

Polymer (Polyanilines) Nanoparticles: A Superior Catalyst for Hydrocarbon Selective Oxidation

Supporting Information

Experimental section

Chemicals used were all reagent grades. Aniline was distilled before use. Doubly distilled water was used to prepare solutions.

1. Preparation of PANI with different sizes and redox states

In a typical microemulsion polymerization reaction, polyethylene glycol 2000 (0.2 M) in cyclohexane (10 mL) was taken, and 0.03 g ammonium persulfate (APS) in 20 mL of hydrochloric acid (0.1 M) was added to it under constant stirring to obtain a milky white emulsion. Then n-butanol was added to the mixture, followed by dropwise addition until the solution turned transparent, homogeneous suddenly. Finally, aniline monomer (0.1 M) was added to the homogeneous solution. During the progress of reaction, the colorless emulsion turned dark blue in a few minutes. The reaction was allowed to proceed for 2 h to obtain 10-20 nm nanosized emeraldine base PANI (NEB), 6 h to obtain 30-50 nm NEB, and 12 h to obtain 80-100 nm NEB. The viscous dark blue solution was added into 1.5 L acetone to induce demulsification and precipitation. After filtering and washed with acetone and water, dark green NEB was obtained and dried under vacuum for 12 h.

For the preparation of nanosized leucoemeraldine base PANI (NLB), NEB was dispersed into 40 mL N, N-dimethylformamide, into which 20 mL phenylhydrazine was added. The reaction was carried out for 8 h. Finally, the mixture was recrystallized by 80 mL isopropanol and then filtered. The NLB was obtained by drying under vacuum for 24 h.

For the preparation of nanosized pernigraniline base (PB) PANI (NS), 0.05 g raw NEB was dispersed into 30 mL H₂SO₄ (18 M), and then placed into a round-bottomed flask with a water condenser. The refluxed reaction was carried out at 110 °C for 6 h in air. After that, the solution was cooled to room temperature, and the product was neutralized and demineralized. The NS was obtained by drying under vacuum at 60 °C for 8 h.

For the preparation of bulk emeraldine base PANI (BEB), in a typical synthesis, solution A was prepared by dissolving 0.03 g APS in 10 mL H₂O by stirring at room temperature. Solution B was prepared by adding 500 µL aniline monomer (Beijing Chemical Reagent Ltd., China) into the mixed solution of 3 mL hydrochloric acid (0.1 M) and 50 mL water. After cooled to room temperature, 10 mL of solution B was mixed with solution A quickly. The reaction was carried out for 12 h. The green solid was obtained by centrifugation and washed with water and ethanol thoroughly to remove excess ions and monomers. The final product was dried in vacuum at room

temperature for 24 h.

The bulk leucoemeraldine base PANI (LB) were obtained by the method for preparing NLB using BEB as the precursor.

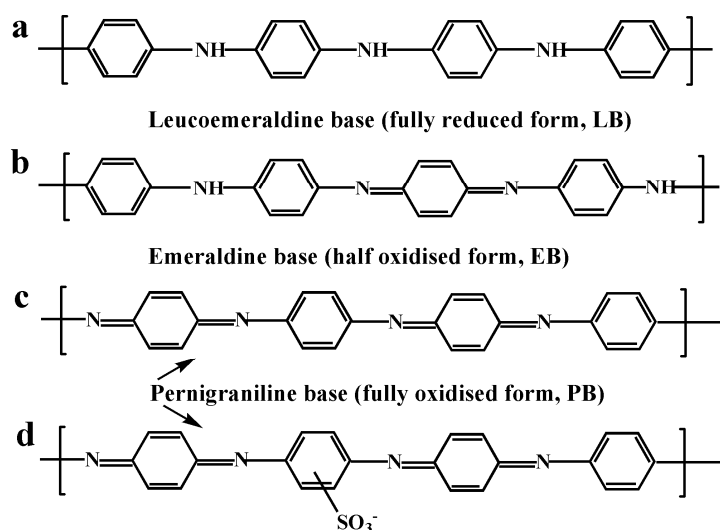
The bulk pernigraniline base (PB) PANI (BS) were obtained by the method for preparing NS using BEB as the precursor.

2. Catalytic selective oxidation of cyclohexene

Cyclohexene (2 mL) and different states PANI catalyst (0.10 g) were stirred at 60 °C in CHCl_3 (10 mL) using hydrogen peroxide (5 mL) as an oxidizing agent for different times. After filtering off the catalyst, the filtrate was analyzed by GC-MS. The varied solvents and oxidants were carried out the corresponding conditions.

3. Characterization

TEM was obtained with a FEI/Philips Tecnai 12 BioTWIN transmission electron microscope. TEM samples were prepared by dropping the sample solution onto a copper grid with carbon and dried in air. Electrochemical measurements were carried out in a conventional three-electrode electrochemical cell. Typically, the working electrode was a modified carbon paste electrode. The auxiliary electrode was a platinum wire and the reference electrode was a Ag/AgCl (saturated KCl) electrode. Cyclic voltammetry measurements were performed with a CHI 832 electrochemical instrument (CHI Inc., USA). The products of the selective oxidation reactions were analyzed using a gas chromatograph. The gas chromatography was performed in a Varian 3400 GC column with a cross-linked 5% PhMe silicone column (25 m × 0.20 mm × 0.33 μm) and a FID detector under the following conditions: carrier gas (N_2) at 140 K; temperature program 60 °C, 1 min, 15 °C/min, 180 °C, 15 min; split ratio, 10:1; injector, 300 °C; detector, 300 °C.



Scheme S1. The molecular structure of PANI with different redox states: (a) leucoemeraldine base (LB, fully reduced form), (b) emeraldine base (EB, half oxidized form), (c) pernigraniline base (PB, fully oxidized form) and sulfonated pernigraniline base (SB, fully oxidized form).

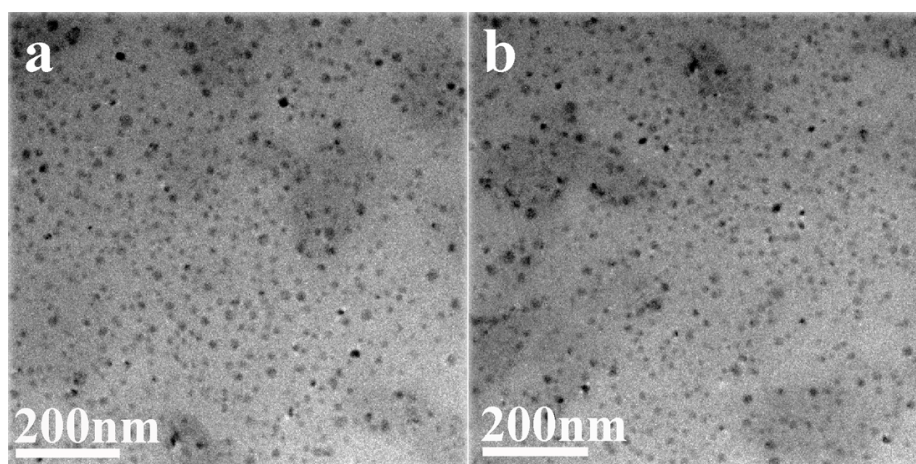


Fig. S1. TEM images of (a) NLE and (b) NS with diameter of about 10 – 20 nm.

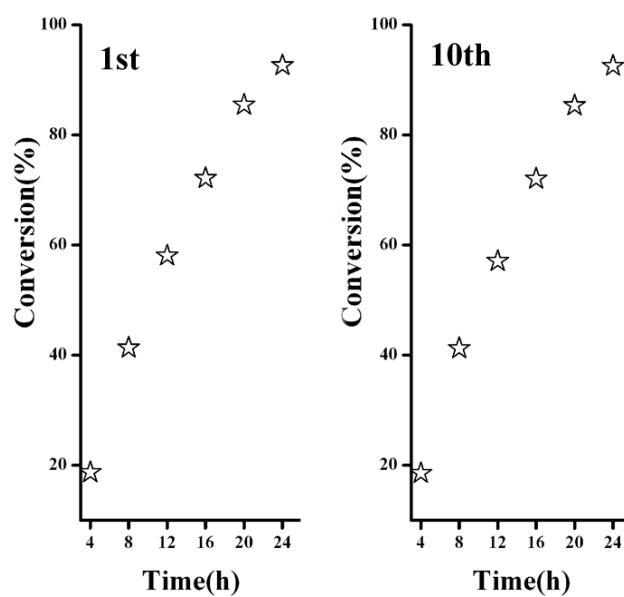


Fig. S2. The repeatability experiments of 10-20 nm NEB in ten times during selective oxidation of cyclohexene at 60 °C using H₂O₂ as an oxidant and chloroform as solvent (24 h).



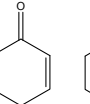
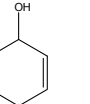
Catalyst	Product Selectivity(%)				Conversion(%)	$\Sigma_{\text{sel}}\text{C}_6^{\S}$
						
No PANI particles	0	0	0	0	0	0
NEB	21.67	64.22	1.75	10.56	92.63	98.2
NLB	31.46	68.54	trace	trace	9.38	100
NS	19.81	70.82	trace	9.37	2.07	100
BEB	28.64	63.60	0.67	6.59	13.11	99.5
BLB	7.39	72.74	0	19.87	1.46	100
BS	8.36	77.76	0	13.88	1.97	100

Table S1. Effect of different redox states and particle sizes of PANI as a catalyst on selective oxidation of cyclohexene.

Reaction conditions: 0.1 g catalyst, cyclohexene (2 mL), CHCl_3 (10 mL), hydrogen peroxide (5 mL), 60 °C, 24 h.

\S Total selectivity to C6 partial oxidation products.



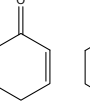
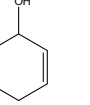
NEB Size	Product Selectivity(%)				Conversion(%)	$\Sigma_{\text{sel}}\text{C}_6^{\S}$
						
10-20 nm	21.67	64.22	1.75	10.56	92.63	98.2
30-50 nm	28.02	56.05	2.19	12.64	82.29	98.9
80-100 nm	30.35	61.72	1.35	5.78	31.43	99.2

Table S2. Effect of different particle sizes of NEB as a catalyst on selective oxidation of cyclohexene.

Reaction conditions: 0.1 g catalyst, cyclohexene (2 mL), CHCl_3 (10 mL), hydrogen peroxide (5 mL), 60 °C, 24 h.

\S Total selectivity to C6 partial oxidation products.





Reaction time(h)	Product Selectivity(%)				Conversion(%)	$\Sigma_{\text{sel}}\text{C}_6^{\S}$
						
0	0	0	0	0	0	0
4	92.61	7.39	trace	trace	18.67	99.9
8	78.16	21.06	0.68	trace	41.32	99.9
12	52.82	44.01	1.78	0.89	58.09	99.5
16	31.56	58.04	4.47	4.93	72.14	99.0
20	24.74	61.86	2.18	9.82	85.46	98.6
24	21.67	64.22	1.75	10.56	92.63	98.2

Table S3. Effect of variety of reaction time on selective oxidation of cyclohexene using 10-20nm NEB as a catalyst.

Reaction conditions: 0.1g catalyst, cyclohexene (2 mL), CHCl_3 (10 mL), hydrogen peroxide (5 mL), 60 °C.

\S Total selectivity to C6 partial oxidation products.





Solvent	Product Selectivity(%)				Conversion(%)	$\Sigma_{\text{sel}}\text{C}_6^{\S}$
						
Chloroform	21.67	64.22	1.75	10.56	92.63	98.2
Cyclohexene	87.22	12.58	0	trace	11.32	99.8
Water	14.63	78.46	trace	4.91	1.96	98.0

Table S4. Effect of different solvents on selective oxidation of cyclohexene using 10-20 nm NEB as catalyst.

Reaction conditions: 0.1 g catalyst, cyclohexene (2 mL), hydrogen peroxide (5 mL), 60 °C, 24 h.

\S Total selectivity to C6 partial oxidation products.


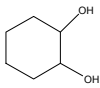
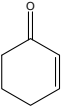
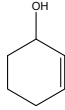
Reagent	Product Selectivity(%)				Conversion(%)	$\Sigma_{\text{sel}}\text{C}_6^{\text{§}}$
						
H ₂ O ₂ -30%	21.67	64.22	1.75	10.56	92.63	98.2
H ₂ O ₂ -15%	16.09	78.93	trace	3.28	38.66	98.3
O ₂	trace	0	0	0	0	0
Air	0	0	0	0	0	0

Table S5. Effect of different oxidants on selective oxidation of cyclohexene using 10-20 nm NEB with as catalyst.

Reaction conditions: 0.1 g catalyst, cyclohexene (2 mL), CHCl₃ (10 mL), 60 °C, 24 h.

§Total selectivity to C6 partial oxidation products.