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Dendritic Amphiphile Mediated One-Pot Preparation of 3D Pt Nanoparticles-Decorated PolyHIPE as a Durable and Well-Recyclable Catalyst

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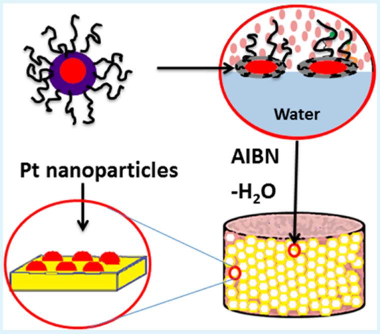
S *Supporting Information*

ABSTRACT: Straightforward organization of platinum nanoparticles (PtNPs) onto a macroscopic and robust material is described. PtNPs are in situ produced and stabilized by a dendritic amphiphile, where the latter consists of a hyperbranched polyethylenimine (PEI) as core and poly(styrene-co-2-ethylhexyl acrylate (P(St-EHA)) as shell. The resulting Pt@PEI@P(St-EHA), upon mixing with biphasic water and oil (a mixture of EHA and a dimethacrylate cross-linker in toluene), can self-assemble along the water/oil (W/O) interface and result in a stable emulsion. At W/O = 80/20 (volume ratio), a high internal phase emulsion (HIPE) forms and can be radically transformed into an open-cellular and elastic monolith termed Pt-polyHIPE, with PtNPs decorated on the surface. The Pt-polyHIPE is mechanically robust, and the cross-linking homogeneity by the dimethacrylate is responsible for the strength. The Pt-polyHIPE shows an active catalytic property, as evaluated by reduction of 4-nitrophenol. The material is conveniently and well recyclable, showing no decrease in catalytic activity at least within 20 cycles. Energy-dispersive X-ray spectra and thermogravimetric analysis also support sufficient retaining of the Pt species, where the multivalent and multiligand PEI should be responsible for this property.



KEYWORDS: *polyHIPE, dendritic amphiphile, platinum, recycle, supported catalyst, self-assembly*

1. INTRODUCTION

Noble-metal nanoparticles are well-known as excellent catalysts, but the recycle remains a general challenge.[1−5] The recycle is not only important for cost-effective chemical production but is also favorable to environmental protection and quality products. Support of these particles on a macroscopic and porous material such as polyHIPE[6−10] (high internal phase emulsion) and graphene-based material[11−17] is an alternative strategy. It is known that polyHIPE can be readily prepared at large scale and at any size.[18−21] A polyHIPE usually has interconnected pores and channels, which are large enough to allow permeation of gases and liquids and, thus, a functional polyHIPE may find applications in water remediation[22] and gas adsorption. Conventional as-made polyHIPEs are produced with the aid of small surfactants, but the surfactants populated on the surface of the polyHIPE are ready to run off and can poorly act as functional groups. Postmodification of a polyHIPE usually suffers from drawbacks such as the tedious synthesis arising from multistep functionalization of the preformed support and the inefficiency of heterogeneous reactions. The poor functionalization of polyHIPEs limits their application (e.g., inefficient adsorption and poor performance on metal supporting). Use of amphiphilic block copolymers in place of the small surfactants may directly bring about functional polyHIPEs, but a challenge remains.[23] In contrast, the use of a dendritic amphiphile in place of the small surfactants in a HIPE system can confer the surface of the resulting polyHIPE both functional and topological features at a microscopic scale. Very recently, we reported the first example that a dendritic amphiphile alone could lead to a functionalized polyHIPE in a one-pot manner.[22] With the finely tunable hydrophobicity, functionality, and topology of a dendritic amphiphile, it should be able to bring about additional benefits to a polyHIPE. It is known that a dendritic amphiphile can act as a multivalent and multiligand stabilizer to interact with a metal nanoparticle,[24−27] resulting in a more stable nanocomposite than that by small surfactants. Now, our concern is if dendritic amphiphiles with impregnated noble metal nanoparticles can still stabilize a HIPE system; then, organization of them at a macroscopic scale is possible via a polyHIPE route, and the unique feature of a dendritic amphiphile may bring about robust immobilization of a metal species.

Currently, most polyHIPEs suffer from poor mechanical strength, which significantly limits their applications. A typical polyHIPE is of porous structure (the volume fraction of the cellular voids makes up over 70% of the bulk material) and of low bulk density (around 0.1 g mL^{-1}), each contributing to the poor mechanical strength. Additionally, the hydrophobic chemical structure of the matrix, the inhomogeneity of cross-linking, and the small cellular size of a polyHIPE may

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contribute to the weak mechanical strength as well. The most extensively studied St/divinylbenzene (DVB)-based polyHIPE is a representative one known for brittle and chalky property. Much effort has been devoted to improve the mechanical strength, for example, using a living radical technique,[28] selection of a cross-linker,[29] employing special monomers,[30] addition of inorganic particles,[31] or using a miniemulsion template[32] is found favorable to a better strength. Additionally, decreasing the relative amount of a stabilizer in a HIPE recipe favored stronger mechanical strength but tended to result in a close-cell structure.[33] It was recommended that using an elastomeric monomer, such as EHA,[34−38] to build the matrix framework could alleviate the issue. However, it seems that the use of EHA has to be accompanied with reinforcing particles, or rigid comonomers, or else the resulting polyHIPE is labile to collapse and no longer retains the porous framework. Here, we show that dendritic amphiphiles impregnated with platinum nanoparticles (PtNPs) can act as a stabilizer to mediate an EHA-based HIPE system to directly lead to 3D PtNPs-decorated polyHIPE (Pt-polyHIPE). Additionally, without any additives or rigid comonomers, the EHA alone-based Pt-polyHIPE can be mechanically robust if an appropriate species of cross-linker is used at an appropriate amount in the recipe. The Pt-polyHIPE is a durable and well-recyclable catalyst.

2. EXPERIMENTAL SECTION

2.1. Materials. Hyperbranched polyethylenimine (PEI, M_n = 1×10^4, M_w/M_n = 2.5, degree of branch (DB) = 60%) and Span 80 (Sorbitane monooleate) were purchased from Aldrich. Divinylbenzene (DVB), K_2PtCl_4, *p*-nitrophenol (4-NP), and 2-ethylhexyl acrylate (EHA, 99%) were purchased from Aladdin (China). Styrene (St, 99%), azodiisobutyronitrile (AIBN), sodium borohydride (96%), methyl orange (MO), and toluene were purchased from SCRC (China). St and EHA were distilled under vacuum to remove the inhibitor and were stored at 4 °C until use. AIBN was recrystallized in ethanol and was stored at 4 °C until use. Polyethylene glycol dimethylacryalte (PEGMA, $CH_2 = C(CH_3)COO(CH_2CH_2O)_4H$) was purchased from TCI and was used as received. Phosphate buffer (pH 7.4, 0.02 M) was prepared by dissolution of 0.889 g $NaH_2PO_4{\cdot}2H_2O$ and 5.80 g $Na_2HPO_4{\cdot}12H_2O$ in deionized water and was diluted to 1 L.

2.2. Measurements. UV/vis spectra were recorded on a Mapada UV-6300 spectrophotometer (Shanghai Mapada Instruments Co., Ltd.). ^1H and ^{13}C NMR spectra were recorded on Bruker (400 MHz for ^1H and 100 MHz for ^{13}C) with tetramethylsilane as a reference. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC) using a Waters 2414, calibrated with standard poly(styrene); eluent: chloroform; flow rate: 1 mL/min; sample concentration: 10 mg/mL; injection volume: 200 μL; column temperature: 40 °C. Element analysis was conducted on a JY/T017-1996 elemental analyzer. The size of metal NPs was recorded using H-800 Omega transmission electronic microscopy (TEM) operating at an acceleration voltage of 200 kV on a carbon-coated copper grid. The X-ray powder diffraction (XRD) patterns were recorded at a scanning rate of 4° $\min^{-1}$ in the 2θ range of 20−80° using a Rigaku D/max2550VB3+/PC X-ray diffractometer with Cu Kα radiation (λ = 1.54178Å). Thermogravimetry analysis (TGA) was performed using a Netzsch STA 449 C thermogravimetric analyzer with air purging and a heating rate of 20 °C/min over the temperature range of ca. ambient to 1000 °C. Field emission scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were recorded on Magellan 400 (FEI Co. Ltd.). The porosity and surface area of polyHIPE were measured with a mercury intrusion porosimetry (MIP) of Pore Master 60-GT (Quantachrome Corp). Crush strengths were recorded on a SANS CMT5105 equipment at a compress rate of 5 mm/min, and samples were prepared in size of 20 mm (diameter) × 15 mm (height). For bristle samples whose strength is out of the measuring range of the equipment, a rough value was obtained by adding weight on the sample while observing the crush with a magnifying lens. Atomic force microscopy (AFM) was recorded on an SPA-300HV via a dynamic force mode, and the sample was prepared by dropping chloroform solution on fresh mica and by evaporating the solvent.

2.3.1. Synthesis of P(St-EHA). Typically, a solution of 4-glycidyloxy-2,2,6,6-tetramethyl- piperidine-1-oxyl[39,40] (0.6066 g, 2.657 mmol), St (18.77 g, 0.1802 mol), EHA (11.25 g, 0.061 mol), and AIBN (0.2182 g, 1.329 mmol) was prepared, was degassed by N_2 bubbling for 0.5 h, was sealed, and was heated at 75 °C for 2.5 h and then at 125 °C for 2 d. The mixture was cooled to 0 °C, was dissolved in chloroform, and was precipitated in excess ethanol. Purification was carried out by repeated dissolution/precipitation with chloroform/ethanol before drying in vacuum to afford a solid (19.07 g, 61.7%). M_n = 10580, M_w/M_n = 1.35 (GPC). ^1H NMR (400 MHz, $CDCl_3$, δ): 6.25−7.6 (m, 5 H, C_6H_5), 3.25−4.20 (m, 0.80 H, OCH_2), 0.5−0.95 (m, 2.6 H, CH_3), 0.95−2.5 (m, 7.0 H, CH_2, and CH). The molar ratio of St unit and EHA unit in the polymer can be obtained by comparing the signal intensity at 6.25−7.6 and 3.25−4.20 ppm, which was derived to be 2.9:1.0.

2.3.2. Synthesis of PEI@P(St-EHA). A solution of PEI (0.5 g, 11.6 mmol NH) and P(St-EHA) (13.542 g, 1.88 mmol) in chloroform (25 mL) was prepared and was subjected to stirring for 4 d. The mixture was dialyzed against chloroform (spectro/pro, molecular weight cutoff: 8000−14 000) to yield 13.82 g (98.4%) viscous liquid, equivalent to a grafting ratio of 13%. ^1H NMR (400 MHz, $CDCl_3$, δ): 6.25−7.6 (m, 5 H, C_6H_5), 3.25−4.20 (m, 0.95 H, OCH_2), 0.5−0.95 (m, 2.3 H, CH_3), 0.95−2.5 (m, 7.1 H, CH_2, CH, and NH). Element analysis: C 61.20%, H 7.622%, and N 0.66%.

2.3.3. Synthesis of Pt@PEI@P(St-EHA). A solution of PEI@P(St-EHA) (1.35 g) in chloroform (150 mL) was mixed with K_2PtCl_4 (0.0133 g, 0.032 mmol) in water (10 mL) and was allowed to stir for 4 h. An aqueous solution of $NaBH_4$ (51 mL, 0.06 M) was dropped in under rigorous stirring within 15 min, and the mixture was allowed to stir for another 4 h. The mixture was washed with deionized water (3 × 150 mL) at pH 10 (adjusted with aqueous NaOH), and the organic layer was separated and dried over anhydrous sodium sulfate. After removal of the inorganic salt and chloroform, a gray rubber (1.269 g, 84.6%) was obtained. ^1H NMR (400 MHz, $CDCl_3$, δ): 6.25−7.6 (m, 5 H, C_6H_5), 3.25−4.20 (m, 0.95 H, OCH_2), 0.5−0.95 (m, 2.3 H, CH_3), 0.95−2.5 (m, 7.1 H, CH_2, CH and NH).

2.3.4. Synthesis of Pt-PolyHIPE. Typically, to a homogeneous oil phase containing the stabilizer of Pt@PEI@P(St-EHA) (0.1 g), AIBN (0.005 g), EHA (0.48 mL), toluene (0.3 mL), and PEGMA (0.120 mL), water (4 mL, pH = 7.4, PB buffer) was dropped in under rigorous stirring. The mixture was stirred for 5 min after the water addition before the emulsion was transferred into a beakerlike vessel and was heated at 70 °C in an oil bath for 1 d. The resulting elastomer was sufficiently washed with ethanol to yield 0.34 g elastomer (50.5%).

In a control experiment, EHA and PEGMA were replaced by St and DVB, respectively, at equal volume, and St-based polyHIPE was similarly prepared. In another control experiment, the stabilizer of Pt@PEI@P(St-EHA) was further replaced by Span 80 at equal mass weight while the other conditions remained intact to prepare St-based polyHIPE.

2.3.5. Unimolecularity of PEI@P(St-EHA)..[39,41] To learn whether polymer PEI@P(St-EHA) exists as aggregate or as unimolecular inverted micelle (UIM), the dependence of encapsulating capacity on the concentration of the polymer was measured. A stock solution of aqueous MO was prepared; the polymer in chloroform at a diversity of concentrations (10^{-8}–10^{-4} M) was prepared and was mixed with equal volume of aqueous MO for phase equilibration. MO was charged in excess to ensure a saturated encapsulation. After a phase balance was reached, the oil layer was separated, and the amount of MO transferred to the oil was obtained from a UV/vis spectrometer. The encapsulating capacity was obtained by comparing the moles of MOs and polymers in the oil phase.

2.3.6. Catalytic Property of Pt-PolyHIPE. Typically, a slice of Pt-PolyHIPE monolith (0.015 g, equivalent to 0.4 mg Pt) was suspended in a N_2-bubbled aqueous solution containing 4-NP (3 mL, 0.06 mM) and $NaBH_4$ (0.077 g), and the mixture was charged in a cuvette and was monitored around 400 nm with a UV/vis spectrometer. The Pt-polyHIPE monolith was fished out, was packed in a filter paper, and was forced out the inside water before using in another cycle.

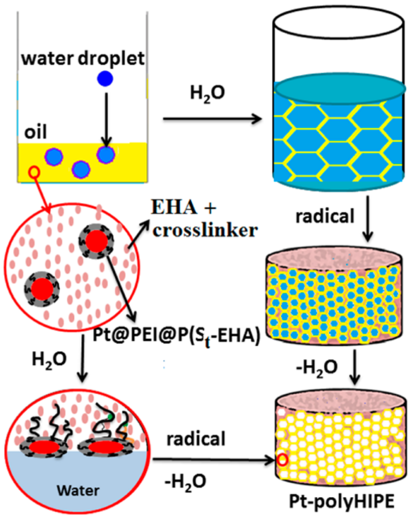
3. RESULTS AND DISCUSSION

3.1. Synthesis of Pt-polyHIPE. Generally speaking, if the disperse phase makes up over 74 volume % of the total system, the water/oil (W/O) emulsion is called a HIPE system. With a polymerizable oil phase, the emulsion can be transformed into a porous material termed polyHIPE. An appropriate stabilizer is critical to the success of a polyHIPE, where the surface is dictated by the stabilizer. Here, dendritic amphiphiles with impregnated PtNPs are used to replace conventional surfactants in a HIPE system to directly prepare a PtNPs-decorated polyHIPE (Pt-polyHIPE). The concept is outlined in Scheme 1.

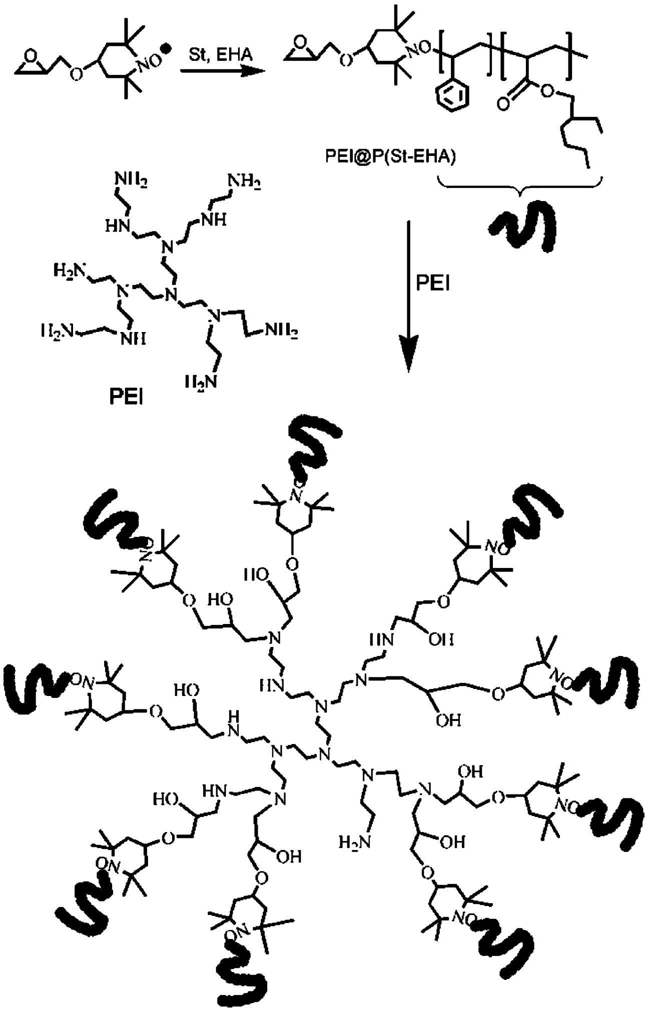
The chemical structure of a dendritic amphiphile is pivotal to this strategy. The synthesis of a PEI-based dendritic amphiphile is outlined in Scheme 2. A glycidyl end-capped copolymer of St and EHA (P(St-EHA)) is prepared by a nitroxide mediated living radical polymerization technique. The polymerization is well controlled, as shown by the narrow polydispersity of the molecular weight (M_w/M_n = 1.35 from GPC), agreeing with the living feature of a typical nitroxide mediated polymerization.[40] With the glycidyl group, P(St-EHA) can be readily attached to PEI via the well-known quasi click reaction between the glycidyl and the aliphatic amino groups, and the unreacted P(St-EHA) chains, if any, are removed by dialysis.

The emulsion-stabilizing ability of PEI@P(St-EHA) is dependent on the functional degree of PEI units by P(St-EHA). Under current conditions, if the functional degree is less than 8%, it is inefficient to stabilize the emulsion. Optimization shows that when the functional degree is over 10%, the emulsion is stable. One possible reason is that a high functional degree of PEI can alleviate the aggregation tendency of the reverse micellelike dendritic amphiphiles. Additionally, the functional degree determines the hydrophilic lipophilic balance of the stabilizer, which is important to the stability of a HIPE. AFM measurement shows that PEI@P(St-EHA) in chloroform mainly exists as rather uniform particles at 5×10^{-7} M (Figure 1). To learn if the polymer exists as UIM, the polymer is used

Scheme 1. Outline of the Preparation of Pt-polyHIPE



Scheme 2. Schematic Presentation of the Synthesis of PEI@P(St-EHA)



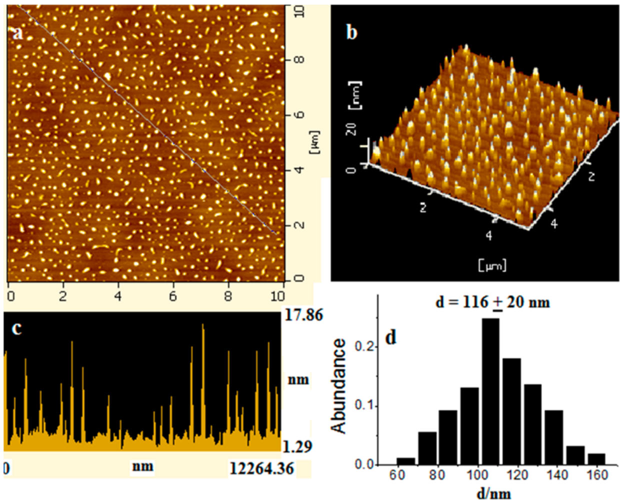


Figure 1. (a−c) AFM of PEI@P(St-EHA) and (d) statistics of the diameters of the pielike particles on mica. Conditions: a sample prepared by evaporation of a chloroform solution (5×10^{-7} M) on mica at room temperature.

as a host to encapsulate an anionic and chloroform-insoluble dye of MO. If the polymer exists as a UIM, the encapsulating capacity will remains intact.[39,41] Experimentally, PEI@P(St-EHA) in chloroform is found to transfer MO in water to the chloroform phase, with a capacity of 20 MOs per PEI@P(St-EHA) unless the concentration of polymer is above 1.6×10^{-5} M (Figure s1). This is the critical aggregation concentration of PEI@P(St-EHA). The PEI@P(St-EHA) is used as a multiligand to synthesize and stabilize PtNPs (Pt@PEI@P(St-EHA). The preparation is conducted via a water/chloroform biphasic system, where PEI@P(St-EHA) is dissolved in the chloroform and K_2PtCl_4 is dissolved in water. Under stirring, the anionic $PtCl_4^{2-}$ will migrate to the oil phase and be captured by the protonated PEI and be reduced to metallic PtNPs by the subsequent addition of aqueous $NaBH_4$. The formation of PtNPs is supported by the appearance of red-shifted absorbance in a UV/vis spectrum (Figure s2) and by XRD detection (Figure s3). As shown in Figure 2a, the size of the resulting PtNPs falls within 20−65 nm, with an average size at 32 nm. Because the size of the PEI core is usually within 5 nm,[42] the above fact suggests that one PtNP is stabilized by several PEI@P(St-EHA).

After loading of a PtNP in PEI@P(St-EHA)s, the emulsion-stabilizing ability of Pt@PEI@P(St-EHA) slightly decreases. This should arise from an enhanced hydrophobicity, and thus a very high functional degree of PEI by P(St-EHA) is not recommended for the stabilizer. Anyway, it is found that 10−20% functionalization of PEI by P(St-EHA) is appropriate for the stabilizing ability of Pt@PEI@P(St-EHA). The emulsion-stabilizing ability of Pt@PEI@P(St-EHA) should stem from its self-assembly along the W/O interface. To prove this, a conventional emulsion is prepared by dropping one droplet of water into an oil solution (1 mL, see Table 1 for the recipe but without AIBN) under rigorous stirring, and the conventional emulsion is found stable. An aliquot is drawn from the emulsion and is dropped on a carbon-coated copper grid, and the sample is dried in vacuum before TEM measurement. As shown in Figure 2b, the PtNPs are found mainly self-assembled along the W/O interface, while PtNPs are rarely detectable in the oil bulk. If much more water is added, the conventional emulsion is transformed into a HIPE system, which is not ready for TEM measurement, but assembly should not be influenced. Optimization of the emulsion stability leads to a typical recipe for the preparation of Pt-polyHIPE (Table 1). With this recipe, a porous and elastic Pt-polyHIPE can be readily obtained. Experimentally, if the cross-linker of PGDMA is at lower dosage, the porous structure tends to collapse, while a lower dosage of Pt@PEI@P(St-EHA) tends to result in a close-cell structure.

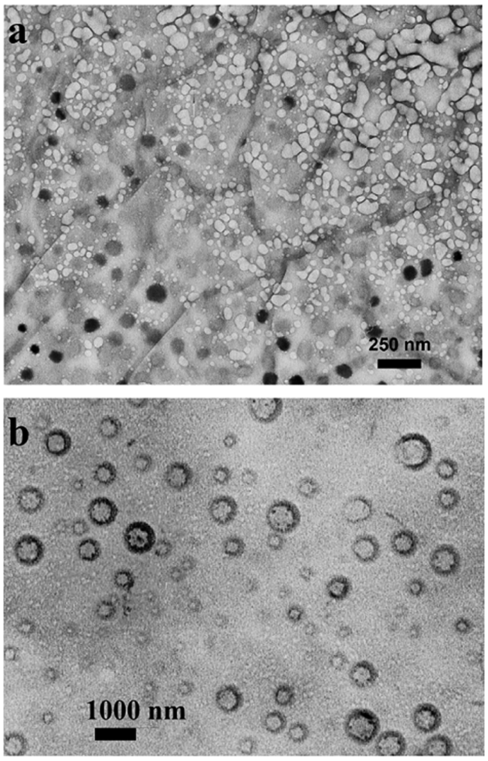


Figure 2. TEM micrograph of (a) Pt@PEI@P(St-EHA) particles and (b) their assembly along the W/O interface.

Table 1. Typical Recipe for the Preparation of Pt-polyHIPE

organic phase (1 mL)	EHA (monomer)	0.48 mL
	PEGMA (cross-linker)	0.12 mL
	toluene	0.30 mL
	Pt@PEI@P(St-EHA)	0.10 g
	AIBN	5.0 mg
aqueous phase (4 mL)	H_2O (PB buffer)	4.0 mL
	pH 7.4	

SEM detection suggests that the resulting Pt-polyHIPE is porous with the pores interconnected, as shown in Figure 3a. This conclusion is further supported by MIP measurement (Figure s4), from which a surface area as large as 5.64 $m^2\ g^{-1}$ is derived and a porosity of 81.4% is found. Diameters of most cells center around 75 μm, which should favor the permeation of liquids. Moreover, after sufficient immersing in aqueous rose Bengal (a red and anionic dye), the inside of the Pt-polyHIPE is found colored as well as that of the outer, also supporting the permeable structure. The formation of pores should be related with toluene and cross-linking in the system.

3.2. Mechanical Property of Pt-polyHIPE. The EHA-based Pt-polyHIPE is elastic and can be repeatedly compressed to at least one-third of the original height (Figure 3b) while the framework remains intact. One can find from the SEM

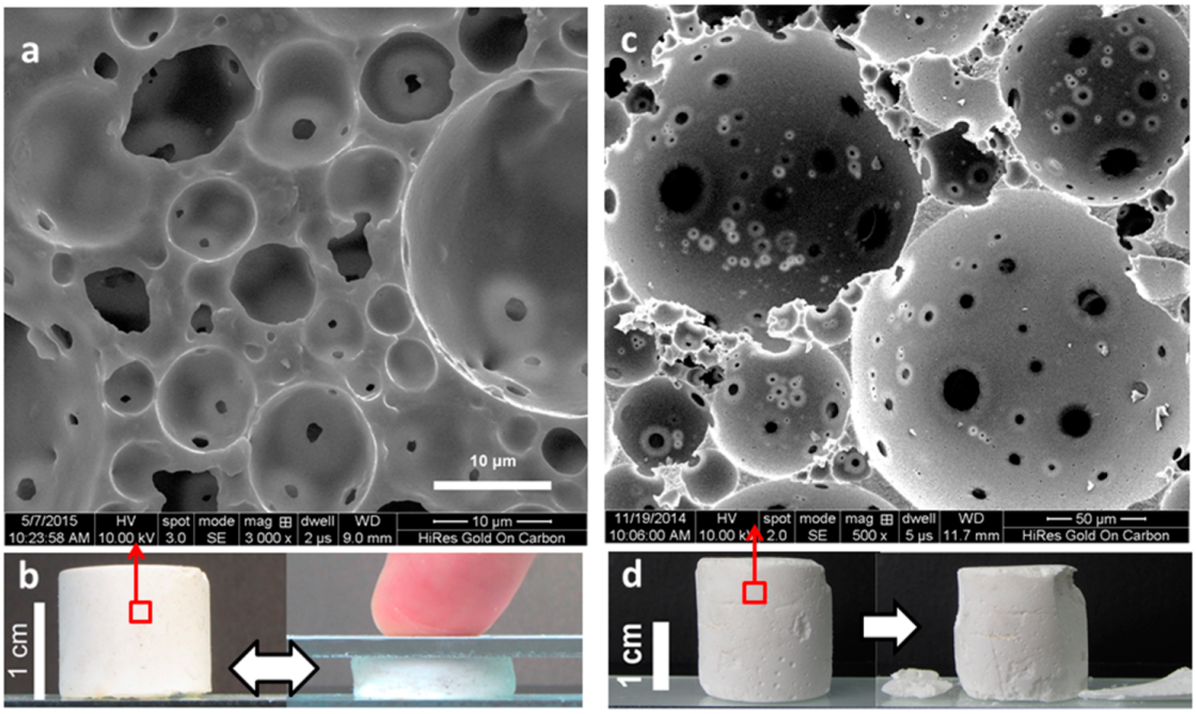


Figure 3. EHA/PGDMA-based Pt-polyHIPE is mechanically robust, as judged from (a) SEM micrograph (b) after repeated compression; while the St/DVB-based polyHIPE is (c) chalky and (d) brittle. Conditions: see the Experimental Section for sample preparation; the red region means part of the sample is subjected to SEM measurement.

micrograph that the surface of EHA-based Pt-polyHIPE is smooth, an indicator of strong mechanical strength, and no chalky debris is found after repeated compression (Figure 3b). This should be attributed to the elastic of the matrix, which results in high crush strength. To elucidate this behavior, the Pt@PEI@P(St-EHA) is similarly used to mediate the classic St/DVB system to prepare St-based Pt-polyHIPE, but the latter is found bristle, and chalky debris can be clearly seen on the surface (Figure 3c) of the as-made material. The appearance of the chalky debris implies that crush occurs upon slight scratch during preparation. In the case of St-based Pt-polyHIPE, crush occurs at very low strength of 0.146 MPa (out of the measuring range of the machine but can be roughly obtained by observing with a magnifying lens under weighting), while in the case of EHA-based Pt-polyHIPE, no chalky debris is found up to 19.9 MPa regardless of the fact that full elastic restore is no longer possible. The over 100-fold stronger crush strength of EHA-based Pt-polyHIPE is very beneficial to recycle the catalyst. It seems that Pt-polyHIPE mediated with Pt@PEI@P(St-EHA) is slightly different from that mediated with PEI@P(St-EHA) in terms of mechanical strengths (Figure 4).

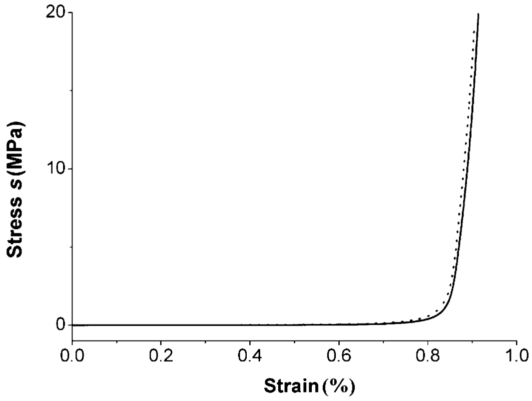


Figure 4. Compression strain−stress curve of EHA-based polyHIPE with (dash line) or without PtNPs (solid line).

The cross-linker of PEGMA is critical to the robust framework: at lower dosage of PEGMA, the structure is very soft and will collapse. Interestingly, when a rigid cross-linker of DVB is used in place of PEGMA at the same recipe, collapse still occurs. One very probable reason is inhomogenity of cross-linking by DVB: PEGMA has a polymerization activity close to that of EHA while DVB has a much higher activity than that of EHA. As a consequence, DVB is consumed at the initial stage and leads to inhomogeneous cross-linking.

3.3. Catalytic Property of the Pt-polyHIPE. The Pt-polyHIPE is used as a catalyst for the aqueous reduction of 4-NP to 4-aminophenol, a well-known test reaction for a catalyst.[43−46] A primary test shows that an induction period exists in the reaction, but if the reaction mixture is bubbled with nitrogen before reduction, the induction period is almost eliminated, suggesting that oxygen is responsible for the induction. UV/vis monitoring shows that the reduction finishes within 25−40 min (Figure s5). Regarding the catalytic mechanism, it is generally believed that both reactants of BH_4^- and 4-NP are adsorbed by the PtNP for electron transfer, followed by dissociation of the product (Langmuir−Hinshelwood model).[46] Accordingly, in case the reductant is in excess, the kinetics complies with a pseudo-first-order form:

$$-\ln(A_t/A_0) = k_{app}t \qquad (1)$$

where A_t and A_0 represent the absorbance at 400 nm at t and 0 moments, respectively, and k_{app} represents the apparent rate constant. Treatment of the kinetic data with eq 1 shows a linear relationship (Figure s5b), implying that the reaction follows a Langmuir−Hinshelwood model. The average rate constant is derived to be k_{app} = 3.5 × 10^{-3} s^{-1}, comparable to most reported noble metal nanoparticles.[47] Generally, the k should be normalized on the amount of Pt content for comparison.[46] The normalized k of our system is 3.69-fold higher in catalytic activity than PtNPs with a similar size (21 nm vs 20 nm) reported by other researchers.[48] The Pt-polyHIPE is repeatedly used as catalyst, and within the tested 20 cycles, no decrease of activity is noticeable (Figure 5), where the conversion is invariably over 97%.

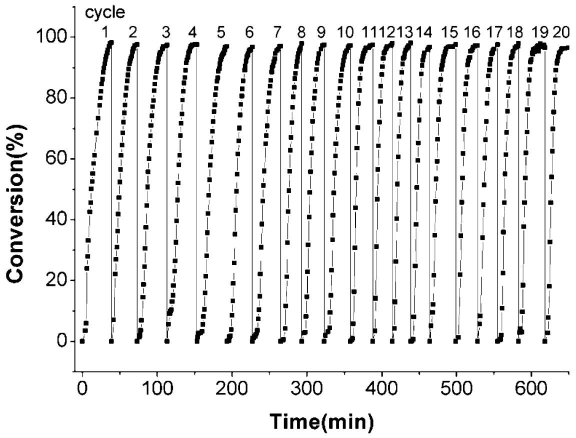


Figure 5. Pt-polyHIPE is repeatedly used as catalyst for the reduction of 4-NP to 4-aminophenol, as monitored around 400 nm with a UV/vis spectrometer. Conditions: see the Experimental Section.

EDX monitoring can provide certain information about the solid-supported catalyst. One slice of the Pt-polyHIPE after 20 catalytic cycles is subjected to EDX detection of the Pt species (Figure 6d), and the signal intensity shows little appreciable change as compared with that of the as-made one (Figure 6c), suggesting robust immobilization of the Pt species. Meanwhile, the signal distribution of Pt species remains rather homogeneous, suggesting that ripening of PtNPs is slight, if any. One can also find that the signal pattern of carbon is very different from that of the Pt species. This is understandable because carbon atoms are abundant in the matrix but are less on the surface, and thus, the carbon signal mainly outlines the framework, while the distribution of Pt species, on the contrary, mainly outlines the surface pattern. It can be clearly seen from the carbon signals (Figure 6a and c) that the porous framework remains regardless of repeated compression during catalytic cycles. The above facts imply that the catalyst should be able to be used far more than 20 cycles. Moreover, TGA detection shows that the incombustible part (attributed to Pt species) makes up 2.9% of the material (Figure s6, agreeing with that in feeding), supporting ignorable leakage of the immobilized Pt species.

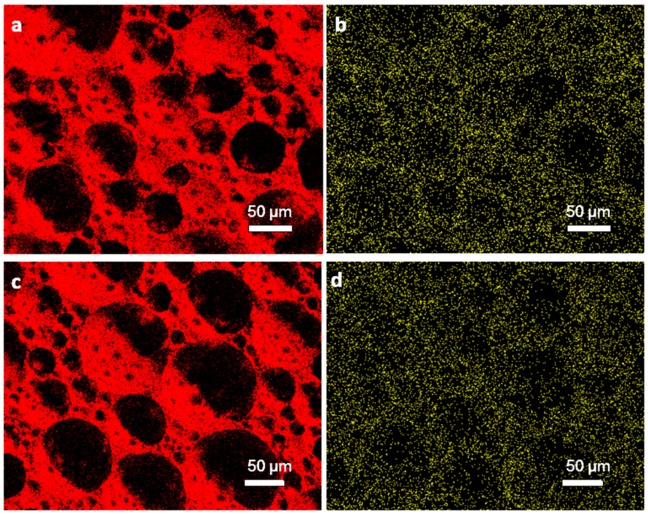


Figure 6. EDX signal of (a, c) carbon and (b, d) Pt of Pt-polyHIPE (a, b) before and (c, d) after 20 cycles using as a catalyst.

4. CONCLUSION

The dendritic amphiphile of PEI@P(St-EHA), even impregnated with PtNPs, retains certain amphiphilicity and can self-assemble along the interface of water-in-oil emulsion and, thus, can be used as a stabilizer of a HIPE system to directly prepare PtNPs-decorated polyHIPE. This strategy provides a straightforward route to organize nanoscale PtNPs onto the surface of a macroscopic and porous material. The resulting Pt-polyHIPE shows excellent catalytic property and can be facilely and repeatedly recycled. It is found that an appropriate cross-linker can lead to a homogeneous cross-linking; as a result, no extra additive or comonomer is necessary while a robust mechanical strength can be ensured. The highly recyclable property also should be related with the multivalent and multiligand property of the dendritic amphiphile toward the metal species.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b06283.

> UV/vis and XRD of PtNPs, unimolecularity of PEI@P(St-EHA), MIP, TGA analyses of Pt-polyHIPE, catalytic kinetics, and spectra (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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