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

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One dimensional polyaniline@halloysite (PANI@HA) nanotubes with enhanced selective oxidation activity of cyclohexene are fabricated by employing aniline (ANI) chemical polymerization on halloysite nanotubes *in-situ*. By facilely controlling the doping acid, acidity and ANI/HA weight ratio in the fabrication, PANI with controllable doping degree, redox state and content are growing on halloysite nanotubes. The cyclohexene selective oxidation result shows PANI@HA nanotubes are effective catalysts in solvent-free reaction system with H_2O_2 as oxidant and their catalytic activity is relied on the doping acid, acidity and ANI/HA weight ratio in the fabrication. Wherein, PANI@HA synthesized with HCI as doping acid to condition the acidity at 1 M and 2.04 ANI/HA weight ratio (PANI@HA/1 M/2.04-HCI) demonstrates the highest catalytic activity (98.17% conversion and 99.50% selectivity to 1, 2-cyclohexanediol). The cyclohexene selective catalystic, 2.5 mL H_2O_2 , 70 °C and 24 h. Furthermore, PANI@HA/1 M/2.04-HCI has exhibit superior dihydroxylation activity toward 2,3-dimethyl-2-butene and cycling performance with 99.11% conversion and 96.92% selectivity to 1, 2-cyclohexanediol after five cycles. CV of PANI@HA indicates cyclohexene selective oxidation is attributed to reversible redox reaction of PANI in PANI@HA to catalytic decomposition of H_2O_2 .

Introduction

1,2-Cyclohexanediol has played an important role in the synthesis of pharmaceuticals intermediate, polyester resins, catechol¹ and liquid crystals.² It can also be acted as a diluter for epoxy resins and a chiral auxiliary or ligand in asymmetric synthesis.³ Therefore, the synthesis of 1,2-cyclohexanediol has been extensively studied. Generally, there are two typical synthetic methodologies for 1.2cyclohexanediol: hydrolysis of epoxy cyclohexane^{4,5} and dihydroxylation of cyclohexene.⁵⁻⁹ The straightforward and benchmarked route is cyclohexene dihydroxylation with OsO4 and RuO_4 as catalyst/oxidants. 10,11 However, it is costly, toxic or difficult to control and nonselective, which prevent further application in industry. On the another aspect, with the increasingly serious environmental pollution, developing environmentally friendly synthesis process, such as solvent-free reaction process, using green oxidants, higher catalytic efficiency to certain product and excellent

recycling performance, has became important for fine chemical, food and pharmaceutical industry.¹²⁻¹⁴ For the green oxidants, the typical ones are air, O₂ and hydrogen peroxide (H₂O₂) ascribed to them or their by-product harmless to the environment.5,7-9,15 Although various dihydroxylation processes of cyclohexene involving a great number of catalysts and oxidants have been developed, metal-based catalysts, expensive oxidants or toxic solvents are still used extensively and low conversion or selectivity to 1,2-cyclohexanediol are usually accompanied by.¹⁶⁻²⁰ For example, Nowak et al.¹⁶ use mesoporous FDU-1 supported Nb(Co) for cyclohexene oxidation with H₂O₂ as oxidant and CH₃CN as solvent, resulting in 61% conversion and 56% selectivity to 1,2-cyclohexanediol. Kang et al.17 adopt a solvent-free synthesis process for cyclohexene oxidation with Augrapheme core-shell nanostructures as catalyst and air as oxidant, but the conversion and selectivity to 1,2-cyclohexanediol are, respectively, 55.5% and 61.6%. Recently, Luo⁵ and Shi⁹ et al apply Ti-Beta zeolite and peroxophosphotungstate-ionic liquid brush assembly to cyclohexene oxidation under solvent-free condition with H_2O_2 as oxidant to achieve higher cyclohexene conversion and selectivity to 1,2-cyclohexanediol (90.2% cyclohexene conversion and 66.2% selectivity to 1,2-cyclohexanediol for Ti-Beta zeolite, 99% 1,2-cyclohexanediol yield for peroxophosphotungstate-ionic liquid brush assembly).

On the other side, metal-free catalysts gradually become the research hotspot, because they have the advantage of low-cost, facilely fabrication, corrosion resistance and conveniently modification.²¹⁻²⁴ Some pioneering studies have demonstrated metal-free catalyst can present comparable or superior catalytic

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Electronic Supplementary Information (ESI) available: [Data of HA; FT-IR and TEM of PANI@HA/1 M/W-H; chemical composition, mass ratio, doping degree and Q/B of PANI in PANI@HA/A/W-H; C1s deconvoluted spectra of PANI@HA/1 M/2.04-H; effect of ANI/HA weight ratio in the fabrication, reaction time, reaction temperature, solvent, oxidant and catalyst amount on selective oxidation of cyclohexene with PANI@HA/1 M/W-HCI as catalyst; recycling study with PANI@HA/1M/2.04-HCI as catalyst; GC, GC-MS and ¹H NMR spectra of the reaction products for olefin oxidation]. See DOI: 10.1039/x0xx00000x

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activity to the metal-based catalyst. For example, Afonso et al have reported *p*-toluenesulfonic acid can promote cyclohexene oxidation with H_2O_2 as oxidant in a biphasic system to achieve 97.9% conversion and 80.7% selectivity to 1,2-cyclohexanediol, and ptoluenesulfonic acid is also efficient for the dihydroxylation of substituted acyclic olefins and alkyl cyclic olefins.^{7,8} Legros *et al* have shown supramolecular fluorous catalyst can used as recyclable catalyst for the Morita-Baylis-Hillman reaction.²² And 1,2-bis[3,5bis(trifluoromethyl) phenyl]diselane can also be used to catalyze cyclohexene oxidation to 1,2-cyclohexanediol in acetonitrile.23 Nitrogen-doped CNTs exhibit 59.0% cyclohexene conversion and 52.3% selectivity to allylic products using molecular oxygen as oxidant in CH₃CN.²⁴ So it proposes whether or not polymer material can present enhanced or comparable catalytic oxidation activity for cyclohexene oxidation. Recently, nano-polyaniline (PANI) with different redox state has been used as catalyst directly to selective oxidation of cyclohexene to 1,2-cyclohexanediol with H₂O₂ as oxidant in CHCl₃ and exhibit excellent catalytic activity.²⁵ The study shows the catalytic activity of nano-PANI is correlated with the size and redox state. Among them, 10-20 nm emeraldine base PANI (NEB) possesses highest catalytic activity (92.63% conversion and 64.22% selectivity to 1,2-cyclohexanediol), whereas bulk leucoemeraldine base PANI shows lowest catalytic activity (1.46% conversion and 72.74% selectivity to 1,2-cyclohexanediol). However, in this study, to synthesize nano-PANI and avoid the nano-PANI from aggregation, microemulsion polymerization is adopted, which will lead to the residual emulsifier on the surface of nano-PANI and thereby interfere with the catalytic activity. Furthermore, toxic and volatile CHCl₃ is chosen as the solvent, and the selectivity to 1,2-cyclohexanediol is still lower than 70% under the highest conversion.

The nanostructure can also be synthesized by supporting active species on nano-support, which not only can avoid the use of stabilizer or emulsifier, but also sometimes can enhance the properties of active species owing to the synergistic effect of nanosupport and active species.^{16,17,19} In our previous studies, it has shown that nano-Ag, crystalline TiO₂, a-Ni(OH)₂ and PANI can be induced in-situ to grow on the exterior surface of halloysite nanotubes to synthesize halloysite nanotubes supported nanostructure in virtue of the negative charged exterior surface and massive surface hydroxyl groups of halloysite nanotubes.²⁶⁻³⁰ Compared with carbon nanotubes, halloysite nanotube is an abundantly widespread natural clay with different outside/inside surface chemical properties, which endow them facilitating modification and growing functional materials.^{31,32} So using halloysite nanotube as the support for growing nano-PANI will have the economic and resource advantage. Furthermore, the redox state and doping degree of PANI associated with the chain nitrogens can be controlled by the synthesis/redoping conditions (concentration/variety of oxidants/doping acid).^{30,31} It has demonstrated that the visible light photocatalytic dye degradation PANI/TiO₂/halloysite nanotubes activity of and Cr(VI) adsorption/reduction properties of halloysite nanotube@PANI are dependent on doping acid' concentration/variety in the synthesis/redoping process.^{30,33} And compared with nano-TiO₂ and bulk PANI prepared under the comparative condition, they all exhibit enhanced visible light photocatalytic dye degradation activity and Cr(VI) adsorption/reduction properties, respectively. So it proposes

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the question whether halloysite nanotube supported PANL has enhanced or comparative cyclohexene oxidation detivity than that of nano-PANI and the doping acid' concentration/variety can give an impact on the cyclohexene oxidation activity. Although nano-PANI prepared by microemulsion polymerization has recently been applied in cyclohexene oxidation, it is conducted with toxic and volatile CHCl₃ as solvent and the selectivity to1,2-cyclohexanediol is lower than 70%.²⁵ For all we know, the influence of doping acid with the same or different acidity in the fabrication on the cyclohexene oxidation activity of halloysite nanotubes supported PANI, especially its green cyclohexene oxidation process (solvent-free and H₂O₂ as oxidant) and superior catalytic activity (>98% conversion and selectivity to 1,2-cyclohexanediol) have rarely been reported.

In this study, the heterogeneous polyaniline@halloysite nanotubes (PANI@HA) are fabricated in different doping acid through aniline chemical polymerization in-situ on the parent halloysite nanotubes (HA) at room temperature. By conveniently controlling the variety and concentration of doping acid in the fabrication, heterogeneous PANI@HA nanotubes with various PANI redox state and doping degree can be achieved. The impact of catalyst (the variety and concentration of doping acid and ANI/HA weight ratio in the fabrication) and reaction condition (reaction time/temperature, solvent, oxidant and catalyst amount) on the cyclohexene selective oxidation properties of PANI@HA are investigated in detail. Furthermore, the cycling performance of PANI@HA is also investigated. According to the results of CV, a mechanism of reversible redox reaction of PANI in PANI@HA to catalytic decomposition of H2O2 is suggested for cyclohexene selective oxidation by PANI@HA.

Experimental

Materials

Parent halloysite (HA) nanotubes were obtained from Fenghui Minerals Trade Co., Ltd. Aniline (ANI) and ammonium persulfate $((NH_4)_2S_2O_8)$ were obtained from Sinopharm Chemical Reagent Co., Ltd. Trichloromethane (CHCl₃) was obtained from Guangzhou Jinhuada Chemical Reagent Co., Ltd. Cyclohexene (99%) was obtained from J&K Scientific Ltd. Hydrogen peroxide (H₂O₂, 30%) were purchased from Tianjin Fengchuan Chemical Reagent Technology Co., Ltd. All the chemical reagents were analytical grade and used without any further purification.

One-pot fabrication of PANI@HA nanotubes

In the fabrication of PANI@HA nanotubes, the amount of halloysite nanotube in various system was constant and the acidity of the reaction system was controlled by the feeding amount of 2 M inorganic acid. A typical procedure with HCl as doping acid to control the acidity at 1 M and 2.04 ANI/HA weight ratio was as follows:³³ HCl solution (2 M, 200 mL) was added into a PP container with continuously stirring at room temperature. Then deionized water (200 mL) was added to achieve 1 M HCl solution. After 1 h, HA (0.8 g), ANI (1.63 g) and (NH₄)₂S₂O₈ (4 g) (molar ratio of ANI to (NH₄)₂S₂O₈ was 1:1) were added to the above 1 M HCl solution with continuously stirring 24 h at room temperature to form PANI@HA nanotubes. Then the PANI@HA heteroarchitectures were separated by centrifugation, washed with water several cycles to neutral and dry at 65 °C. This sample was labelled as PANI@HA/1 M/2.04-HCl, in

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which 1 M, 2.04 and HCl, respectively, represent acidity, ANI/HA weight ratio and doping acid. The weight ratio of PANI in PANI@HA can be adjusted by the ANI/HA weight ratio in the fabrication. By the similar process, PANI@HA nanotubes with 2.04 ANI/HA weight ratio in the presence of H_3PO_4 , HNO₃ and H_2SO_4 were prepared and labelled as PANI@HA/1 M/2.04-H ("H" standards for doping acid). For comparison, bulk PANI and PANI@HA with various acidity and ANI/HA weight ratio in the presence of HCl (PANI@HA/A/W-HCl, in which A and W, respectively, standard for acidity and ANI/HA weight ratio) were also prepared in the similar way.

Characterization

The morphology of the fabricated PANI@HA nanotubes (PANI@HA/A/W-H) was characterized by TEM (JSM-2100) under an accelerating voltage of 200 kV. FT-IR was conducted on a Thermo Nicolet iS10 instrument with KBr pellet as background and 2 cm⁻¹ spectral resolution. The diffuse reflectance spectra of UV-vis were performed on a Hitachi U-4100 PC photometer in the range from 200 to 800 nm. The X-ray photoelectron spectroscopy (XPS) was conducted on a PHI5000 Versaprobe-II electron spectrometer with 50 W Al K_{α} radiations and C 1s line at 284.6 eV as reference. Cyclic voltammetry measurements were conducted on a CHI760E electrochemical equipment (CHI Inc., China) with modified carbon paste electrode, platinum wire and Ag/AgCl, respectively, as working electrode, auxiliary electrode and reference electrode. Cyclohexene and 2,3-dimethyl-2-butene oxidation reaction product was detected by a gas chromatograph (Agilent 7890A). The gas chromatography was performed in a Agilent 19091J-413 column with a cross-linked 5% Phenyl Methyl Siloxan (30 m×320 um×0.33 mm) and a FID detector under the following conditions: carrier gas (N₂, 40mL/min); temperature program-40 °C holding for 2 min, then heating to 50 °C at 10 °C /min, finally further heating to 300 °C at 50 °C /min. Other olefin oxidation reaction product was identified by GC-MS (TRACE DSQ). GC-MS was performed in a Agilent DB-17 column (30 m×0.25 um×0.25 mm) and a EI ion source under the following conditions: carrier gas (He, 1.0 mL/min); temperature program-40 °C holding for 3 min, then heating to 250 °C at 20 °C /min, finally further heating to 280 °C at 5 °C /min. ¹H-NMR spectra were recorded on a Bruker AVANCE300-MHz spectrometer with CDCl₃ as solvent and tetramethylsilane as an internal standard.

Selective oxidation of cyclohexene by PANI@HA nanotubes

Method A: in a typical experiment, catalyst (PANI@HA, 20 mg), oxidant (30% H_2O_2 , 2.5 mL) and cyclohexene (1.23 mL) are added to a 20 mL dry round-bottom flask equipped with a magnetic stirrer. After the flask was sealed with rubber turnover stopper, parafilm "M" and electric insulation tape consecutively, the flask is placed in an oil bath thermostated at 70 °C. After 24 h, the reaction system was extracted by CHCl₃ or CH₂Cl₂ (5 mL) three times and the extract was collected together and analyzed by gas chromatograph. For the GC-MS characterization, the extract was rotary evaporated at room temperature to remove CHCl₃ or CH₂Cl₂, then 15 mL ethyl acetate was added. During the range of reaction experiments, explosion and leakage of reaction medium did not occur even the oxidation reaction was conducted at 90 °C as the cushioning/sealing effect of rubber turnover stopper. The oxidation reaction also can be conducted in screw glass tube.

Method B: catalyst (PANI@HA, 20 mg), oxidant (30% H₂O₂, 2.5 mL), cyclohexene (1.23 mL) and solvent are added to a 20 mL roundbottom flask with a condenser and were continually stirred at 70 °C.

Results and discussion

Characterization of PANI@HA nanotubes

As the parent support of PANI, halloysite consists of cylindrical nanotubes with about 1-2 μm length, 40-60 nm diameter and 20-30 nm lumen diameter (Fig. S1). The chemical composition of halloysite is 17.5% Si, 17.6% Al and 64.9% O as detected by XPS and EDX (Fig. S2, S3) and with 38.6 m²/g BET surface area. According to our previous reports, the outer surface of the halloysite nanotube is negatively charged under pH<2 and can induced the growing of PANI and inorganic TiO₂ nanocrystals under various inorganic acid with (NH₄)₂S₂O₈ as oxidant of ANI at low temperature.³⁰ In the present work, the PANI@HA nanotubes were prepared with H₃PO₄, HNO₃, HCl, and H_2SO_4 as the doping acid/acidity tuning agent and (NH₄)₂S₂O₈ as the oxidant. The various redox state and doping degree of PANI can be achieved by changing the doping acid and acidity in the fabrication. The PANI@HA nanotubes prepared in 1 M acidity and with 2.04 ANI/HA weight ratio are firstly synthesized and characterized.



Fig. 1 TEM images of PANI@HA nanotubes fabricated in 1 M acidity with 2.04 ANI/HA weight ratio (PANI@HA/1 M/2.04-H): the doping acid/acidity tuning agents are respectively (a) H_3PO_4 , (b) HNO₃, (c) H_2SO_4 and (d) HCI.

Fig. 1 shows the TEM images of PANI@HA nanotubes fabricated in 1 M acidity with 2.04 ANI/HA weight ratio (PANI@HA/1 M/2.04-H). Obviously, the external surface of PANI@HA/1 M/2.04-H is rough and the outside diameter increases significantly when compared with that of the parent halloysite nanotube. By a closer observation, PANI@HA synthesized in different doping acid also has similarity in morphology without blocking the lumen of halloysite nanotube. TEM demonstrates that the PANI has been successfully germinated on the surface of the halloysite nanotube *in-situ*. The polymerization mechanism of aniline on the surface of halloysite nanotube can be explained as follows:^{33,34} at the beginning of polymerization, the surface of halloysite nanotube is mostly occupied by the oligomer of ANI; the new nucleation sites are arising on the external surface of the halloysite nanotubes due to the faster polymerization activity of

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oligomer species than that in the solution. Finally, the PANI chains grow vertically to the axis of the halloysite nanotube due to the steric hindrance effect.

FT-IR spectra of the synthesized PANI@HA nanotubes (PANI@HA/1 M/2.04-H) are present in Fig. 2. When compared with the spectrum of halloysite nanotubes (line a in Fig. 2), new characteristic bands attributed to PANI (3446 cm⁻¹-N-H stretching mode, 1566 cm⁻¹-C=C stretching vibration of quinoid ring, 1492 cm⁻¹-C=C stretching vibration of benzenoid ring, 1300 cm⁻¹-C–N stretching vibration of benzenoid ring, 1244 cm⁻¹-C-N⁺ stretching vibration of benzenoid ring, 1140 cm⁻¹-=N⁺-stretching vibration in guinonoid unit) are observed in PANI@HA/1 M/2.04-HCl. The existing characteristic peaks at 1566, 1492 and 1300 cm⁻¹ signify there are two form PANI unit-pernigraniline (PB) and leucoemeraldine (LB) concomitant in PANI@HA/1 M/2.04-HCl. Furthermore, the Q/B (indicating the redox state of PANI) and the doping degree of PANI can be, respectively, estimated roughly by the peak intensity of C=C stretching vibration of quinonoid ring at 1566 cm⁻¹ to that of the C=C stretching vibration of benzenoid ring at 1492 cm⁻¹, and the peak intensity of doped PANI at 1140 cm⁻¹ and 1244 cm⁻¹ to that of C=C stretching vibration of quinonoid ring and benzenoid ring at 1566 cm⁻¹ and 1492 cm⁻¹. It can be seen from Fig. 2 that PANI @HA with H_3PO_4 , HNO_3 and H_2SO_4 as doping acid tuning the acidity at 1 M in the synthesis take on analogous spectra



Fig. 2 FT-IR spectra of the fabricated PANI@HA/1 M/2.04-H: (a) HA; the acidity of the starting solutions are respectively adjusted by (b) $H_3PO_{4_7}$ (c) HNO_{3_7} (d) H_2SO_4 and (e) HCl.

as that of PANI@HA/1 M/2.04-HCl (Fig. 2b-e). However, they have differences in doping degree and redox state (Q/B): the doping degree of PANI in the PANI@HA/1 M/2.04-H follows the order of PANI@HA/1 M/2.04-HCl > PANI@HA/1 M/2.04-H_2SO_4 > PANI@HA/1 M/2.04-H_3PO_4, whereas Q/B demonstrates the reverse order. Higher doping degree indicates higher electrical conductivity of the fabricated PANI@HA/1 M/2.04-HCl.^{30,33} The different redox state and doping degree of PANI in the PANI@HA/1 M/2.04-H may exert an impact on the catalytic activity of cyclohexene oxidation.

The FT-IR spectra of PANI@HA nanotubes fabricated in 1 M HCl with different ANI/HA weight ratio (PANI@HA/1 M/W-HCl) has also been presented (Fig. S4). It manifests the characteristic peak

intensity of PANI in PANI@HA/1 M/W-HCl fortifies, Awithothe increasement on ANI/HA weight ratio, which states that the content of PANI can be adjusted by ANI/HA weight ratio in the fabrication. From FT-IR (Fig. 2 and Fig. S4), the characteristic peaks of halloysite nanotubes (3799 cm⁻¹, 3622 cm⁻¹, 910 cm⁻¹, 535 cm⁻¹ and 470 cm⁻¹) still maintain in PANI@HA/1 M/W-H,²⁶⁻³³ illustrating the physical structure of halloysite nonutubes remain stable by the PANI growing under different doping acid. Furthermore, the tunable PANI content by adjusting the ANI/HA weight ratio in the preparation is further proved by the increase of PANI layer thickness with the ANI/HA weight ratio increasing (Fig. S5).

The redox state of PANI in the heterogeneous PANI@HA nanotubes is further studied by UV-vis absorption spectra (Fig. 3). Compared with the parent spectra of halloysite nanotube, PANI@HA/1 M/2.04-H appear new three peaks (352 nm assigning to π - π * transition of benzenod ring, 432 nm attributing to π -polaron of benzenod ring, and the broad peak of 470-800 nm ascribing to the polaron- π^* transitions of quinonoid ring), demonstrating the growing of PANI on the halloysite nanoubes.^{30,35-37} The intensity ratio of peak at 470-800 nm and 350 nm in PANI@HA/1 M/2.04-H is much close to one, indicating the PANI on HA is in the form of emeraldine salt.37 However, they still have slight differences in the starting of broad band and the band intensity ratio of 470-800 nm/350 nm even if they are synthesized in the comparative acidity, which is in accordance with the results of FT-IR. The above data indicates that the PANI@HA with various doping acids adjusting the acidity in the synthesis process has varied redox state and doping degree.



Fig. 3 UV-vis spectra of the fabricated PANI@HA/1 M/2.04-H: (a) HA; the acidity of the starting solutions are respectively adjusted by (b) H_3PO_4 , (c) HNO_3 , (d) H_2SO_4 and (e) HCl.

In order to deeply analyze the redox state and doping degree of PANI in PANI@HA/1 M/2.04-H, the XPS spectra is further used to characterize PANI@HA/1 M/2.04-H (Fig. 4, Table S1). It shows that the fabricated PANI@HA/1 M/2.04-H is mainly constituted of Si, Al, O, C and N and the corresponding doping counter-ion element, such as P, N, S and Cl also can be observed for PANI@HA/1 M/2.04-H_3PO₄, PANI@HA/1 M/2.04-HNO₃, PANI@HA/1 M/2.04-H_2SO₄ and PANI@HA/1 M/2.04-HCl, respectively. The high-resolution N 1s spectra of PANI@HA/1 M/2.04-H demonstrate three peaks at 398.9/398.7/398.9/398.8, 399.9/399.7/399.8/399.7 and

400.8/400.5/400.8/400.5 eV, which are respectively attributed to nitrogen atoms in quinonoid imine (-N=), benzenoid amine (-NH-) and doped imine/amine group (-N⁺=/-NH⁺).^{33,35,36,38} Moreover, the doping degree and redox state of PANI in PANI@HA/1 M/2.04-H can be quantitatively calculated according to the deconvoluted N 1s XPS spectra. The doping degree and Q/B, respectively, follow a descendant order and elevatory order of PANI@HA/1 M/2.04-HCl, PANI@HA/1 M/2.04-H_2SO_4, PANI@HA/1 M/2.04-HNO_3 and PANI@HA/1 M/2.04-H_3PO_4 (Table S2), which tie greatly in with the FT-IR spectra data. Whereas PANI@HA/1 M/2.04-H has similar high-resolution C 1s spectra (Fig. S6).



Fig. 4 XPS survey spectra (A) and the corresponding N 1s deconvoluted spectra (B) of PANI@HA/1 M/2.04-H: a) HA, the acidity of the starting solutions are adjusted by b) H_3PO_4 , c) HNO_3 , d) H_2SO_4 and e) HCl, respectively.

Element analysis shows the mass ratio of PANI in PANI@HA/1 M/2.04-H is in the range of 37-52% (Table S2). Among them, PANI@HA/1 M/2.04-HCl has the lowest PANI content, whereas PANI@HA/1 M/2.04-H₃PO₄ has the highest PANI content. It is worthy to be mentioned that the PANI content is lower than 67.1% (the PANI content considering all the feeding ANI has been grown on HA). As there is no PANI in the bulk (Fig. 1) and it has been proved the PANI@HA synthesized by the purified or unpurified ANI has similar PANI content,³³ so the lower PANI content than 67.1% may caused by the removal of the oligomer in the purification process.

Meanwhile, the PANI content in PANI@HA/A/2.04-HCL prepared in different acidity with HCl as doping acid and 2:04 ANI/PFA Weight Fatio is fairly near in 35-37%, meaning acidity in the fabrication has little effect on the PANI content. The above results demonstrate the redox state and doping degree of PANI in the fabrication can be regulated by the variety of doping acid.

Selective oxidation of cyclohexene to 1,2-cyclohexanediol by the PANI@HA nanotubes

The above PANI@HA nanotubes with H₃PO₄, HNO₃, H₂SO₄, and HCl as doping acid/acidity adjusting agent in the fabrication are directly applied to selective oxidation of cyclohexene in solvent-free reaction system at 70 °C with H₂O₂ as oxidant. And for comparison, the cyclohexene oxidation activities of the parent HA and the bulk PANI fabricated in 1 M doping acid solution without adding HA are also investigated. The reaction products are analyzed by gas chromatograph (GC). The GC spectra of the reaction products with PANI@HA/1 M/2.04-H3PO4, PANI@HA/1 M/2.04-HNO3, PANI@HA/1 M/2.04-H₂SO₄ and PANI@HA/1 M/2.04-HCl as catalyst are given in Fig. S8. And to facilitate the analysis, the GC spectra of 99% cyclohexene, epoxy cyclohexane, 2-cyclohexen-1-ol, 2-cyclohexen-1one and 1,2-cyclohexandiol are also given (Fig. S7). It is demonstrable the reaction products of cyclohexene oxidation with PANI@HA as catalyst mainly appear two peaks around the retention time of 1.25 and 4.60 min, which are ascribed to cyclohexene and 1,2cyclohexandiol, respectively, indicating the main oxidation product is 1,2-cyclohexandiol. And the peak intensity of 1,2-cyclohexandiol increases with the order of PANI@HA/1 M/2.04-HCl, PANI@HA/1 M/2.04-H₂SO₄, PANI@HA/1 M/2.04-HNO₃ and PANI@HA/1 M/2.04-H₃PO₄.

The reaction products are further characterized by ¹H NMR spectra (Fig. S10). The signal assignment of cyclohexene, epoxy cyclohexane, 2-cyclohexen-1-ol, 2-cyclohexen-1-one and 1,2-cyclohexandiol is given in Fig. S9. The signals at 5.74-5.58 ppm, 5.91-5.67 ppm and 6.11-5.96 ppm are respectively corresponded to the two vinyl protons (-CH=CH-) of cyclohexene, 2-cyclohexen-1-ol and 2cyclohexen-1-one. The signal at 3.20-3.02 ppm is assigned to the two methylidyne protons (-<u>CH</u>-O-<u>CH</u>-) of epoxy cyclohexane.³⁹ The signals at 3.85-3.65 ppm and 3.44-3.26 ppm are ascribed to the two methylidyne protons (-CHOH-CHOH-) of cis-1,2-cyclohexanediol and trans-1,2-cyclohexanediol, respectively.7,40 So cvclohexene conversion can be calculated by the sum of the integral values of the signals at 5.91-5.67, 6.11-5.96, 3.20-3.02, 3.85-3.65 and 3.44-3.26 ppm to that at 5.74-5.58, 5.91-5.67, 6.11-5.96, 3.20-3.02, 3.85-3.65 and 3.44-3.26 ppm. The selectivity to 1,2-cyclohexanediol can be estimated by the sum of the integral values of the signals at 3.85-3.65 and 3.44-3.26 ppm to that at 5.91-5.67, 6.11-5.96, 3.20-3.02, 3.85-3.65 and 3.44-3.26 ppm. Based on the ¹H NMR spectra, the cyclohexene conversion/selectivity to 1,2-cyclohexanediol for PANI@HA/1 M/2.04-H₃PO₄, PANI@HA/1 M/2.04-HNO₃, PANI@HA/1 M/2.04-H₂SO₄ and PANI@HA/1 M/2.04-HCl are respectively 43.42%/96.71%, 48.44%/94.40%. 52.61%/98.35% and 97.64%/98.34%, which are in accordance with the results of GC (entry 1-3 and 7, Table 1) . Considering the efficiency of GC characterization, the reaction products are characterized by GC in the following.

The detailed cyclohexene conversion and selectivity for various

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products based on GC are summarized in Table 1. It is obvious cyclohexene oxidation by HA and catalyst-free is extremely remote (3.66% and 0.1% cyclohexene conversion, respectively). Whereas with PANI@HA/1 M/2.04-H as catalyst, cyclohexene oxidation is noteworthy, especially with PANI@HA/1 M/2.04-HCl as catalyst, the cyclohexene conversion is 98.17% within 24 h, indicating the growing PANI on HA can enhance the cyclohexene oxidation activity of HA. However, the cyclohexene oxidation activity of PANI@HA/1 M/2.04-H fabricated under various doping acids is different. PANI@HA/1 M/2.04-HCl performs the highest conversion (98.17%) and high selectivity toward 1,2-cyclohexanediol (99.50%) when compared with those with H₂SO₄, HNO₃ and H₃PO₄ as doping acid (entry 1-3, Table 1). The reason may be due to the highest doping degree of PANI in PANI@HA/1 M/2.04-HCl. Cyclohexene conversions of the PANI@HA nanotubes are keeping the following order as PANI@HA/1 M/2.04-HCl > PANI@HA/1 M/2.04-H₂SO₄ > PANI@HA/1 M/2.04- $HNO_3 > PANI@HA/1 M/2.04-H_3PO_4$, accordance with the redox state and doping degree of PANI obtained by FT-IR and XPS. It is demonstrable that cyclohexene conversion of PANI@HA/1 M/2.04-HCl is higher than that of the bulk PANI prepared under 1 M HCl solution (entry 13, Table 1) due to the induction of HA to achieve nanostructure PANI, which is consist with the reported work that nano-PANI has improved cyclohexene oxidation activity.²⁵ Obviously,

Table 1 Cyclohexene conversion and selectivity of PANI@HA, PANI and HA.

the doping acid in the fabrication will produce a significant effection the cyclohexene oxidation activity of PANI@RA/11M/204-HA02605F

Furthermore, the acidity in the fabrication will also affect the cyclehexene oxidation activity, for example, when the acidity is in the range of 0.03-1 M, the cyclohexene conversion increases with the acidity increasing and then when the acidity is between 1 and 2 M, the cyclohexene conversion decreases with the acidity increasing. An optimal acidity in the fabrication is 1 M, which is coincided with the Cr(VI) adsorption/reduction result.33 And the effect of ANI/HA weight ratio in the fabrication (PANI@HA/1 M/W-HCl) on the cyclohexene oxidation activity are further studied (Table S3). It shows that the conversion increases with the ANI/HA weight ratio significantly when the ANI/HA weight ratio lower than 2.04, then it increases indistinctively when the ANI/HA weight ratio higher than 2.04. Although the cyclohexene conversion (98.32%) with a 2.24 ANI/HA weight ratio (PANI@HA/1 M/2.24-HCl) is slight higher than that (98.17%) with a 2.04 ANI/HA weight ratio (PANI@HA/1 M/2.04-HCl), a 2.04 ANI/HA weight ratio is still chosen for further studies when considering economy and effectiveness. The effect of ANI/HA weight ratio on the conversion is owing to a synergy of PANI content and PANI dispersion on the HA. From the point of selectivity to 1,2cyclohexanediol, it is on the slight increase with the ANI/HA weight ratio increasing and finally stable with a

	Selectivity (%)				_		
Catalyst	0	ОН	o	OH	Conversion (%)	TONª	r ^{"b} (mmol/g/h)
PANI@HA/1 M/2.04-H ₃ PO ₄	0	99.43	0	0.57	38.70	41.69	18.88
PANI@HA/1 M/2.04-HNO₃	0.43	96.47	0.46	2.64	43.42	56.96	25.80
PANI@HA/1 M/2.04-H ₂ SO ₄	0	99.61	0	0.39	54.42	66.10	29.94
PANI@HA/0.03 M/2.04-HCl	0.12	99.51	0	0.37	49.89	80.32	36.38
PANI@HA/0.3 M /2.04-HCl	0.12	99.42	0.05	0.41	52.07	82.43	37.33
PANI@HA/0.5 M/2.04-HCl	0.16	99.57	0	0.28	53.53	-	-
PANI@HA/1 M/2.04-HCl	0	99.50	0.05	0.45	98.17	148.66	67.33
PANI@HA/1.5 M/2.04-HCl	0	97.95	0.80	1.25	88.61	-	-
PANI@HA/2 M/2.04-HCl	0.13	99.52	0.10	0.27	58.86	-	-
PANI/1 M-H ₃ PO ₄	0.40	99.31	0.17	0.18	55.00	30.68	13.90
PANI/1 M-HNO3	0.12	99.75	0	0.12	51.40	28.68	12.99
PANI/1 M-H ₂ SO ₄	0.20	99.60	0	0.20	51.74	28.86	13.07
PANI/1 M-HCl	0.12	99.59	0	0.28	62.82	35.05	15.87
НА	1.15	94.61	0	4.24	3.66	-	-
Catalyst-free	54.68	0	11.74	33.58	0.10	-	-
10-20 nm emeraldine base PANI (NEB) ^c	21.67	64.22	1.75	10.56	92.63	16.81	7.61
Au-graphene core-shell nanostructure ^d	0.69	61.61	7.24	30.23	55.50	107.80	22.80

^aTON (turnover number) is defined as total mol of cyclohexene molecules converted per mol of catalyst.

^bInitial reaction rate of cyclohexene consumption normalized by catalyst mass.

^c Reaction conditions: 0.1g catalyst, 2 mL cyclohexene, 10 mL CHCl₃, 5 mL H₂O₂, 60 °C, 24 h (ref. 25).

^d Reaction conditions: 50 mg catalyst, 5 mL cyclohexene, O₂, 60 °C, 24 h (ref. 17).

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

2.04 ANI/HA weight ratio. In combination of the FT-IR result that the intensity of PANI characteristic peaks increases with the ANI/HA weight ratio increasing (Fig. S4), the cyclohexene oxidation activity of PANI@HA/1 M/W-HCI will be influenced by the PANI content in PANI@HA (ANI/HA weight ratio in the fabrication).

It is deserved to be mentioned that the selectivity to 1,2-

cyclohexanediol of cyclohexene oxidation by PANI@HA/A/W-H exceeds 95%, regardless of the doping acid, acidity and ANI/HA weight ratio in the fabrication. The high selectivity to 1,2cyclohexanediol will facilitate the later separation and purification. It is interesting that the cyclohexene conversion and selectivity to 1,2cyclohexanediol of PANI@HA/1 M/2.04-HCl are respectively 98.17% Published on 01 August 2017. Downloaded by Queen Mary, University of London on 03/08/2017 01:33:58

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and 99.50% within 24 h under the above reaction condition. indicating PANI@HA/1 M/2.04-HCl is an effective catalyst and can selectively oxidize cyclohexene to 1,2-cyclohexanediol. Both of the cyclohexene conversion and selectivity to 1,2-cyclohexanediol are higher than that of nanosized 10-20 nm PANI (emeraldine base, 92.63% conversion and 64.22% selectivity to 1,2-cyclohexanediol),²⁵ even the dosage of PANI@HA/1 M/2.04-HCl to cyclohexene (16.3 g/L) is lower than that of nanosized PANI to cyclohexene (50.0 g/L). Concluded on the above results, cyclohexene oxidation performance of PANI@HA/A/W-H is dependent on the acidity, variety of doping acid and ANI/HA weight ratio in the fabrication. Among them, PANI@HA/1 M/2.04-HCl shows the highest catalytic activity for cyclohexene oxidation, corresponding to a 67.33 mmol g⁻¹h⁻¹ massnormalized activity and 148.66 TON. This activity is significantly higher than that of 10-20 nm emeraldine base PANI (NEB, 7.61 mmol g⁻¹h⁻¹ and 16.81 TON) (entry 17, Table 1)²⁵ and comparable to that of supported nano-metal catalyst (entry 18, Table 1).17 Therefore, PANI@HA/1 M/2.04-HCl is an effective catalyst for cyclohexene oxidation and selected for further studies.



Fig. 5 Effect of reaction time on cyclohexene oxidation with PANI@HA/1 M/2.04-HCl as catalyst.

In the following, we will further explore the effect of reaction condition (including reaction time/temperature, solvent and oxidant and catalyst amount) on the cyclohexene selective oxidation performance of PANI@HA/1 M/2.04-HCl. Firstly, the effect of reaction time (0-48 h) on the catalytic activity of cyclohexene oxidation is investigated while keep other reaction conditions unchanged. It shows that the cyclohexene conversion increases markedly with the reaction time increasing and it achieves 98.17% conversion with 99.50% selectivity to 1,2-cyclohexandiol when the reaction time is 24 h (Fig. 5, Table S4). Then the cyclohexene conversion increases in an obscure when the reaction time is longer than 24 h, for example, the conversion only slightly increases to 99.69%, while with a drop off of the selectivity for 1,2-cyclohexandiol to 94.07%. It is deserved to mention that the selectivity to 1,2cyclohexandiol is over 83% throughout the whole reaction stage, indicating 1,2- cyclohexandiol is the main oxidation product even at a short reaction time, for example, 0.5 h (83.90% selectivity to 1,2cyclohexandiol). So considering the practical application and the catalytic activity, the reaction time is chosen as 24 h in the subsequent studies.

Reaction temperature is an important factor affecting the catalytic

activity, so in the following, cyclohexene selective, oxidation, by PANI@HA/1 M/2.04-HCl is also investigated: With 38 he77 reaction temperature in the range of 30-80 °C (Table S5). Obviously, cyclohexene conversion is dependent on the reaction temperature: when cyclohexene oxidation is conducted on below 50 °C, the conversion is lower than 1.2%; whereas when cyclohexene oxidation is underway at 60 °C, the conversion is fleetly raised to 46.78%; when the reaction temperature is 70 °C, the conversion is 98.17%. The increase of catalytic activity with the reaction temperature can be explained by the fact that high temperature can provide sufficient energy to deeply catalyze oxidation of cyclohexene.⁴¹ However, no obvious conversion promotion of cyclohexene is observed with the increase of reaction temperature to 80 °C (Table S5). The relationship between selectivity to 1,2-cyclohexandiol and reaction temperature is similar with that between conversion and reaction temperature, but the selectivity to 1,2-cyclohexandiol remains at high level (>90%) in the range of 30-80 °C. So the reaction temperature is fixed at 70 °C for cyclohexene oxidation.



Fig. 6 Effect of solvent on cyclohexene selective oxidation with PANI@HA/1 M/2.04-HCl as catalyst.

Besides, a series of solvents such as n-heptane, tetrahydrofuran (THF), trichloromethane (CHCl₃), acetonitrile (CH₃CN) and dimethyl sulfoxide (DMSO) have been used as solvents for the selective oxidation of cyclohexene and compared with that of solvent-free system. As shown in Fig. 6 and Table S6, the catalytic activity has reliance on the solvent. Maximum cyclohexene conversion (98.17%) and high selectivity to 1,2-cyclohexandiol (99.50%) is achieved in the solvent-free reaction system. The low conversion of the reaction system with solvent could be attributed to segmental decomposition of H₂O₂ with solvent in the present condition.⁴² In solvent-free reaction system, as the main product can dissolve in the water, thus accelerate cyclohexene conversion and the water in H₂O₂ can promote decompose of O-O bonds of peroxo-species, resulting in the high selectivity to 1,2-cyclohexanediol. It can also be observed that high polar solvent (for example, DMSO) can lead to the decrease of selectivity to 1,2-cyclohexanediol (65.63%) accompanying the increasing of selectivity to epoxy cyclohexane (24.35%) and 2cyclohexen-1-one (10.01%) (Table S6). It is probably due to the enhanced active oxygen species formation under the high polar solvent and thus facilitates allylic oxidation and epoxidation.^{41,43,44}

It is well known that oxidants play an important role in the

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cyclohexene oxidation. The detailed results of conversion of cyclohexene and selectivity to various products are concluded in Fig. 7 and Table S7. It is demonstrable there is a maximum conversion of 98.17% when the added volume of 30% H₂O₂ is 2.5 mL. While the selectivity to 1,2-cyclohexanediol is up to 99% with 1.25 mL 30% H_2O_2 and changes little with the increase of 30% H₂O₂ volume. Furthermore, other oxidants, such as O2 and air are also used to cyclohexene oxidation. However, the conversion of cyclohexene is poor (only 5.20% and 2.91% conversion for O_2 and air, respectively, Table S7), signifying PANI@HA/1 M/2.04-HCl is unable to activate O₂ under the current reaction conditions. In combination of 2.91% cyclohexene conversion with PANI@HA/1 M/2.04-HCl as catalyst but without H₂O₂ (Entry 1, Table S7) and 3.66% cyclohexene conversion with HA as catalyst and 30% H₂O₂ as oxidant (Entry 15, Table 1), we conclude that the role of different redox state/doping degree of PANI in PANI@HA should be catalytic decomposition of H2O2 to achieve active oxygen species. Therefore, the optimized oxidant is H₂O₂ and the effective volume of H_2O_2 is 2.5 mL for selective oxidation of cyclohexene in the present catalytic reaction system.



Fig. 7 Effect of H_2O_2 volumes on cyclohexene oxidation with PANI@HA/1 M/2.04-HCl as catalyst.

And also, the influence of catalyst amount on the cyclohexene oxidation activity of PANI@HA/1 M/2.04-HCl is investigated. There are strong signs that a demonstrable increase in the cyclohexene conversion is observed when the used catalyst amount is lower than 20 mg (Fig. S11). Exceeding this amount, cyclohexene conversion decreases distinctly. This could be explained by the possibility that competent interaction of PANI in PANI@HA/1 M/2.04-HCl with cyclohexene will inhibit the catalytic reaction and overdose catalyst will afford excess active sites to accelerate the occurrence of side reaction.⁴⁵ Therefore, the optimum catalyst amount is 20 mg in the present reaction system. What is worthy to be mentioned that cyclohexene oxidation is usually accompanied by many side products, but in this study 1,2-cyclohexanediol is the main product while other product can be ignored.

Moreover, the dihydroxylation scope of PANI@HA toward a range of olefins such as 2,3-dimethyl-2-butene (tetrasubstituted alkyl acyclic olefin), 1-hexene (monosubstituted alkyl acyclic olefin), (R)-(+)-limonene (trisubstituted cyclic olefin), cyclooctene (disubstituted alkyl cyclic olefin), styrene and 1,1-diphenylethylene is investigated under the optimized conditions (20 mg PANI@HA/1 M/2.04-HCl, 1.23 mL olefin, 2.5 mL H₂O₂, 70 °C, 24 h). The 2,3-dimethyl-2-butene oxidation product was characterized by GC and ¹H NMR (Fig. S12, Fig.

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S13). For other olefin oxidation, as the complicated application

product and the high boiling point of olefin, Dthe lexthadt was dotaby evaporated at room temperature to remove CHCl₃ or CH₂Cl₂, then 15 mL ethyl acetate was added for the GC-MS characterization. The GC-MS spectra are given as Fig. S14, Fig. S16, Fig. S18 and Fig. S20. Furthermore, ¹H NMR spectra of extract (note: in order to reflect the authenticity of the oxidation reaction, the extract is directly characterized by ¹H NMR, so some spectra will appear strong peak around 5.3 ppm when using CH₂Cl₂ as extractant) are also given as Fig. S15, Fig. S17, Fig. S19 and Fig. S21. And to facilitate the analysis, ¹H NMR spectra of olefin and some main reaction product are also given. The analysis of the spectra (including MS and ¹H NMR) was based on the data from Spectral Database for Organic Compounds (SDBS). The oxidation result is summarized in Table 2. The values outside and inside the bracket are respectively calculated based on the GC/GC-MS and ¹H NMR data. It is clearly the olefin conversion and selectivity to 1,2-diol calculated based on the GC/GC-MS and ¹H NMR data is consistent. Generally, higher olefin conversion and 1,2diol selectivity are achieved for substituted alkyl acyclic olefin than for terminal alkyl acyclic olefin (entry 1-2, Table 2), for example, 98.25% 2,3-dimethyl-2-butene conversion and 100% selectivity to pinacol for 2,3-dimethyl-2-butene catalytic oxidation (Fig. S12, Fig. S13), whereas 0.24% 1-hexene conversion and 30.68% selectivity to 1,2-hexanediol for 1-hexene catalytic oxidation. Compared with cyclohexene oxidation, the efficiency of cyclooctene oxidation (12.90% conversion) is much decreased and the main oxidation product is 1,2epoxycyclooctane (100% selectivity), which may be in virtue of its poor water solubility and higher activation energy (entry 4, Table 2).^{8,9} Furthermore, olefin conversion and selectivity to 1,2-diol will be influenced by the steric hindrance of olefin,^{8,9} for example, the (R)-(+)-limonene conversion is 0.55% with 39.22% selectivity to 1methyl-4-(1-methylethenyl)-1,2-cyclohexanediol (entry 3, Table 2), whereas the cyclohexene conversion is 98.17% with 99.50% selectivity to 1,2-cyclohexanediol (entry 7, Table 1). Aryl olefins, styrene and 1,1- diphenylethylene, also demonstrate steric effect will exert influence on the olefin conversion and the selectivity (entry 5,6, Table 2). For styrene oxidation, the main product is 1-phenyl-1,2ethanediol (45.89% selectivity), whereas for 1,2-diphenylethene oxidation, the main product are benzophenone (47.24% selectivity) and 2,2-diphenyl-2-hydroxyacetic acid (43.17% selectivity). Although not all the olefins are oxidized into their corresponding 1,2-diols and certain olefin oxidation achieve poor conversion catalyzed by PANI@HA under the optimized conditions for cyclohexene oxidation, the conversion and selectivity to certain product can be tuned by the reaction conditions, for example the reaction temperature (entry 3-6, Table 2). Further optimization of the reaction conditions for various olefins is undergoing.

 Table 2
 Olefin conversion and selectivity to 1,2-diol with PANI@HA/1 M/2.04-HCl as catalyst.

-				
Entry	Substrate	1,2-Diol	Selectivity to 1,2- diol (%)	Conversion (%)
1	\succ	но🔶 🔶 он	100.00 (100.00)	98.25 (99.35)
2	$\sim \sim $	ОН НО	30.68	0.24

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^aReaction conditions: 20 mg catalyst, 1.23 mL olefin, 2.5 mL H₂O₂, 80 °C, 24 h. ^bReaction conditions: 20 mg catalyst, 1.23 mL olefin, 2.5 mL H₂O₂, 90 °C, 24 h. ^cFor cyclooctene oxidation, 100% selectivity for 1,2-epoxycyclooctane; whereas for 1,1-diphenylethylene oxidation, >37% selectivity for benzophenone and 2,2-diphenyl-2-hydroxyacetic acid at the present reaction condition.

Reaction conditions: 20 mg catalyst, 1.23 mL olefin, 2.5 mL H_2O_2 , 70 °C, 24 h. Recycling study of PANI@HA

As an excellent catalyst, it should be stable and recyclable in the repeated use.¹⁶⁻²⁴ To illustrate the recycling performance of PANI@HA, five times recycling experiments are conducted on PANI@HA/1 M/2.04-HCl and the reaction time of each cycle is 24 h. It presents the cyclohexene conversion and selectivity to 1,2-cyclohexandiol still can achieve 99.11% and 96.92%, respectively, after five cycles (Fig. 8), which indicates that the PANI@HA/1 M/2.04-HCl and can be recycled effectively in the



Fig. 8 Cyclohexene selective oxidation recycling study with PANI@HA/1 M/2.04-HCl as catalyst. Reaction condition: 20 mg catalyst, 1.23 mL cyclohexene, 2.5 mL H₂O₂, 70 °C, 24 h.

repeated cyclohexene oxidation. With these unique advantages of green catalytic reaction system (solvent-free and green oxidant), high catalytic performance and excellent cyclic stability, it will facilitate to the purification and separation of oxidation products and have potential application in the fine chemical industry.

Cyclohexene selective oxidation mechanism of PANI@HA

In order to study the enhanced catalytic activity of PANI@HA/1

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M/2.04-HCl, cyclic voltammetry (CV) measurements of PANL@HA/1 M/2.04-H are made to investigate electron Transport and possible cyclohexene selective oxidation mechanism. It is notable three redox peaks of 0.23/-0.43 V, 0.53/0.07 V, 0.80/0.76V are appeared in the CV of PANI@HA/1 M/2.04-HCl and no anodic peak (black line) exists in HA (Fig. 9A). Among them, the 0.23/-0.43V redox couple is ascribed to the redox process between LB and EB, and the rest ones are respectively owing to quinone intermediates and the redox



Fig. 9 CV of the fabricated PANI@HA (20 mg) with 50 mV•s⁻¹ scan rate in 2.5 mL 1.0 M H₂SO₄ solution (A) and in 2.5 mL 30% H₂O₂ solution (B): a) HA, b) PANI@HA/1 M/2.04-H₃PO₄, c) PANI@HA/1 M/2.04-HNO₃, d) PANI@HA/1 M/2.04-H₂SO₄ and e) PANI@HA/1 M/2.04-HCl.

potential of PANI@HA/1 M/2.04-HCl has shifted respectively 56, 5, reaction of EB and PB.⁴⁶ The CV of PANI@HA/1 M/2.04-H₃PO₄, PANI@HA/1 M/2.04-HNO₃ and PANI@HA/1 M/2.04-H₂SO₄ also demonstrate three redox peaks, but differ in the potential and current. By a closer comparison of the curves, the first anodic peak 29 mV from that of PANI@HA/1 M/2.04-H₃PO₄, PANI@HA/1 M/2.04-H₁NO₃ and PANI@HA/1 M/2.04-H₃PO₄, and while the second and the third peak potential have at least, respectively, shifted 26 mV and 15 mV from those of PANI@HA/1 M/2.04-H (H=H₃PO₄, HNO₃ and H₂SO₄). Besides, the anodic peak current of PANI@HA/1 M/2.04-HCl is maximum among the PANI@HA/1 M/2.04-H SAMI@HA/1 M/2.04-HCl > PANI@HA/1 M/2.04-H₂SO₄ > PANI@HA/1 M/2.04-HNO₃ > PANI@HA/1 M/2.04-H₃PO₄, which is in agreement on the cyclohexene catalytic activity/doping degree order of PANI@HA/1 M/2.04-H.

The shifts of anodic peak potential and the highest peak currents indicate that PANI@HA/1 M/2.04-HCl has a favourable electrical conductivity, which can be ascribed to high doping degree, surface area and electron transfer of the nanocomposite.^{30,47,48} The CV of PANI@HA/1 M/2.04-H confirms the transition of emeraldine salt (EB) to pernigraniline (PB) and leucoemeraldine (LB). As halloysite nanotube shows no demonstrable redox reactivity under the same testing potential range and PANI@HA/1 M/2.04-HCl shows the maximum anodic peak current, whereas PANI@HA/1 M/2.04-H₃PO₄ shows the minimum anodic peak current, the above results also manifest the doping acid in the fabrication can exert a demonstrable effect on the cyclohexene catalytic activity of PANI@HA/1 M/2.04-H.

Furthermore, electrocatalysis behaviors of PANI@HA/1 M/2.04-H for H_2O_2 decomposition by three-electrode electrochemical cell measurements are also investigated. The CV of PANI@HA/1 M/2.04-H fabricated under different doping acid with the same concentration of H_2O_2 is presented in Fig. 9B. We can observe obviously that the anodic peak current/reduction potential of PANI@HA/1 M/2.04-HCl are the highest among the PANI@HA/1 M/2.04-H samples, implying the electron transfer from EB to LB is more active than others.²⁵ In combination of no anodic peak in HA, we can conclude the catalytic decomposition of H_2O_2 is to a great extent dependent on the PANI@HA.

In light of the above results, the probable catalytic mechanism of cyclohexene by PANI@HA is proposed in Scheme 1: at first, H₂O₂ is chemical adsorbed onto the surface of PANI in PANI@HA, and then owing to the catalytic decomposition of PANI, molecular H_2O_2 is rapidly decomposed into water and the oxygen atom species to form active oxygen [O]. Finally, the active oxygen [O] would fleetly attack the double bond of cyclohexene to form epoxy cyclohexane (which will be further oxidated into 1,2-cyclohexanediol or other higher oxidation state products). From the relationship between reaction time and the selectivity to various oxidation product, it can be seen that the selectivity to 1,2-cyclohexandiol is over 83% throughout the whole reaction stage, indicating 1,2-cyclohexandiol is the main oxidation product even at a short reaction time, for example, 0.5 h, 83.90% selectivity to 1,2-cyclohexandiol (Fig. 5, Table S4). It also can be seen the selectivity to epoxy cyclohexane decreases with the reaction time increasing in the range of 0-12 h and finally stable to 0%, whereas the selectivity to 1,2-cyclohexandiol increases correspondingly. Considering the low selectivity to epoxy cyclohexane (5.54%) and high selectivity to 1,2-cyclohexandiol (83.9%) at 0.5 h reaction time, the oxidation process is that when the active oxygen [O] attack the double bond of cyclohexene, epoxy cyclohexane is firstly formed as the reaction intermediate, and then the reaction intermediate is quickly oxidated into 1,2cyclohexanediol.



Scheme 1 Proposed mechanism of selective oxidation of cyclohexene to 1,2cyclohexandiol with PANI@HA nanotubes as catalyst.

Conclusions

The PANI@HA nanotube has been successfully synthesized by the insitu chemical polymerization of aniline on the surface of halloysite nanotubes. PANI with various redox state and doping degree in PANI@HA nanotube can be achieved by merely adjusting the acidity and the doping acid in the fabrication. The PANI@HA fabricated with 2 M HCl as doping acid tuning the acidity at 1 M and 2.04 ANI/HA weight ratio (PANI@HA/1 M/2.04-HCl) demonstrates the maximum doping degree. The effect of doping acid, acidity and ANI/HA weight ratio in the synthesis of PANI@HA on the selective oxidation of cyclohexene are investigated in detail. The result shows PANI@HA/1 M/2.04-HCl exhibits the highest catalytic activity for the selective oxidation of cyclohexene. And the main oxidized product is 1,2cyclohexanediol (99.50% selectivity) with 98.17% conversion in solvent-free reaction system with H₂O₂ as oxidants. It turns out that cyclohexene catalytic oxidation activity is dependent on varieties of doping acid, acidity and ANI/HA weight ratio in the fabrication. And the optimal reaction condition is 20 mg catalyst, 2.5 mL H₂O₂, 70 °C and 24 h. Furthermore, PANI@HA/1 M/2.04-HCl demonstrates higher catalytic activity for the selective oxidation of 2,3-dimethyl-2butene and styrene to the corresponding 1,2-diol. In light of the CV result, a mechanism of cyclohexene selective oxidation attributed to reversible redox reaction of PANI in PANI@HA to catalytic decomposition of H₂O₂ is proposed. This findings not only indicates HA can act as an powerful substrate support to achieve nanostructure PANI@HA, which avoids the use of surfactant and simplifies the synthesis process of nanostructure PANI, but also PANI@HA can enhance cyclohexene oxidation and the selectivity to 1,2-cyclohexanediol. In combination of the solvent-free reaction system and environmentally friendly oxidant, this work may open a new path for the fabrication of polymer based green catalyst system with high performance.

Conflicts of interest

There are no conflicts to declare

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Enhanced solvent-free selective oxidation of cyclohexene to 1,2-cyclohexanediol was achieved by polyaniline@halloysite nanotubes with H_2O_2 as oxidant at 70°C.

Graphical Abstract

