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Supporting Information

Enhanced solvent-free selective oxidation of cyclohexene to 1,2-cyclohexanediol by polyaniline@halloysite nanotubes

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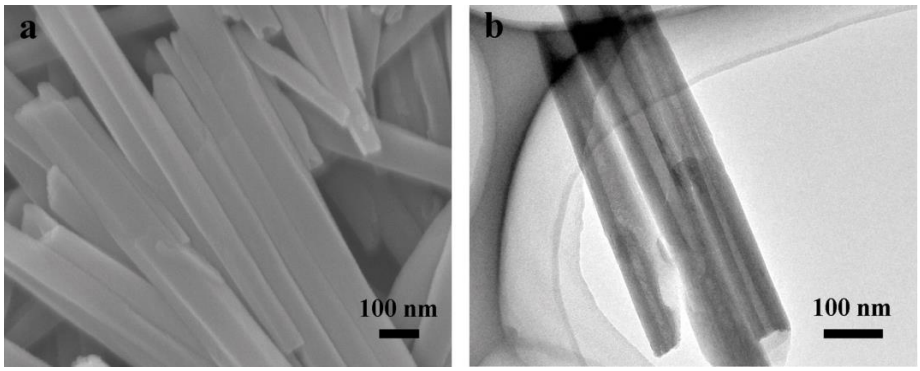


Fig. S1 SEM (a) and TEM (b) of halloysite nanotubes (HA).

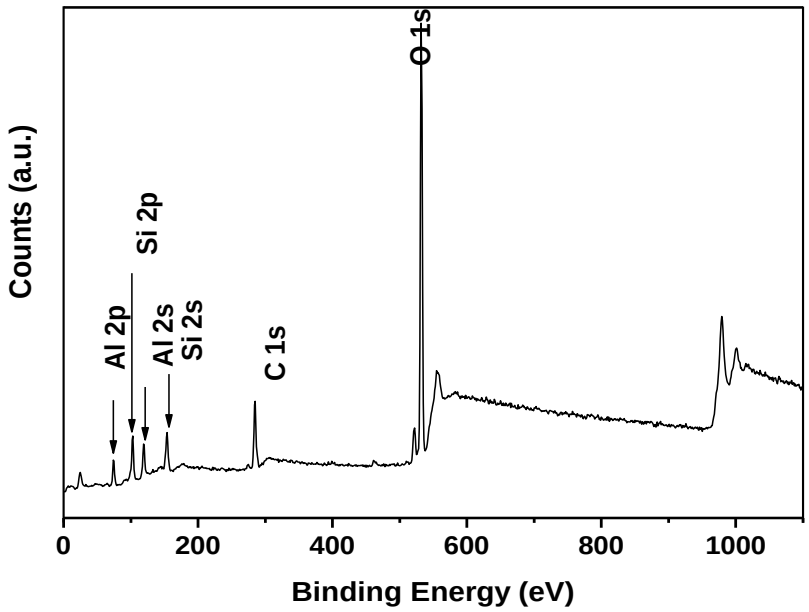


Fig. S2 XPS spectra of halloysite nanotubes (HA) (C peak from the adventitious elemental carbon).

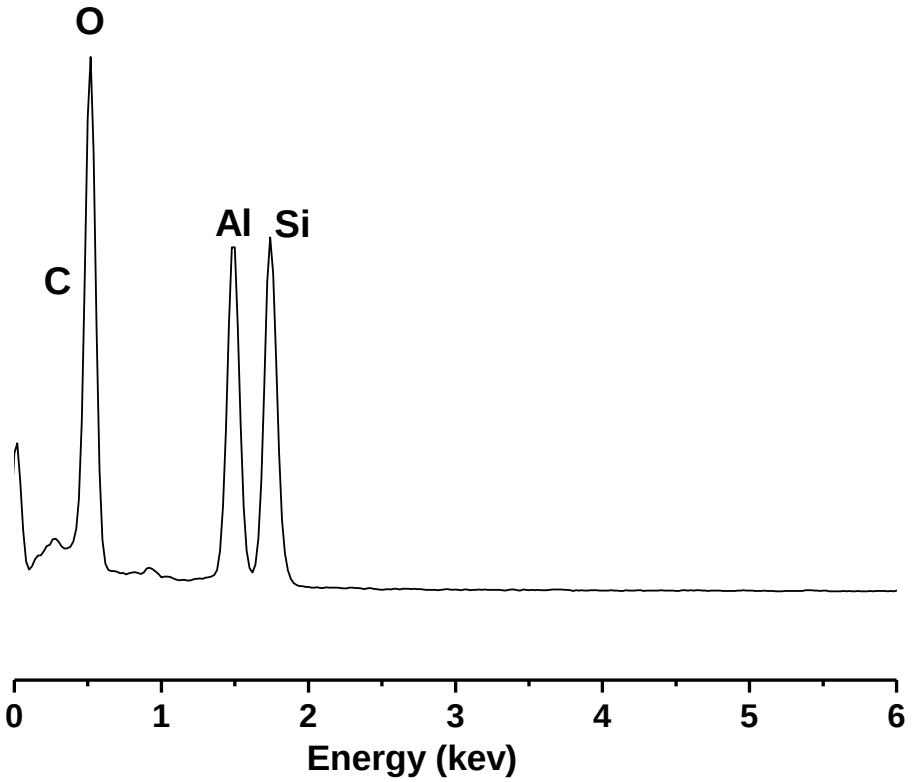


Fig. S3 EDX spectroscopy of halloysite nanotubes (HA) (C peak from the carbon-coated copper grids).

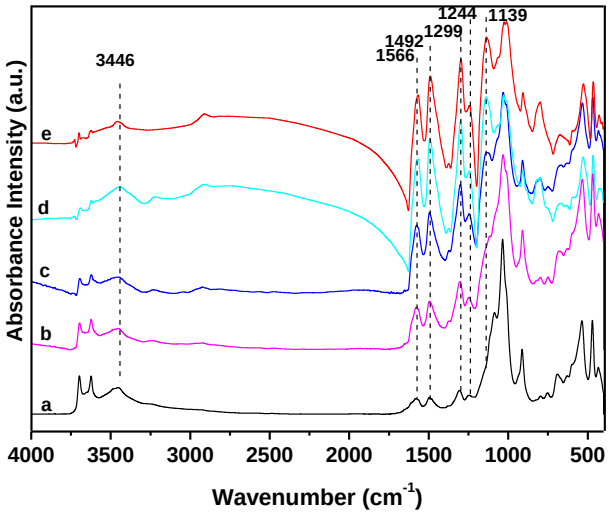


Fig. S4 FT-IR spectra of the PANI@HA nanotubes fabricated in 1 M HCl with different ANI/HA weight ratio: (a) 0.10, (b) 0.41, (c) 1.02, (d) 2.04, (e) 2.24.

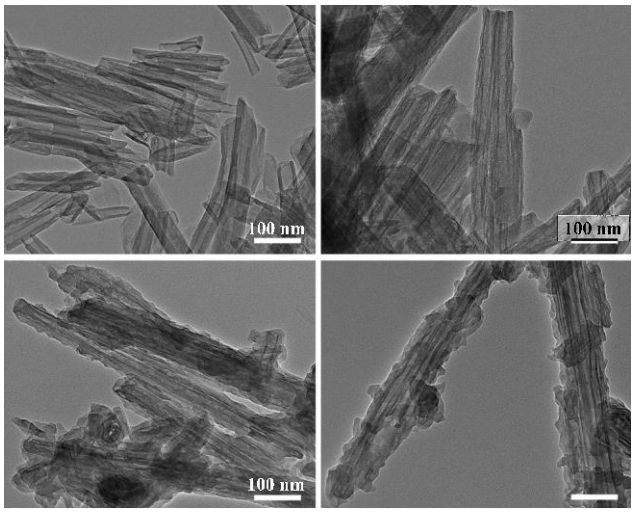


Fig. S5 TEM images of the PANI@HA nanotubes fabricated in 1 M HCl with different ANI/HA weight ratio: (a) 0.10, (b) 0.41, (c) 1.02 and (d) 2.04.

Table S1 Chemical composition of HA and PANI@HA/1 M/2.04-H.

Sample	Atomic concentration (%)							
	Si	Al	O	C	N	Cl	S	P
HA	13.7	10.1	55.5	20.7	-	-	-	-
PANI@HA/1M/2.04-H_3PO_4	0.9	0.8	13.5	76.3	8.4	-	-	0.1
PANI@HA/1M/2.04-HNO_3	1.7	1.4	14.7	74.2	8.0	-	-	-
PANI@HA/1M/2.04-H_2SO_4	1.0	1.0	15.6	71.7	10.0	-	0.7	-
PANI@HA/1 M/2.04-HCl	1.0	1.0	13.8	71.8	11.5	0.8	-	-

Table S2 Mass ratio, doping degree and Q/B of PANI in PANI@HA/A/W-H.

Sample	The acidity tuned by	Mass ratio of PANI (%)	Doping degree of PANI (%)	Q/B
PANI@HA/1 M/2.04-H_3PO_4	H_3PO_4	51.8	26.6	1.32
PANI@HA/1 M/2.04-HNO_3	HNO_3	42.5	27.3	1.24
PANI@HA/1 M/2.04-H_2SO_4	H_2SO_4	45.9	29.1	1.20
PANI@HA/1 M/2.04-HCl	HCl	36.8	34.7	1.00
PANI@HA/0.3 M/2.04-HCl	HCl	35.2	-	-
PANI@HA/0.03 M/2.04-HCl	HCl	34.7	-	-

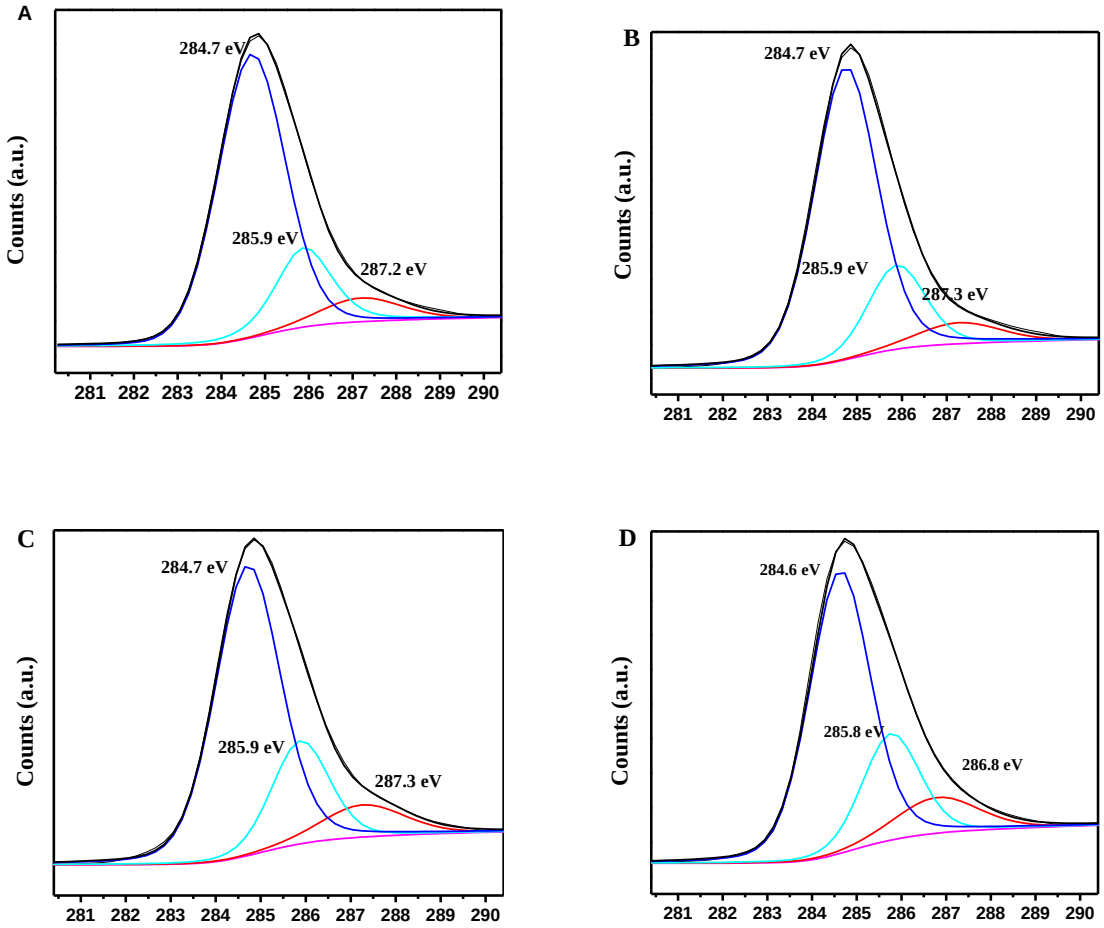


Fig. S6 C1s deconvoluted spectra of PANI@HA/1 M/2.04-H: the acidity of the starting solutions is respectively adjusted by A) H_3PO_4, B) HNO_3, C) H_2SO_4 and D) HCl.

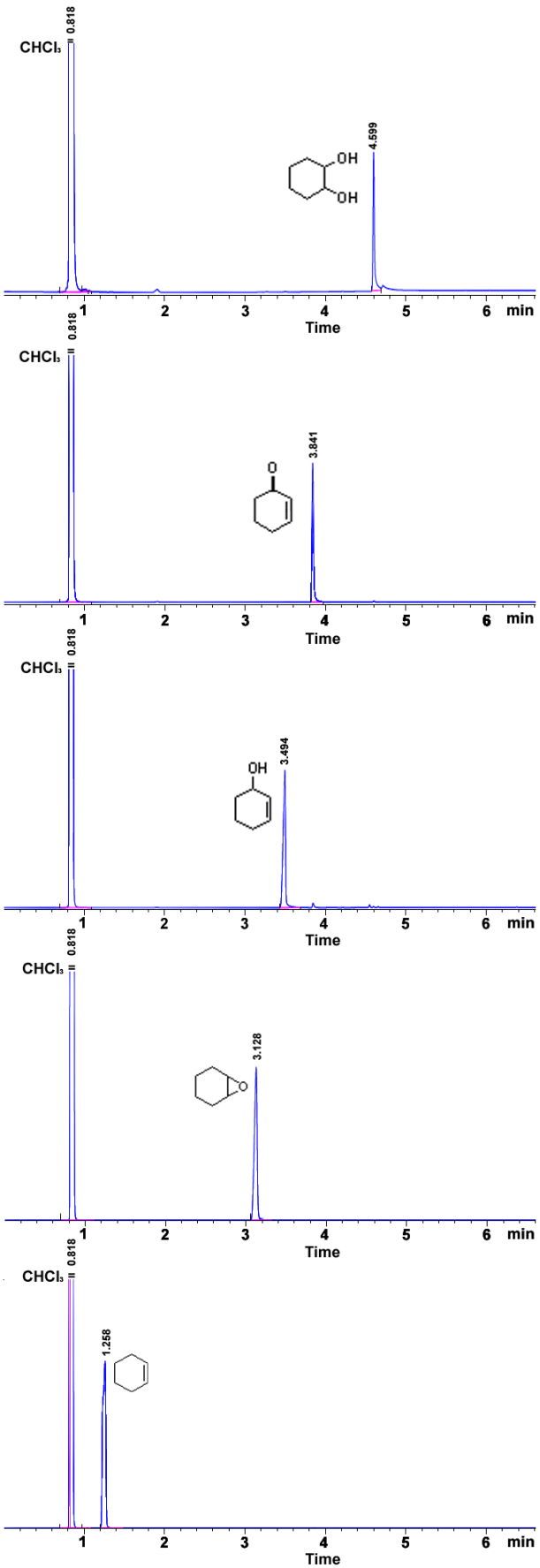


Fig. S7 GC spectra of 99% cyclohexene, epoxy cyclohexane, 2-cyclohexen-1-ol,

2-cyclohexen-1-one and 1,2-cyclohexandiol.

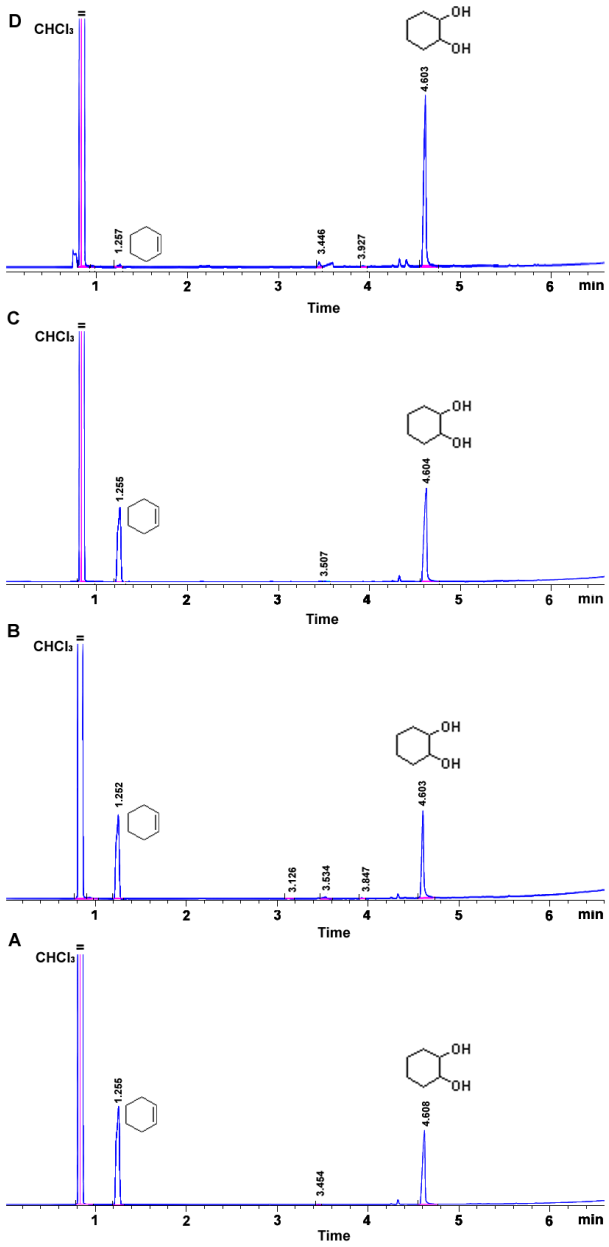


Fig. S8 GC spectra of the reaction products for cyclohexene oxidation with A) PANI@HA/1 M/2.04-H_3PO_4, B) PANI@HA/1 M/2.04-HNO_3, C) PANI@HA/1 M/2.04-H_2SO_4 and D) PANI@HA/1 M/2.04-HCl as catalyst.

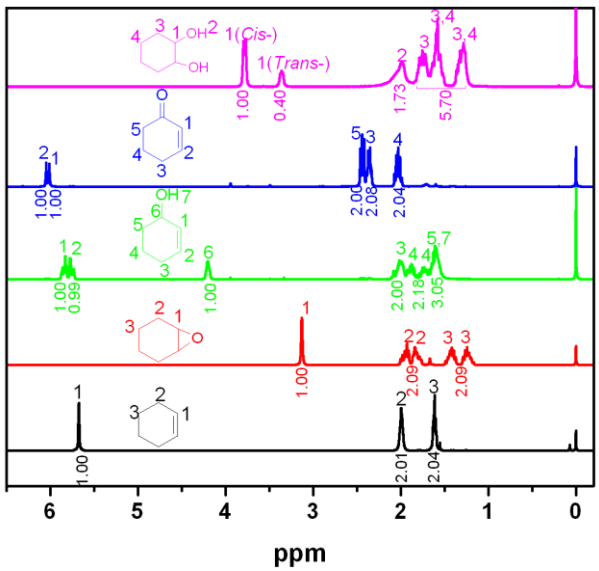


Fig. S9 ^{1}H NMR spectra (300MHz, $CDCl_3$) of cyclohexene, epoxy cyclohexane, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, and 1,2-cyclohexandiol.

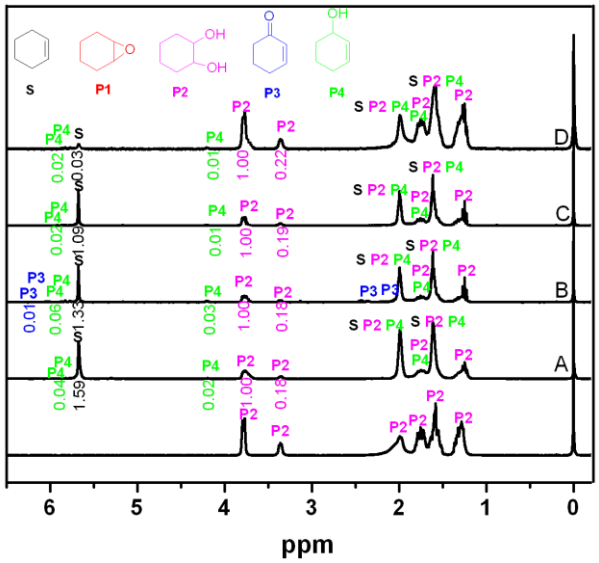
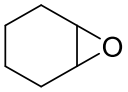
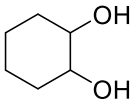
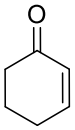
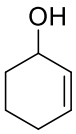


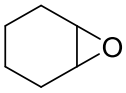
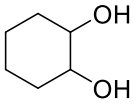
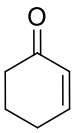
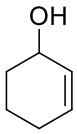
Fig. S10 ^{1}H NMR spectra (300MHz, $CDCl_3$) of the reaction products for cyclohexene oxidation with A) PANI@HA/1 M/2.04-H_3PO_4, B) PANI@HA/1 M/2.04-HNO_3, C) PANI@HA/1 M/2.04-H_2SO_4 and D) PANI@HA/1 M/2.04-HCl as catalyst. The bottom ^{1}H NMR spectrum is 99% 1,2-cyclohexandiol.

Table S3 Effect of ANI/HA weight ratio in the fabrication on selective oxidation of cyclohexene with PANI@HA/1 M/W-HCl as catalyst.

PANI@HA/1 M/W-HCl	Product selectivity (%)				Conversion (%)
					
PANI@HA/1 M/0.20-HCl	1.57	95.87	0	2.56	4.26
PANI@HA/1 M/0.41-HCl	0.85	96.72	0	2.43	12.77
PANI@HA/1 M/1.02-HCl	0.57	97.28	0	2.16	32.87
PANI@HA/1 M/2.04-HCl	0	99.50	0.05	0.45	98.17
PANI@HA/1 M/2.24-HCl	0	99.05	0	0.95	98.32

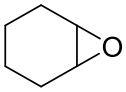
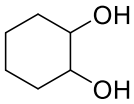
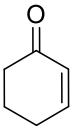
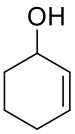
Reaction conditions: 20 mg catalyst, 1.23 mL cyclohexene, 2.5 mL H_2O_2, 70 °C, 24 h.

Table S4 Effect of reaction time on selective oxidation of cyclohexene with PANI@HA/1 M/2.04-HCl as catalyst.

Reaction time (h)	Product selectivity (%)				Conversion (%)
					
0.5	5.54	83.90	2.99	7.56	0.31
1	4.12	86.88	4.75	4.25	0.38
2	2.74	89.21	1.11	6.94	0.40
4	0.79	97.46	0.34	1.39	0.83
8	0.45	98.38	0	1.17	7.35
12	0.14	99.07	0	0.79	44.64
16	0	99.23	0	0.77	87.12
20	0	99.38	0	0.62	92.34
24	0	99.50	0.05	0.45	98.17
48	0	94.07	0	5.93	99.69

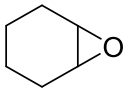
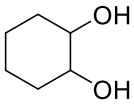
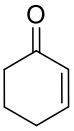
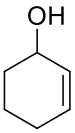
Reaction conditions: 20 mg catalyst, 1.23 mL cyclohexene, 2.5 mL H_2O_2, 70 °C.

Table S5 Effect of reaction temperature on selective oxidation of cyclohexene with PANI@HA/1 M/2.04-HCl as catalyst.

T (°C)	Product selectivity (%)				Conversion (%)
					
30	0.95	90.91	3.07	5.08	0.49
40	0.89	95.09	0.60	3.41	0.65
50	0.62	97.6	0	1.79	1.17
60	0.21	99.49	0	0.30	46.78
70	0	99.50	0.05	0.45	98.17
80	0	99.71	0	0.29	99.00

Reaction conditions: 20 mg catalyst, 1.23 mL cyclohexene, 2.5 mL H_2O_2, 24 h.

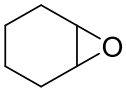
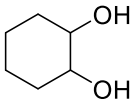
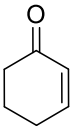
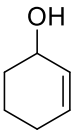
Table S6 Effect of solvent on selective oxidation of cyclohexene with PANI@HA/1 M/2.04-HCl as catalyst.

Solvent	Product selectivity (%)				Conversion (%)
					
Solvent-free	0	99.50	0.05	0.45	98.17
n-Heptane	0.78	98.33	0	0.89	3.79
THF	1.09	96.50	0.32	2.08	3.63
CH_2Cl_2[a]	3.39	88.59	4.49	3.54	1.66
$CHCl_3$	3.88	91.79	0.63	3.70	5.32
CH_3CN	0.66	94.61	2.71	2.02	29.01
DMSO	24.35	65.63	10.01	0	40.68

[a]Cyclohexene oxidation according to the oxidation process of method B.

Reaction conditions: 20 mg catalyst, 1.23 mL cyclohexene, 2.5 mL H_2O_2, 70 °C, 24 h.

Table S7 Effect of oxidant on selective oxidation of cyclohexene with PANI@HA/1 M/2.04-HCl as catalyst.

Oxidant	Product Selectivity (%)				Conversion (%)
					
H_2O_2-free	1.79	52.39	18.90	26.92	2.91
1.3 mL H_2O_2	0.29	99.27	0.15	0.28	38.62
2.5 mL H_2O_2	0	99.50	0.05	0.45	98.17
5.0 mL H_2O_2	0.48	97.28	0.26	1.99	40.69
7.5 mL H_2O_2	0	98.91	0.16	0.94	26.56
O_2	3.71	67.91	11.89	16.49	5.20
Air	1.79	52.39	18.90	26.92	2.91

Reaction conditions: 20 mg catalyst, 1.23 mL cyclohexene, 70 °C, 24 h.

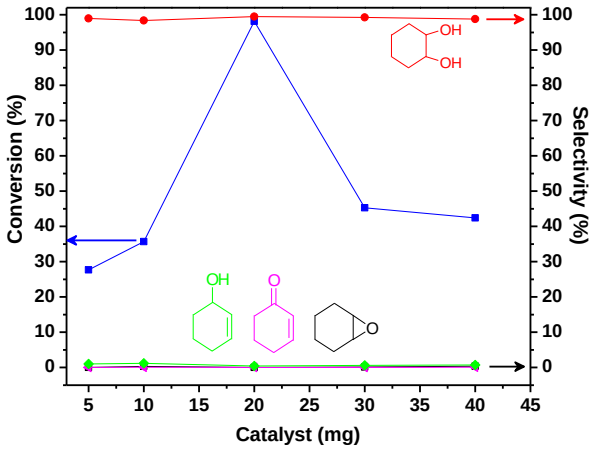


Fig. S11 Effect of catalyst amount on selective oxidation of cyclohexene with PANI@HA/1 M/2.04-HCl as catalyst.

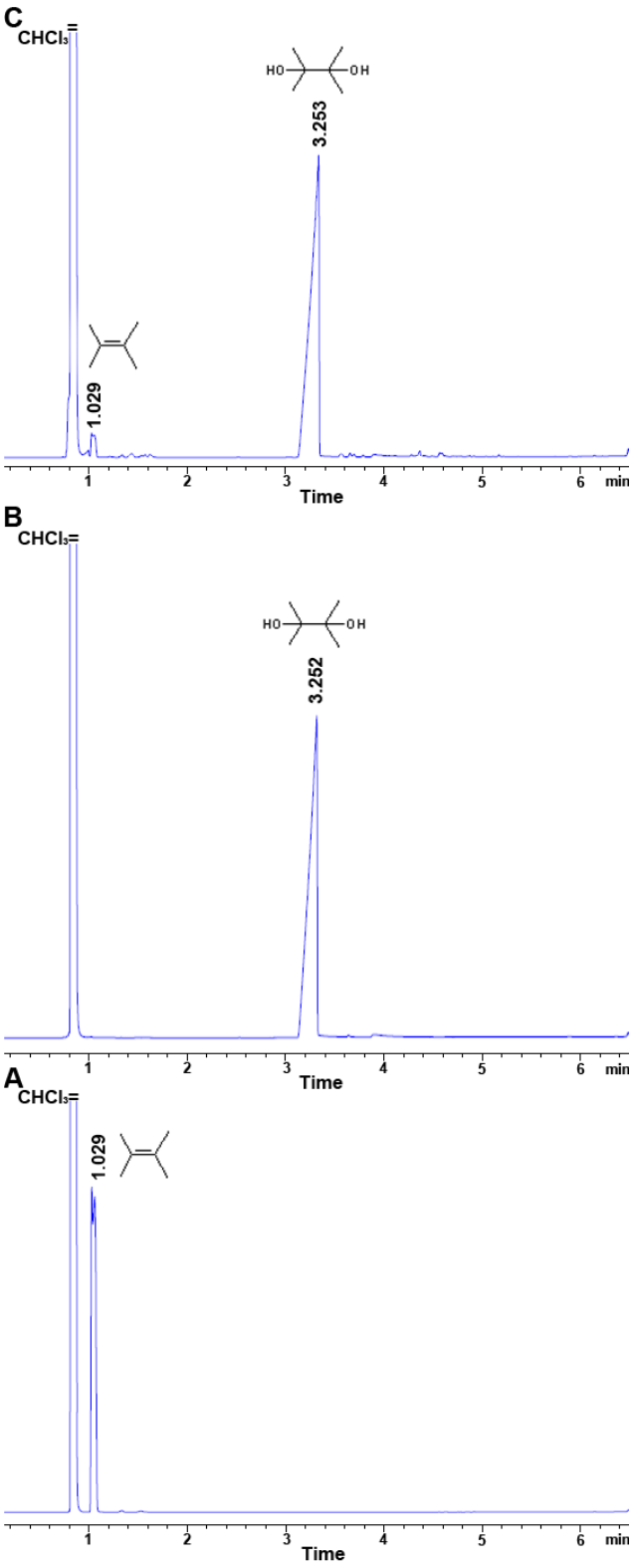


Fig. S12 GC spectra of (A) 98% 2,3-dimethyl-2-butene, (B) 98% 2,3-dimethyl-2,3-butanediol (pinacol) and (C) the reaction products for 2,3-dimethyl-2-butene oxidation with PANI@HA/1 M/2.04-HCl as catalyst at 70 ^{o}C.

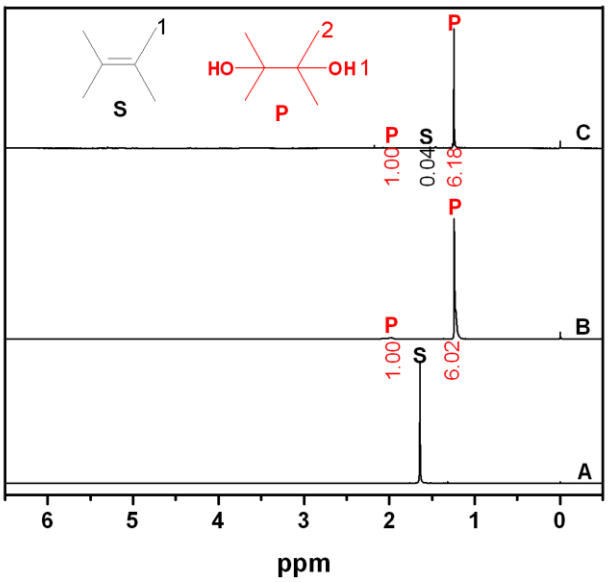


Fig. S13 ^{1}H NMR spectra (300MHz, $CDCl_3$) of (A) 98% 2,3-dimethyl-2-butene, (B) 98% 2,3-dimethyl-2,3-butanediol (pinacol) and (C) the reaction products for 2,3-dimethyl-2-butene oxidation with PANI@HA/1 M/2.04-HCl as catalyst at 70 ^{o}C.

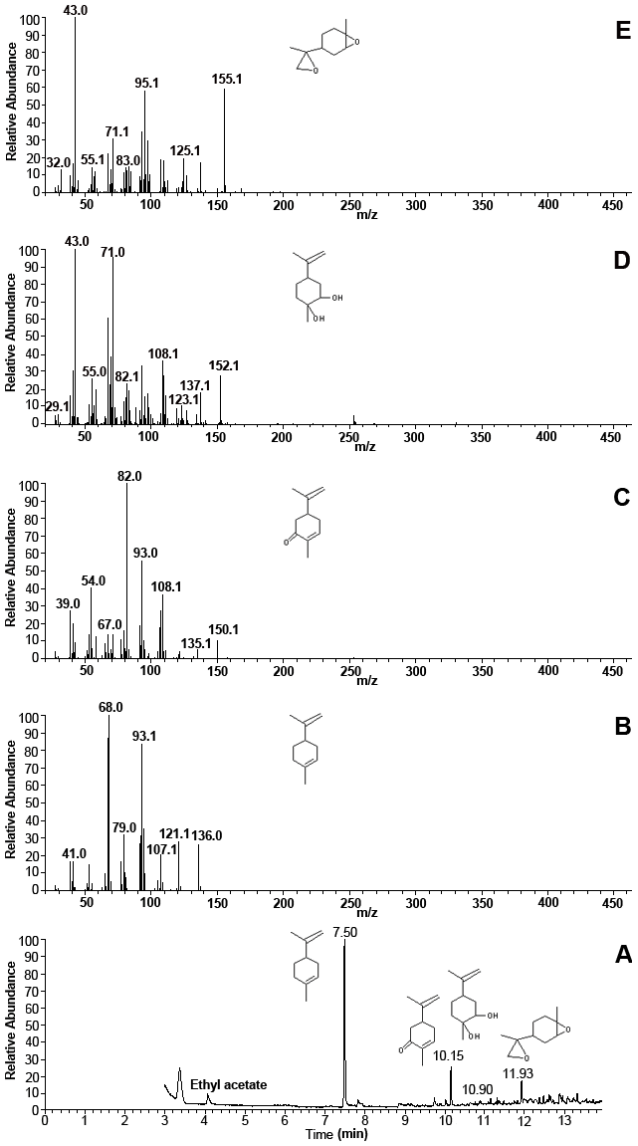


Fig. S14 (A) GC spectra of the reaction products for (R)-(+)-limonene oxidation with PANI@HA/1 M/2.04-HCl as catalyst at 90 °C; (B), (C), (D) and (E) the MS spectra of (A) at the retention time of 7.50, 10.15, 10.90 and 11.93 min, respectively.

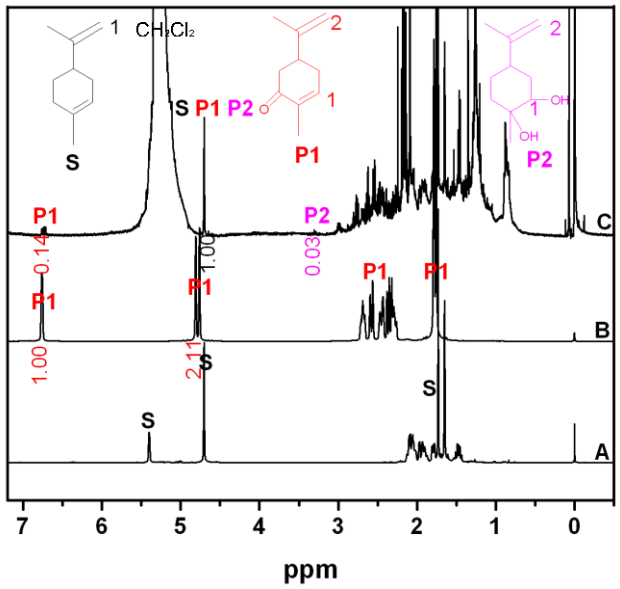


Fig. S15 ^{1}H NMR spectra (300MHz, $CDCl_3$) of (A) 97% (R)-(+)-limonene, (B) 98% (R)-(-)-carvone, (C) the reaction products for (R)-(+)-limonene oxidation with PANI@HA/1 M/2.04-HCl as catalyst at 90 °C.

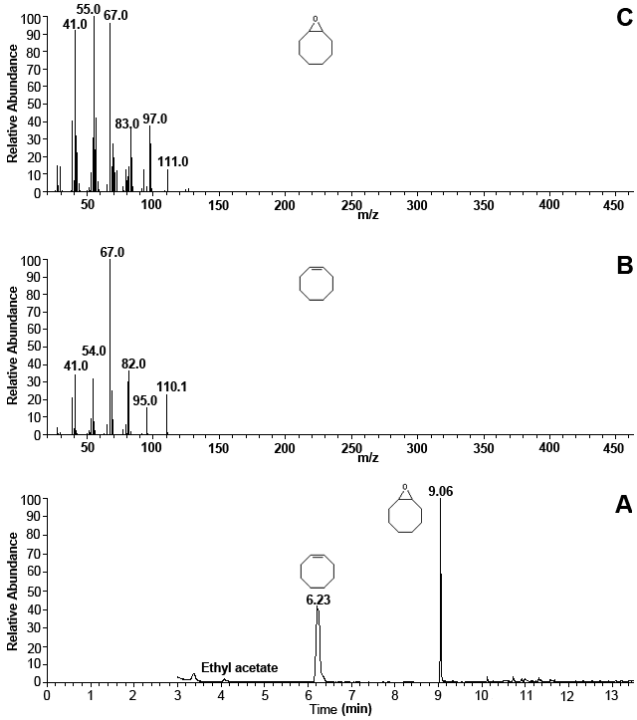


Fig. S16 (A) GC spectra of the reaction products for cyclooctene oxidation with PANI@HA/1 M/2.04-HCl as catalyst at 90 °C; (B) and (C) the MS spectra of (A) at the retention time of 6.23 and 9.06 min, respectively.

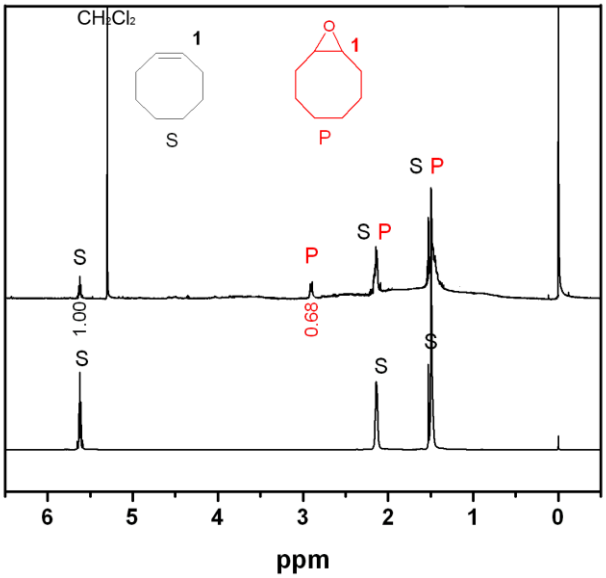


Fig. S17 ^{1}H NMR spectra (300MHz, $CDCl_3$) of the reaction products for cyclooctene oxidation with PANI@HA/1 M/2.04-HCl as catalyst at 90 ^{o}C. The bottom ^{1}H NMR spectrum is 96% cyclooctene.

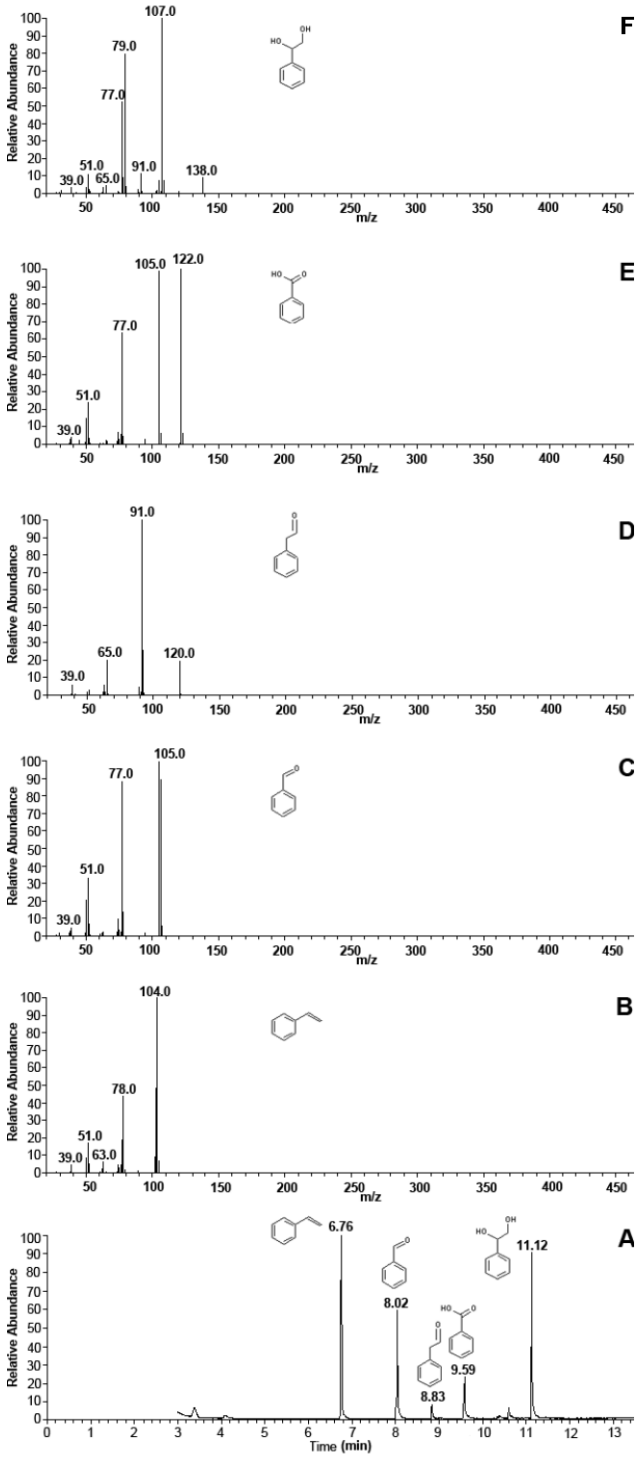


Fig. S18 (A) GC spectra of the reaction products for styrene oxidation with PANI@HA/1 M/2.04-HCl as catalyst at 80 °C; (B), (C), (D), (E) and (F) the MS spectra of (A) at the retention time of 6.76, 8.02, 8.83, 9.59 and 11.12 min, respectively.

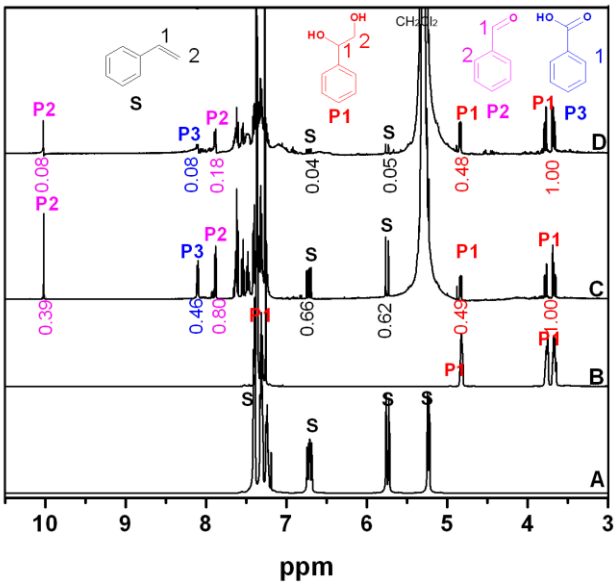


Fig. S19 ^{1}H NMR spectra (300MHz, $CDCl_3$) of (A) 98% styrene, (B) 99% 1-phenyl-1,2-ethanediol; (C) and (D) the reaction products for styrene oxidation with PANI@HA/1 M/2.04-HCl as catalyst at 80 ^{o}C and 90 ^{o}C, respectively.

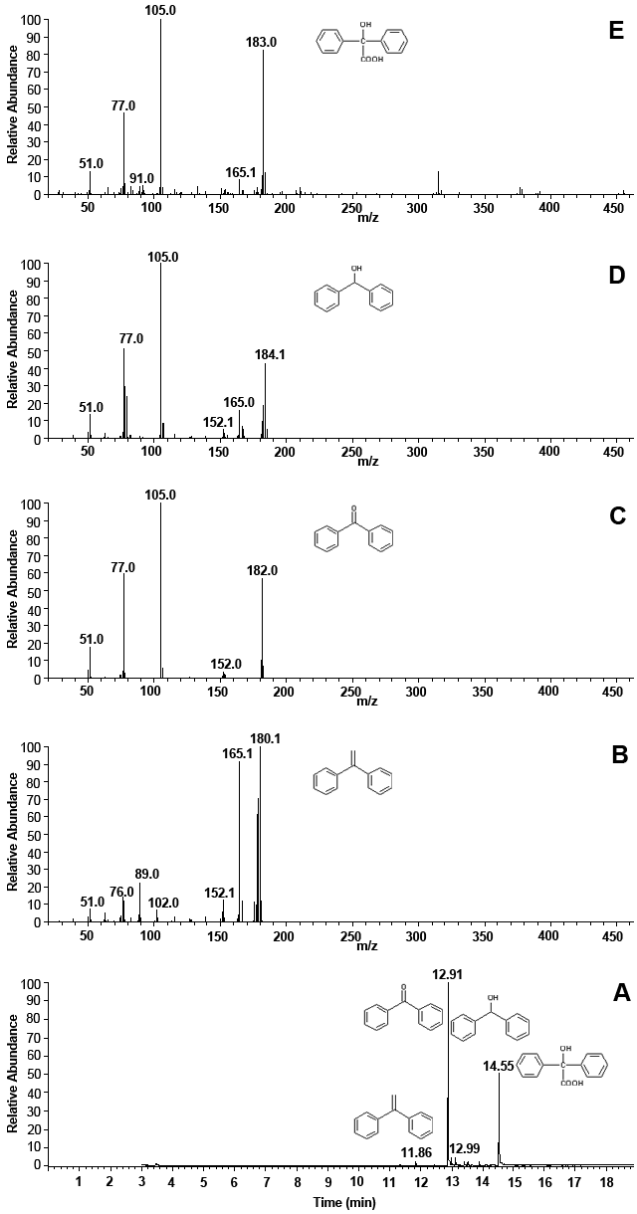


Fig. S20 (A) GC spectra of the reaction products for 1,1-diphenyl ethylene oxidation with PANI@HA/1 M/2.04-HCl as catalyst at 90 ^{o}C; (B), (C), (D) and (E) the MS spectra of (A) at the retention time of 11.86, 12.91, 12.99 and 14.55 min, respectively.

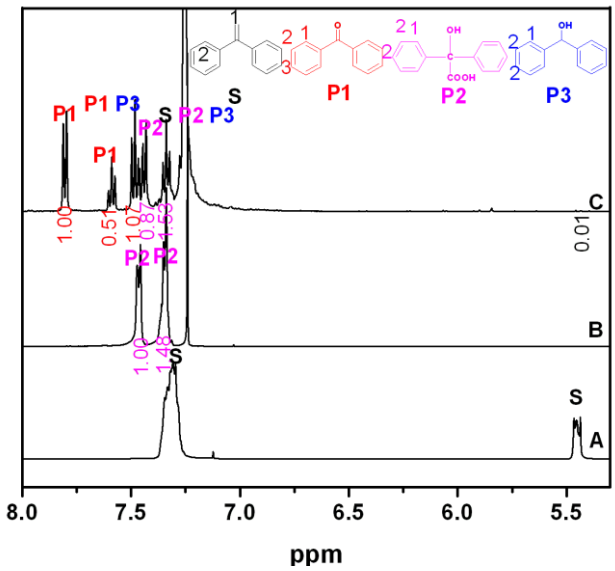
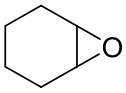
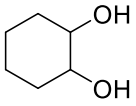
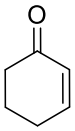
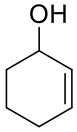


Fig. S21 ^{1}H NMR spectra (300MHz, $CDCl_3$) of (A) 98% 1,1-diphenyl ethylene, (B) 98% 2,2-diphenyl-2-hydroxyacetic acid and (C) the reaction products for 1,1-diphenyl ethylene oxidation with PANI@HA/1 M/2.04-HCl as catalyst at 90 °C.

Table S8 Recycling study with PANI@HA/1M/2.04-HCl as catalyst.

Cycles	Product Selectivity (%)				Conversion (%)
					
1	0	99.50	0.05	0.45	98.17
2	0	97.16	0.52	2.32	98.78
3	0	91.66	0.47	7.91	99.43
4	0	95.15	0.20	4.65	99.45
5	0	96.92	1.21	1.87	99.11

Reaction conditions: 20 mg catalyst, 1.23 mL cyclohexene, 2.5 mL H_2O_2, 70 °C, 24 h.