

Amphiphilic Polyoxometalate-Paired Polymer Coated Fe₃O₄: Magnetically Recyclable Catalyst for Epoxidation of Bio-Derived Olefins with H₂O₂

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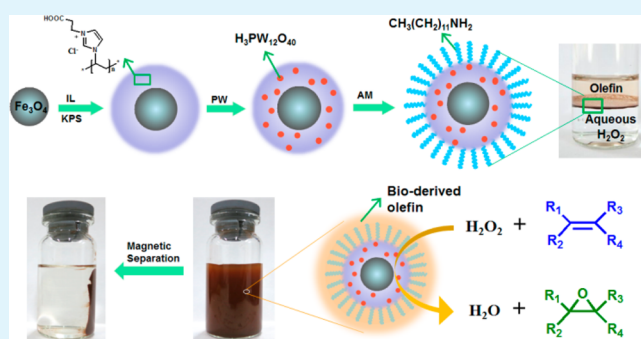
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S Supporting Information

ABSTRACT: An amphiphilic composite with magnetic Fe₃O₄ core and dodecylamine-modified polyoxometalate-paired poly(ionic liquid) shell was synthesized and characterized by ¹H NMR, thermogravimetric analysis (TGA), vibrating sample magnetometry (VSM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, UV–vis spectroscopy, X-ray diffraction (XRD), and digital microscopy. Catalytic tests for H₂O₂-based epoxidation of bioderived olefins, along with comparisons to various counterparts, demonstrate well that this newly designed catalyst exhibits high activity and selectivity, coupled with convenient magnetic recovery, and effective regeneration. The unique amphiphilic catalyst structure and the intramolecular charge transfer between amino groups and heteropolyanions are revealed to be responsible for the catalyst's excellent performances in epoxidation reactions.

KEYWORDS: amphiphilic composite, polyoxometalate, heterogeneous catalysis, poly(ionic liquid), epoxidation



INTRODUCTION

Epoxidized vegetable oils and their derivatives are a class of important bioderived oleochemicals widely applied as plasticizers and stabilizers for plastics, additives in lubricants, and components in cosmetics and pharmaceutical formulations.^{1–4} Industrially, they are generally produced via Prilezhaev reaction using in situ generated peroxyacids from oxidation of carboxylic acid with H₂O₂.^{5,6} Such a process, however, causes severe safety and corrosion problems relative to the peroxyacids. Therefore, great efforts have been devoted to the greener carboxylic acid-free H₂O₂-based epoxidation, for which many transition metal complexes of rhenium, molybdenum, titanium, tungsten, etc. are investigated as catalysts.^{7–11} Nevertheless, most of those systems are homogeneous and affected by poor selectivity.

Many polymeric materials have been developed as novel catalysts or catalyst supports due to their ease of work-up and product/catalyst separation.^{12–14} For example, various polymer-grafted organocatalysts, organometallic compounds, and metal nanoparticles are used as heterogeneous catalysts for organic syntheses.^{15–20} On the other hand, polyoxometalate (POMs) are well-known transition metal oxygen clusters and have been widely used in the catalytic field.^{21–24} Particularly, POMs proved to be highly efficient homogeneous catalysts for H₂O₂-based epoxidation of olefins.^{25,26} To recover POM catalysts, various recyclable catalytic systems have been

reported, including heterogeneous reactions over supported POM catalysts, biphasic systems with ionic liquids (ILs) as solvents, and phase transfer catalyzes involving quaternary ammonium organic cations,^{25,27–30} but they suffer from slow reaction rate,²⁸ leaching of active species,³⁰ or low catalyst recovery ratio.²⁵ Despite the versatile utilizations of organic polymers in developing efficient and recyclable catalytic systems,^{31–33} quite surprisingly, their use in POM-catalyzed epoxidation of bioderived olefins is still unexplored.

Poly(ionic liquids) (PILs), a subclass of polyelectrolytes in the field of polymer science, are emerging as a new research focus. The properties of PILs can be altered more easily and broadly by the counterion exchange.^{34–37} Indeed, POM-anions have been used as the counteranions for preparing task-specific ionic hybrids,³⁸ including our recent work on POM-paired hybrid catalysts for heterogeneous organic transformations.^{39–43} Unfortunately, our already made hybrids only provide very low catalytic activity and selectivity for epoxidation of bioderived olefins. We believe that the high viscosity and hydrophobicity of the unusual substrates of bioderived olefins challenges greatly a solid catalyst in activity due to the poor

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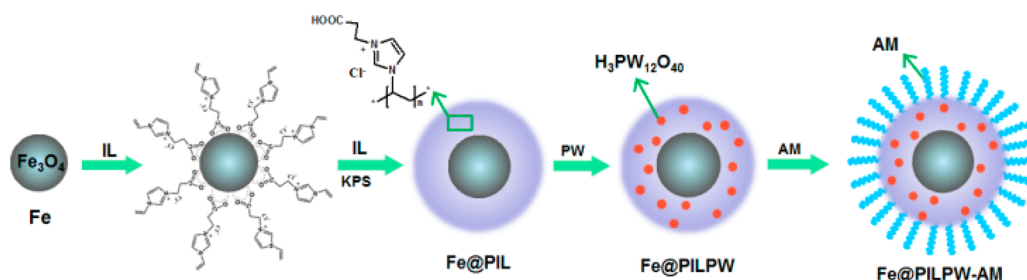


Figure 1. Schematic illustration of the synthetic procedure for the catalyst Fe@PILPW-AM.

mass transfer in the liquid–solid biphasic reaction medium. To solve this problem, constructing an amphiphilic substructure for a solid catalyst should be an effective strategy.

In this paper, we report a novel amphiphilic composite catalyst Fe@PILPW-AM with magnetic Fe₃O₄ core and dodecylamine-modified POM-paired PIL shell. It supplies a unique interfacial amphiphilic microenvironment for H₂O₂-based epoxidation of bioderived olefins, which would accelerate the mass transfer in the liquid–solid media. Moreover, the magnetic core makes it convenient to separate the catalyst by an external magnet. The catalyst is fully characterized by ¹H NMR (Supporting Information (SI), Figure S1), thermogravimetric analysis (TGA), vibrating sample magnetometry (VSM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, UV–vis spectroscopy, X-ray diffraction (XRD) analysis (SI, Figure S5), and digital microscopy. Catalytic tests for H₂O₂-based epoxidation of bioderived olefins, along with comparisons to various counterparts, demonstrate well that this newly designed catalyst exhibits high activity and selectivity, coupled with easy recovery and effective regeneration.

RESULTS AND DISCUSSION

Preparation and Characterization of Catalyst Fe@PILPW-AM. Fe@PILPW-AM was prepared according to the procedures illustrated in Figure 1. First, the COOH-functionalized IL is adsorbed on Fe₃O₄ surface via chemisorption interaction between the functional group –COOH and iron ion.^{44–47} Next, an aqueous phase precipitation polymerization of the vinyl imidazole IL was initiated by potassium peroxydisulfate (KPS) to form a PIL coating on Fe₃O₄ core. Afterward, PW was anion-exchanged into the PIL network to give Fe@PILPW which was further treated with dodecylamine (AM) to provide the final catalyst Fe@PILPW-AM.

The VSM curves for Fe@PILPW-AM showed that its saturation magnetization value was 30 emu/g without the observation of hysteresis curves, indicating the typical superparamagnetic behavior (Figure 2). The TGA patterns for Fe/PIL and Fe@PILPW (Figure 3) showed the drastic weight loss of nearly 70% and 20% for the organic PIL, respectively, from which the content of PW in Fe/PILPW is estimated as ca. 71 wt %, demonstrating a high POM loading for the catalyst.

Figure 4 presents the TEM images for the evolution of catalyst assemblies. Nanoparticles with small size of 20–30 nm were clearly seen for the employed Fe₃O₄ (Figure 4a), and after polymerization treatment on Fe₃O₄ surface, a thick layer of PIL appeared for Fe@PIL (Figure 4b). In the image of Fe@PILPW (Figure 4c), the observed dark micelles indicate that the introduced PW has been uniformly dispersed in the PIL network.⁴⁸ For the final catalyst Fe@PILPW-AM, an obvious AM shell was formed around the composite (Figure 4d) due to

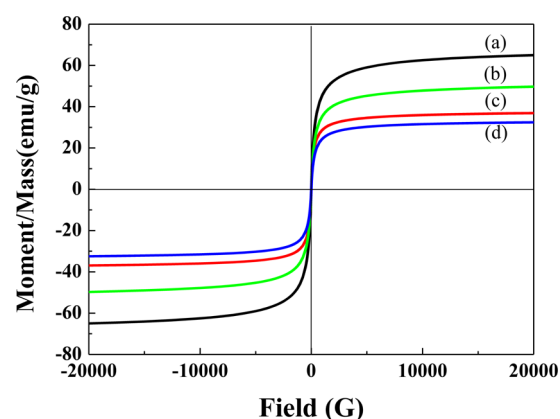


Figure 2. Magnetic hysteresis loops of (a) Fe₃O₄, (b) Fe@PILPW, (c) Fe@PIL, and (d) Fe@PILPW-AM.

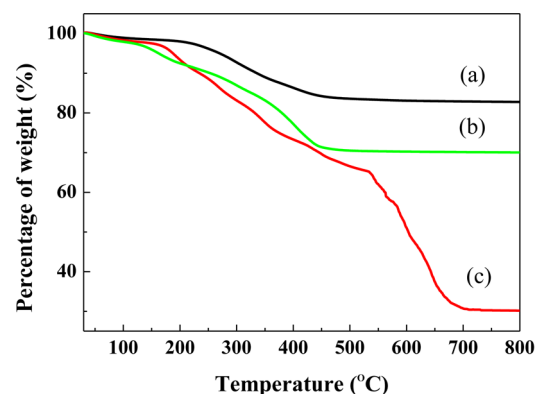


Figure 3. TG patterns of (a) Fe@PILPW, (b) Fe@PILPW-AM, and (c) Fe@PIL.

the AM surface modification for Fe@PILPW. The similar surface morphology change is reflected from the SEM images (Figure 4e,f). Also, the formation of the AM shell is confirmed by the TEM image for the Fe₃O₄-free analogue PILPW-AM (SI, Figure S3).

Catalytic Performance of Fe@PILPW-AM. Table 1 lists the catalytic performance of Fe@PILPW-AM for epoxidation of DL-limonene (Lim) with H₂O₂, together with comparisons with various control samples. Lim is one of the most common naturally occurring monoterpenes presented in citrus oil, and its epoxide product 1,2-epoxy-*p*-menth-8-ene (LimOx) is an important cycloaliphatic epoxide for producing copolymers, pharmaceuticals, fragrances, and food additives.^{49,50} As seen in entry 1 of Table 1, Fe@PILPW-AM offered a high conversion of Lim 97% with selectivity of 98% to LimOx in a solid–liquid heterogeneous catalysis system. In contrast, the parent POM

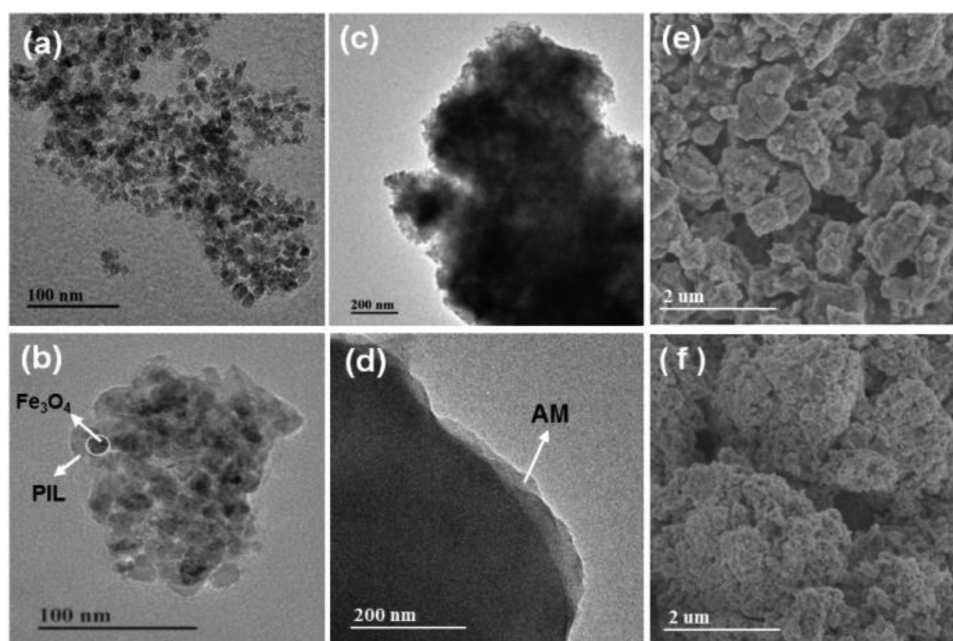
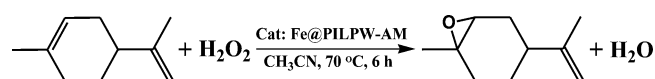


Figure 4. TEM images showing the evolution of catalyst assemblies: (a) Fe_3O_4 , (b) Fe@PIL , (c) Fe@PILPW , (d) Fe@PILPW-AM ; SEM images of (e) Fe@PILPW and (f) Fe@PILPW-AM .

Table 1. Catalytic Performances of Various Catalysts for Epoxidation of DL-Limonene with H_2O_2 ^a



entry	catalyst	phenomenon	con ^b (%)	sel ^c (%)
1	Fe@PILPW-AM	heterogeneous	97	98
2	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	homogeneous	15	85
3	Fe@PIL	heterogeneous	9	83
4	Fe@PILPW	heterogeneous	62	90
5	PILPW-AM	heterogeneous	100	96
6	PILPW	heterogeneous	71	85

^aReaction conditions: acetonitrile (10 mL), catalyst (0.03 mmol), DL-limonene (10 mmol), 30% H_2O_2 (4 mmol), 70 °C, 6 h. ^bConversion based on H_2O_2 . ^cSelectivity for 1,2-epoxy-*p*-menth-8-ene (by products: 1,2:8,9-diepoxy-*p*-menthane and 1,2-ene-*p*-menth-8,9-epoxy, detected by GC-MS).

$\text{H}_3\text{PW}_{12}\text{O}_{40}$ is a homogeneous catalyst, only giving a conversion of 15% with selectivity of 85% (Table 1, entry 2). The precursor Fe@PIL , though with the $-\text{COOH}$ functional group, showed the lowest conversion (Table 1, entry 3). For Fe@PILPW without the surface modification by AM, considerable conversion of 62% and selectivity of 90% were obtained (Table 1, entry 4), still far less active than Fe@PILPW-AM . This implies that the AM shell around the external surface of the composite Fe@PILPW plays an essential role in improving the overall activity.

Further, entries 5 and 6 of Table 1 show that the Fe_3O_4 -free hybrids PILPW and PILPW-AM display comparable catalytic performances to the core-bearing counterparts Fe@PILPW and Fe@PILPW-AM , respectively. Although no contribution to activity from the Fe_3O_4 core could be proposed from the above observation, it enables a magnetic recovery approach for the catalyst that is important for a heterogeneous reaction. Additionally, PILPW-AM gave much higher conversion (100%) and selectivity (96%) than those of PILPW ,

which again suggests a catalytically promotional role of AM for this reaction.

The catalytic reusability of Fe@PILPW-AM for epoxidation of Lim with H_2O_2 is shown in Figure 5. As illustrated in the

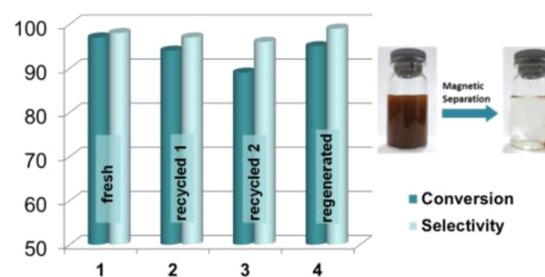
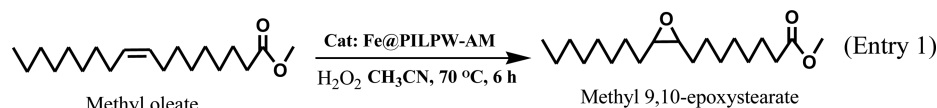


Figure 5. Catalyst recycling in epoxidation of Lim with H_2O_2 over Fe@PILPW-AM (inset: photos for magnetic separation of catalyst by external magnet).

inset of Figure 5, the catalyst Fe@PILPW-AM could be separated easily by an external magnet after reaction. The recycled catalyst in the third run showed conversion of 89% with selectivity of 96%, indicating a slow decrease in activity for the reused one. The result of ICP-AES analysis for the reacted filtrate showed that less than 0.9 wt % W of Fe@PILPW-AM has been leached into the reaction media. Moreover, the profile of IR spectrum for the recovered catalyst was very similar to that of the fresh one, but the intensities of the stretching vibration bands at 2848 and 2922 cm^{-1} for C–H in AM decreased to some extent (SI, Figure S4). This observation indicates that the slow decrease in catalytic activity over the recycled catalyst may associate with the partial leaching of AM groups during the reaction. Therefore, we retreated the third recovered catalyst with AM, and the thus regenerated catalyst almost resumed the initial activity of the fresh one, showing conversion of 95% and selectivity of 99%. This demonstrates a good regenerate capability for Fe@PILPW-AM .

Table 2. Results of Various Epoxidation Reactions over the Catalyst Fe@PILPW-AM^a

entry	substrate	t (h)	con ^b (%)	sel ^c (%)
1	methyl oleate	6	93	95
2	cyclooctene	4	100	99
3	cyclohexene	4	94	97
4	1-hexene	6	77	100
5	1-octene	6	86	100
6	cis-3-hexene-1-alcohol	6	92	96

^aReaction conditions: acetonitrile (10 mL), catalyst (0.03 mmol), substrate (10 mmol), 30% H₂O₂ (4 mmol), 70 °C. ^bConversion based on H₂O₂. ^cSelectivity for the epoxide product; byproducts for entry 1: methyl 9-ol, 10-ol oleate; entry 2: 2-cycloocten-1-ol and 2-cycloocten-1-one; entry 3: 2-cyclohexen-1-ol and 2-cyclohexen-1-one; entry 6: 3,4-epoxyhexane-1-aldehyde.

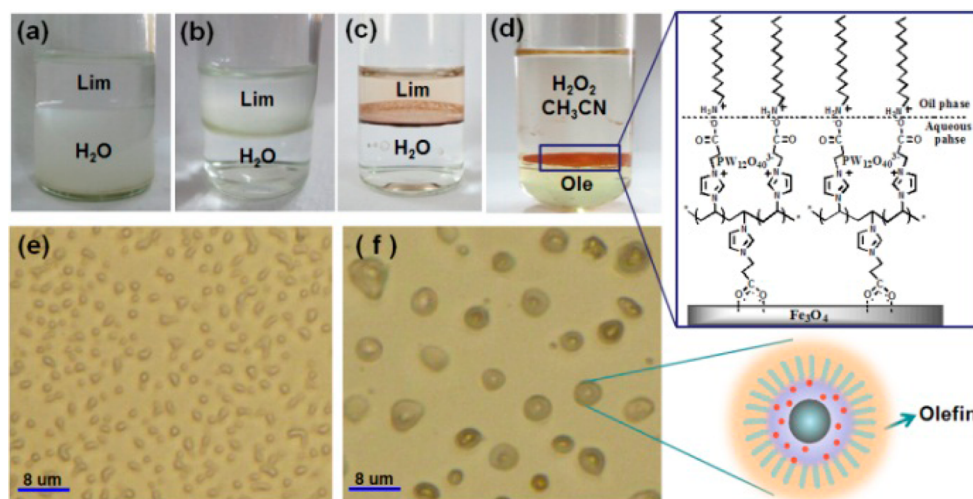


Figure 6. Illustrations of the catalysts in aqueous/Lim biphasic system: (a) PILPW suspended in aqueous layer, (b) PILPW-AM and (c) Fe@PILPW-AM appeared at the water/Lim interface, and (d) Fe@PILPW-AM appeared at the interface of the practical (H₂O₂ + CH₃CN)/Ole reaction system. Digital microscopy images of (e) Fe@PILPW and (f) Fe@PILPW-AM in the reaction system.

Methyl oleate (Ole) is another well-known bioderived olefin with high viscosity, and thereby, its epoxidation conversion is more challenging over a heterogeneous catalyst. When charged into the system of Ole with aqueous H₂O₂, Fe@PILPW-AM resulted in a liquid–liquid–solid triphase system due to immiscibility of Ole in the medium. To our delight, high conversion (93%) and selectivity (95%) were achieved once more over Fe@PILPW-AM (Table 2, entry 1). This finding confirms that the presently designed Fe@PILPW-AM is an excellent heterogeneous catalyst for epoxidation of bioderived olefins. Besides, it also exhibited high conversion and selectivity in epoxidations of other commonly seen olefins, such as cyclooctene, cyclohexene, 1-octene, 1-hexene, and cis-3-hexene-1-alcohol (Table 2, entries 2–6).

The catalytic activity and selectivity of Fe@PILPW-AM are much higher than those of the previously reported heterogeneous catalysts, such as SBA-15 supported peroxophosphotungstate,²⁹ alumina-supported group VI metal oxide,⁵¹ and “tetrakis” phosphotungstate,⁵² as well as the homogeneous molybdenum complex.⁷ It should be mentioned that, for epoxidations of conventional olefins like cyclohexene, base additives (KOH, NaHCO₃, imidazole, etc.) are usually added into reaction media aiming to get high conversion and selectivity.^{53–55} In contrast, our new catalyst provides high

conversion and selectivity without the aid of any additives. Noticeably, the mesoporous silica-grafted titanocene dichloride catalyst is a good heterogeneous catalyst for epoxidation of Ole with conversion of 96% and selectivity of 95%,^{2,8} comparable to our catalyst, but it takes a longer reaction time, 24 h. Clearly, the advantages of this work are higher catalytic efficiency with a shorter time, 6 h, and easier catalyst recovery.

Understanding of the Catalytic Behavior of Fe@PILPW-AM. The dispersion properties of the catalysts in water/oil biphasic media are examined and shown in Figure 6. The hybrid PILPW was found to highly disperse in the aqueous layer of water/Lim biphasic system (Figure 6a), due to the hydrophilic nature of the 3-propionic acid-1-vinylimidazolium moiety of PIL. Interestingly, after the treatment of AM on the external surface of PILPW, assembly of the hybrid PILPW-AM at the water/Lim boundary was observed (Figure 6b) because of the spontaneous change in the hydrophobic long carbon chain of AM interfacially oriented on the hydrophilic PAVM layer. The final catalyst Fe@PILPW-AM showed a similar assembling behavior in the water/Lim boundary (Figure 6c). For the (H₂O₂ + CH₃CN)/Ole mixture, imitating the practical epoxidation of Ole, a thin film of Fe@PILPW-AM was also assembled at the interface of the aqueous and oil phases (Figure

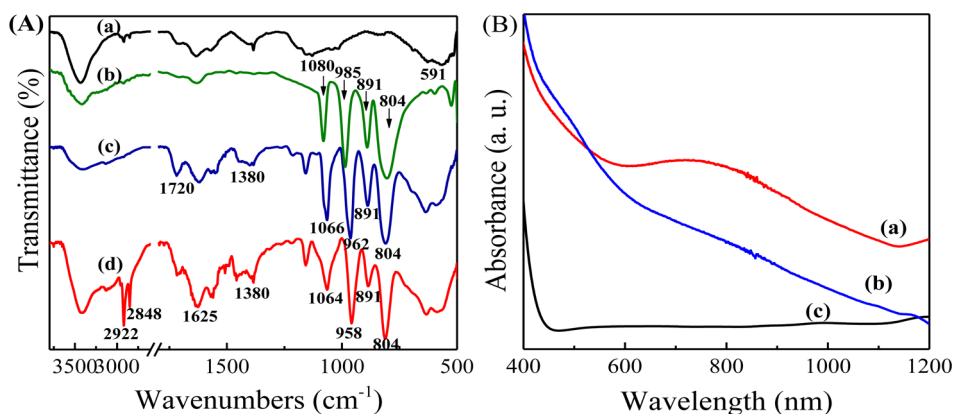


Figure 7. (A) FT-IR spectra of (a) Fe@PIL, (b) H₃PW₁₂O₄₀, (c) Fe@PIL-PW, and (d) Fe@PILPW-AM. (B) UV-vis spectra of (a) PILPW-AM, (b) PILPW, and (c) H₃PW₁₂O₄₀.

6d). These phenomena demonstrate well the amphiphilic nature of PILPW-AM.

More insight into the amphiphilic behaviors of the catalysts in a practical epoxidation reaction solution of Lim is obtained with digital microscopy. In striking contrast to the image for Fe@PILPW (Figure 6e), the digital microscopy for Fe@PILPW-AM clearly revealed a uniform core/shell structure that is similar to a reverse micelle (Figure 6f). In this case, the shell of Fe@PILPW-AM is much thicker than that observed in TEM images. It is thus proposed that the amphiphilic catalyst structure should have supplied a unique microenvironment for the catalyst to involve both the hydrophobic olefin substrates and hydrogen peroxide molecules in aqueous phase, which allows PW in the bulk of the composite to give full play as catalytic centers. It is known that most solid-state heterogeneous catalysts have larger mass transfer resistance than homogeneous or phase-transfer catalysts, and constructing an amphiphilic structure for a solid is one of the most effective solutions to form highly reactive systems.^{56,57} We thus suggest that the excellent catalytic activity of Fe@PILPW-AM for epoxidation of bioderived olefins largely arises from its unique amphiphilic catalyst structure.

As seen above, the carefully designed amphiphilic catalyst structure favors liquid–solid heterogeneous epoxidations of bioderived olefins by accelerating the mass transfer. However, the appropriate electronic property of PW in the catalyst is a prerequisite for enhancing the epoxidation reactivity.⁵⁸ Intramolecular electronic behaviors for selected samples are shown in Figure 7. In the FT-IR spectra of Figure 7A, four IR bands assigned to Keggin structure appeared at 1080, 985, 891, and 804 cm⁻¹ for H₃PW₁₂O₄₀. For Fe@PILPW, the four Keggin peaks also appeared, with the simultaneous occurrence of the stretching vibrations of Fe–O (591 cm⁻¹) for Fe₃O₄ and the characteristic peaks for organic groups (1300–1800 cm⁻¹). However, two of the vibrations for Keggin structure at 1080 and 985 cm⁻¹ shifted to 1066 and 962 cm⁻¹, respectively, implying the distortion of the POM kegging framework, mostly due to the hydrogen bonding and intramolecular charge interaction between –COOH and terminal oxygen of PW.^{59–62} Fe@PILPW-AM presented strong stretching vibration peaks at 2848 and 2922 cm⁻¹ for C–H bands in AM, and the intensity of the band at 1625 cm⁻¹ assigned to the carboxylate –COO⁻ was remarkably enhanced, indicating that AM has been tethered into Fe@PILPW through electrostatic interaction between –COOH and –NH₂ groups. Further, the slight shift

of the bands at 1064 and 958 cm⁻¹ as compared with that of Fe@PILPW is ascribed to the increased hydrogen bonding and intramolecular charge interaction arising from the amino groups in AM.^{59–62} Additionally, in the UV-vis spectra of Figure 7B, the broad absorption band at 600–1000 nm is assigned to the intramolecular charge transfer from organic functional groups to PW anions.⁶³ PILPW-AM showed a stronger band in this area than that of PILPW, which consolidates the evidence for the increased intramolecular charge interactions between PW and amino groups. From the above spectral results, one can conclude that the redox property of PW in the catalyst should have been effectively turned by the intramolecular charge transfer from amino groups in AM, which is essential for the high activity of Fe@PILPW-AM catalyst. The similar electronic effect derived from amino groups has also been revealed in our early work.^{40,41}

CONCLUSIONS

In summary, magnetic Fe₃O₄ core, POM-paired ionic polymer, and surfactant AM have been used to fabricate a novel amphiphilic composite Fe@PILPW-AM that is proved to be a highly efficient heterogeneous catalyst for epoxidation of bioderived olefins with H₂O₂, plus the advantages of convenient recovery and effective regeneration. The amino-functionalized W species act as the active center for epoxidation reactions, while the amphiphilic catalyst structure acts as a “trapping agent” for both the hydrophobic olefin substrates and the H₂O₂ molecules in aqueous phase, and thus, the catalytic activity is largely promoted. Both high efficiency and convenient recycling of Fe@PILPW-AM in epoxidation reactions thoroughly reflect the rational and smart design strategy for the present catalyst, which might be a significant step toward the design of heterogeneous catalysts with integrated and enhanced properties for more catalytic processes.

EXPERIMENTAL SECTION

Reagents and Analysis. All chemicals were analytical grade and used as received. FT-IR spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs) in the 4000–400 cm⁻¹ region. ¹H NMR spectra were measured with a Bruker DPX 300 spectrometer at ambient temperature in D₂O using TMS as internal reference. Elemental analyses were performed on a CHN elemental analyzer (FlashEA 1112). Solid UV-vis spectra were measured with a PE Lambda 950 spectrometer, and BaSO₄ was used as an internal standard. XRD patterns were collected on the Bruker D8 Advance powder diffractometer using Ni-filtered Cu Kα radiation source at 40

kV and 20 mA, from 5° to 80° with a scan rate of 4°/min. TEM images were obtained with a JEOL JEM-2100 electron microscope operated at 200 Kv. TG analysis was carried out with a STA409 instrument in dry air at a heating rate of 10 °C/min. The epoxidation products were analyzed by gas chromatography–mass spectrometry (GC-MS, Trace DSQ) equipped with a capillary column (SE-5). Digital microscopy images were obtained on the VH-Z250R VHX digital microscope. Magnetization measurements were recorded at room temperature on a Lake Shore 7410 vibrating sample magnetometer (VSM). SEM images were performed on a HITACHI S-4800 field-emission scanning electron microscope. The amount of leached tungsten species in the filtrate was measured using a Jarrell-Ash1100 ICP-AES spectrometer.

Preparation of Catalysts. Synthesis of Carboxylic Acid Functionalized IL. [3-Propionic acid-1-vinylimidazolium]Cl/*N*-vinylimidazole (9.42 g, 0.10 mol) and 1-chloropropionic acid (0.10 mol) were dissolved in ethanol (50 mL) with stirring at 80 °C for 24 h. On completion, the white solid product was obtained after the removal of solvent and washing with acetonitrile (Yield: 92%). ¹H NMR (300 MHz, D₂O, TMS) (SI, Figure S1) δ (ppm) = 3.01 (t, 2H, –CH₂), 4.72 (t, 2H, –CH₂), 5.45 (d, 1H, –CH), 5.81 (d, 1H, –CH), 7.17 (m, 1H, –CH), 7.63 (s, 1H, –CH), 7.79 (s, 1H, –CH), 9.12 (s, 1H, –CH).

Synthesis of IL Modified Magnetic Nanoparticles. The Fe₃O₄ nanoparticle was synthesized by a chemical coprecipitation method of ferric and ferrous ions in alkali solution.^{64,65} 23.3 g of FeCl₃·6H₂O and 8.60 g of FeCl₂·4H₂O were dissolved in 500 mL of deionized water under nitrogen at room temperature; then, 100 mL of 25% NH₃·H₂O was added with vigorous stirring. After the color of the solution turned to black, the magnetite precipitates were separated by magnetic decantation and washed several times with deionized water. The fresh particle suspension with 1.0 g of Fe₃O₄ in 50 mL of deionized water was stirred with 1.5 g of the prepared [3-propionic acid-1-vinylimidazolium]Cl for 30 min to form IL modified Fe₃O₄ nanoparticle, and the particles were washed extensively with methanol and deionized water.

Synthesis of Fe@PILPW-AM. The magnetite Fe₃O₄@poly(ionic liquid) (Fe@PIL) was synthesized through precipitation polymerization. Typically, IL modified Fe₃O₄ (1 g) in 50 mL of deionized water was mixed with an aqueous solution (10 mL) of [3-propionic acid-1-vinylimidazolium]Cl (2 g) by mechanical stirring. After degassing with nitrogen for 30 min, the solution was heated up to 75 °C, and potassium peroxydisulfate (KPS) solution (0.05 g/mL, 2 mL) was injected to initiate the polymerization. After 24 h of reaction, the final products were collected using magnetic separation, washed with water, and finally redispersed in deionized water.

Fe@PILPW nanoparticles were prepared as follows: the aqueous solution containing 2 g of H₃PW₁₂O₄₀ (PW) was added to the above solution, followed by 5 h of stirring to allow the anion exchange of PW₁₂O₄₀³⁻ into the polymer network. The obtained Fe@PILPW particles were magnetically separated to remove the excess H₃PW₁₂O₄₀ and dried in a vacuum.

Fe@PILPW-AM nanoparticles were prepared as follows: Fe@PILPW particles (2 g) were redispersed in ethanol (60 mL); the ethanol solution (5 mL) of dodecylamine (AM, 0.4 g) was added to partly neutralize COOH groups to form carboxylate –COONH₃– inside the polymer network, followed by 12 h of stirring. The thus obtained solid catalyst Fe@PILPW-AM was magnetically separated and washed with ethanol for three times, followed by drying in a vacuum.

Preparation of Heteropolyanion-Based Ionic Hybrids. Poly(ionic liquid) (PIL) was prepared according to the literature.^{66,67} In detail, the obtained ionic liquid [3-propionic acid-1-vinylimidazolium]Cl (2 g) and azobis(isobutyronitrile) (AIBN) (0.05 g) were dissolved in methanol (10 mL) under nitrogen atmosphere, and the mixture was refluxed at 65 °C for 24 h with stirring. Then, the solvent was removed by distillation, and the residue was washed with THF to give a white solid. The obtained PIL (0.65 g, monomer molar quantity was 3.0 mmol) was dissolved in deionized water at room temperature with stirring; an aqueous solution of H₃PW₁₂O₄₀(PW) (2.88 g, 1.0 mmol)

was added to the solution of PIL, followed by the stirring of the mixture for 24 h. The white precipitate PILPW was filtered and washed with water for three times, followed by drying in a vacuum. The obtained PILPW (3 g) was redispersed in 30 mL of ethanol. Then, the ethanol solution (5 mL) of AM (0.6 g) was added, followed by 12 h of stirring. The thus obtained solid PILPW-AM was separated and washed with ethanol for three times, followed by drying in a vacuum.

Catalytic Test. DL-Limonene (10 mmol), CH₃CN (10 mL), and catalyst Fe@PILPW-AM (0.03 mmol) were added to a 25 mL flask. The reaction started after the addition of aqueous H₂O₂ (30 wt %, 4 mmol) at 70 °C within 10 min under vigorous stirring. After reaction, the product mixture was analyzed by gas chromatography–mass spectrometry (GC-MS). The concentration of H₂O₂ in the reacted mixture was determined by the titration with sodium thiosulfate (starch as the indicator) in the presence of potassium iodide, sulfuric acid, and ammonium molybdate. No remaining H₂O₂ was detected due to the self-decomposition of H₂O₂ accompanied with the oxidation of the alkene. Other alkene substrates were tested accordingly. For a three-run operation of the epoxidation of DL-limonene to test the catalytic stability of Fe@PILPW-AM, the catalyst was recovered by magnetic separation and directly used for the next run.

■ ASSOCIATED CONTENT

Supporting Information

Figure S1, the ¹H NMR spectra for carboxylic acid-functionalized IL; Figure S2, the TG patterns for PILPW and PILPW-AM; Figure S3, the SEM images of PILPW and PILPW-AM; Figures S4, FT-IR spectra for PILPW, PILPW-AM, Fe@PILPW-AM, and recovered Fe@PILPW-AM; Figure S5, the XRD patterns for H₃PW₁₂O₄₀, Fe₃O₄, Fe@PILPW-AM, and PILPW-AM. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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