pollutant Discharge Standard (GB 18918-2002).

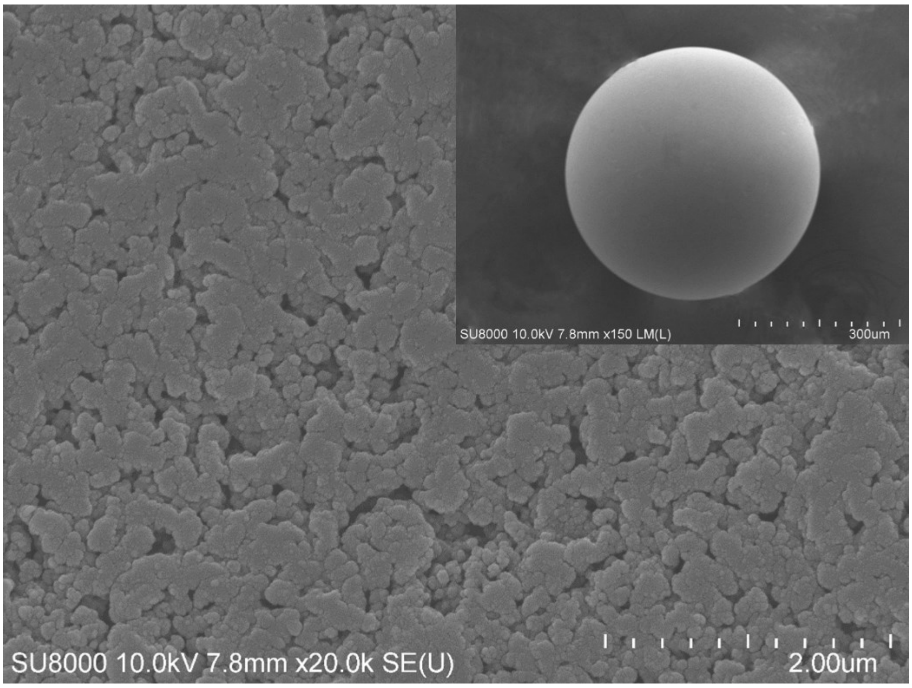

Fig. S15 FESEM image of of raw resin

Table S7 Pd/In mass loading on 0.5 g DOW M4195 Resin in the prepared M-Pd/In(1/0.5) after 5 cycles of reuse by regeneration

	Pd (mg)	In (mg)	Pd/In mass ratio	Pd + In (mg)
M-Pd/In(1/0.5)	58.5	10.2	5.7/1	68.7

Table S8 The mass ratio of Pd to NO_3^--N, In to NO_3^--N, and Pd+In to NO_3^--N at different initial NO_3^--N concentration

Initial NO_3^--N (mg/L)	Initial NO_3^--N (mg)	Mass ratio of Pd/NO_3^--N	Mass ratio of In/NO_3^--N	Mass ratio of Pd+In/NO_3^--N
50	2.5	25.56	5.08	30.64
100	5.0	12.78	2.54	15.32
150	7.5	8.52	1.69	10.21
200	10.0	6.39	1.27	7.66