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Poly(ionic liquid) Core Turns Hollow Silica Spheres into Amphiphilic Nanoreactor in Water

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ABSTRACT: The stressing environmental concerns push us to move traditional organic reactions toward an eco-friendly way. Replacing organic solvents by water seems to be a promising solution yet is very challenging. The main obstacle is the poor solubility of many hydrophobic substrates in water, leading to a restricted accessibility, thus inevitably ending up with low reac-



💶 0, 🕑 Hydrophobic@Hydrophilic Nanoreactor, 👄 Substrates, 🛛 Pd Nanoparticles, 🎱 Products

tion rates. To overcome this problem, we propose a hybrid micelle-like hydrophobic@hydrophilic nanoreactor formed by a poly(ionic liquid) (PIL) core and a mesoporous silica shell. This nanoreactor exhibited high activity (TOF up to 414 h^{-1} , 12.9 times of that for a corresponding silica catalyst) and selectivity (100%) in the oxidation of benzyl alcohol to benzaldehyde using water as solvent.

1. INTRODUCTION

Nanoreactors with tailor-made structure and judicious choice of compositions have shown superior performance in accelerating the reaction kinetics, enhancing the selectivity, and improving the recycling of the catalysts in many traditional organic solvents.¹⁻⁶ Environmental concerns require chemists to develop effective nanoreactors that can operate in more ecofriendly reaction conditions compared to organic solvents, such as solvent-free reactions, using water as solvent or at low energy consumption.⁷⁻⁸ Significant efforts have been made to fabricate nanoreactors that fulfill these requirements. Nevertheless, the relatively low activity of many nanoreactors, in most cases supported noble metal nanoparticles (MNPs), remains a key point to improve. The main issue lies in the poor accessibility of the hydrophobic substrates to the waterdispersible, catalytically active MNPs. Variable attempts have been conducted to tackle these challenges, for example, adding surfactants or amphiphilic agents into the aqueous medium, building emulsion systems, modifying the hydropho-bic/hydrophilic property of the catalyst supports.⁹⁻¹² Among these solutions, micelles and emulsion systems show excellent dispersity in water and high affinity towards hydrophobic substrates; However, these soft matter systems suffer from being liable to external environments and surfaces, and difficulties associated with product separation and reuse.¹³⁻¹⁴

Taking the advantages of heterogeneous catalysts, such as simple separation, high mechanical stability,¹⁵⁻¹⁷ recyclability, and being available to flow reactors in industry, constructing hybrid nanoreactors with a micelle-like amphiphilic feature and a stable framework seems to be a promising approach, yet

very challenging and rarely reported.¹⁸⁻²⁰ The demands for the synthesis of such a nanoreactor are multiple: first of all, it must contain components or "pockets" with hydrophilic and hydrophobic nature for aqueous dispersability and to house the diverse reactants; Secondly, the nanoreactor should possess component that can accommodate MNPs in a stable and highly dispersed fashion; And thirdly, the nanoreactor must be easily separable and recyclable. This reusability adds additional utility value to the catalyst.

Inspired by the micelle nanostructure, we present herein a hybrid nanoreactor composed of a hydrophobic core and a hydrophilic shell fabricated by poly(ionic liquid) (PIL) and mesoporous silica, respectively. The PIL nanoparticles will undergo a unique hydrophilic-to-hydrophobic transition upon processing, which facilitates the fabrication of the nanoreactor greatly. It shows significantly enhanced activity and high selectivity in the oxidation of primary aromatic alcohols to the corresponding aldehydes in water, using molecular oxygen as the oxidizing agent at mild temperature (65 °C) and pressure (2 atm).

The general synthetic scheme and the corresponding electron microscopy images are shown in Figure 1. The synthesis started with PIL nanospheres (~56 nm in diameter, see SI for synthetic approach) with a distinctive multilamellar centric vesicular nanostructure (Figure 1B), consisting of multiple hydrophilic and hydrophobic nanodomains, as reported previously.²¹⁻²⁴ The chemical structure is depicted in Figure 1A and Scheme S1. In our initial attempts, several polymer systems were considered as the core component, such as polymer latexes prepared via emulsion polymerization and microgels

from poly(N-isopropylacrylamide).²⁵ Due to their very favorable properties, finally PIL nanospheres were chosen. PILs are the polymerized products of ionic liquids,²⁶⁻³¹ prepared here via dispersion polymerization of vinylimidazolium ionic liquid monomers with long alkyl chains. They are well dispersible in water, and can stabilize MNPs in their polar domains; However, upon environmental change, they will sporadically undergo

structural rearrangement and turn hydrophobic,³² and no longer dispersible in water.³³ In addition, the ionic nature enables the PIL to complex metal ions and locate the derived catalytically active MNPs around the reactor core. All these structural features are beneficial to the functional nanostructure design.



Figure 1. Schematic illustration of the synthetic route to the PIL@SiO₂–Pd nanoreactor and the corresponding TEM images at each step. (A) Chemical structure of PIL (x denotes Br or dicyanamide anion), (B) PIL nanospheres, (C) after coating a layer of mesoporous silica via using micelles formed by CTAB as template, (D) the formation of PIL@SiO₂ nanostructure and (E) the incorporation of Pd NPs in the PIL core (with CTAB residues inside the mesopores of silica shell). Inset in (B) is a cryo-TEM image. Scale bar in inset in (B) and (E) is 20 nm.

2. EXPERIMENTAL SECTION

PIL nanospheres. PIL nanospheres (56 nm and 70 nm respectively) were made by a previously reported single step precipitation polymerization in aqueous solutions.³⁴

Synthesis of PIL@SiO₂ nanospheres. In a typical procedure, 1.5 mL PIL dispersion solution (50 g/L, water) was added into a mixture of 40 mL of H_2O , 30 mL EtOH, containing CTAB (0.15 g) and NH_3 • H_2O (0.05 mL, 28 wt%). After ultrasonication for 15 min, the mixture was put into an oil bath of 38 °C. Then TEOS (0.2 mL) was added under vigorous stirring, and the mixture was kept at 38 °C for 24 h. Then the mixture was centrifuged and washed with water and ethanol for several times and dried at room temperature.

 $PIL@SiO_2$ nanospheres with different shell thickness (10, 13 and 20 nm) and sizes (78, 102 and 112 nm) were achieved through a similar way by using a larger amount of TEOS (0.4, 0.5 and 1.0 mL) and PIL nanospheres with different sizes as precursors (56, 70 and 70 nm respectively).

Synthesis of PIL@SiO₂-Pd catalyst. Incorporation of Pd NPs into the PIL part as the nanoreactor core: The Pd NPs were incorporated through an anion exchange method (and a partial complexing effect of the Pd ions with the charged PIL chains). A Pd(NO₃)₂ solution (5 mL, 1 mg/mL, H₂O) was added dropwise into a aqueous dispersion of PIL@SiO₂ nanospheres (40 mL, 15 mg/mL, H₂O) under vigorous stirring. After 10 min, the liquid phase was removed by centrifugation. The gray solid was further washed with water for several times to remove free salts. The solid was redispersed in water (20 mL) with the assistance of ultrasonic, in which NaBH₄ solution (2 mL, 5 mol/L) was added quickly. The solution was kept in ultrasonic bath for another 5 min, before the liquid phase was removed by centrifugation. The gray solid was further washed with water and ethanol for several times, and dried under high vacuum till constant weight.

Synthesis of MCM41-Pd catalyst. The synthesis of MCM41 silica nanospheres were according to a literature method.¹ The MCM41-Pd catalyst was made through an immersion and reduction method as follows: 1 g MCM41 silica nanospheres were immersed into 30 mL ethanol solu-

tion containing $Pd(NO_3)_2$ (35 mg). After ultrasonic treatment for 20 min, the solution was stirred for 12 h at room temperature. Ethanol was then removed by rotation evaporation at room temperature. The obtained solids were reduced using NaBH₄ solution, similar to the synthesis of PIL@SiO₂-Pd catalyst.

Synthesis of PIL-Pd catalyst. The PIL-Pd catalyst was synthesized by adding a Pd(NO₃)₂ solution (8 mL, 1 mg/mL, H₂O) dropwise into a dispersion of PIL nanospheres (10 mL, 50 g/L) under stirring. After stirring for 1 h, the transparent colloid solution turned into turbid, due to the deposition of the PIL nanospheres. Gray solid polymeric product was obtained after freeze-drying of the mixture. It cannot be re-dispersed in water anymore. Wash the product with water, until colorless solution was obtained. The solid was reduced by NaBH₄ solution (10 mL, 2 mol/L), then removed from the liquid phase, washed with water for several times, and dried under vacuum.

Catalytic Tests. In a typical oxidation, 0.5 mmol of substrate and 0.0048 mmol of Pd catalysts (calculated by weight) and 1.3 mL of H₂O were added into a 20 mL Schlenk tube, which was fitted with a magnetic stirrer and an oxygen balloon. The reaction was performed at 65 °C in an oil bath with magnetic stirring (stirring rate: 900 r.p.m.) for a given time. When the reaction was finished, the liquid phase of the reaction mixture was collected by filtration. Then the liquid mixture was extracted by CH₂Cl₂ for 3 times, and the mixture of CH₂Cl₂ was dried with anhydrous Na₂SO₄ for 2 h, and used for GC–MS analysis. The oven temperature of GC was programed increasing to 300 °C.

For the recycling test, all the solids were collected by centrifugation after reaction. The residual catalyst was washed with water for several times and used directly for the next catalytic reaction. The reaction time for the third and fourth recycling is 10 h.

3. RESULTS AND DISCUSSION

The PIL nanospheres were then coated by a thin layer of mesoporous silica through the assistance of surfactant cetyltrime-thylammonium bromide (CTAB, which can form

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micelles in water and act as templates for mesopores, as shown in Figure 1) in basic solution.³⁵ The inorganic shell acts as an "exoskeleton" and provides high mechanical/chemical stability and hydrophilic nature to the nanoreactor, while the residual CTAB aggregates inside the mesopores play double roles, *i.e.* preventing the diffusion of PIL chains out of the silica shell and meanwhile assisting the transmission of hydrophobic molecules from water to the hydrophobic PIL core, similar to the solubilization effect of micelles in water. The details will be discussed later in the surface nature investigation part. The transmission electron microscopy (TEM) image of the obtained PIL@SiO₂ nanosphere is shown in Figure 1C. Solid nanospheres with an average size of 66 nm (as determined from TEM characterization) were obtained. This defines an average thickness of the silica shell to be 4-5 nm. Interestingly, small irregular inner voids (indicated by white arrows) are already visible at this stage in these PIL nanospheres, indicating the inner PIL core starts the structural rearrangement, induced by the silica shell. Upon prolonging the reaction time to 24 h, nanospheres with a shrunken hydrophobic hollow PIL core and a hydrophilic mesoporous silica jacket were obtained (Figure 1D).



Figure 2. TEM images of $PIL@SiO_2$ nanospheres with different sizes and shell thickness. The size and shell thickness are: 78 and 10 nm (A, D), 102 and 13 nm (B, E) and 112 and 20 nm (C, F), respectively. The scale bar in D-F is 10 nm.

A probable explanation for this structural rearrangement phenomenon is expected to stem from the uniquely structured PIL nanospheres, bearing a multilamellar centric vesicular morphology, as reported in Figure 1B and our previous work.²¹ Such nanostructure is constructed by multiple alternating hydrophilic (the charged polymer backbone part) and hydrophobic (the long alkyl side chain part) nanodomains, similar to a multilayer liposome. This PIL polymer is intrinsically hydrophobic due to the long alkyl chain and insoluble in water. However, their nanospheres are well-dispersed in water due to the preferential organization of the charged ionic backbone on outer ring, which provides electrostatic repulsion. Upon external environmental variation, such as silica coating, the contact of the hydrophilic outer surface with water is replaced by silica-PIL interface. To fit the new environment, the PIL chains started rearrangement to rebalance its surface tension, which initiated a structural evolution. This is the phenomenon of the self-adaptive ability of PIL nanospheres under confinement in silica.³⁶

The dimension and shell thickness of the PIL@SiO₂ are easily tunable by changing the size of the used PIL nanosphere templates and the amount of silica precursor (TEOS) added for the silica shell formation (Figure 2). PIL@SiO₂ nanospheres with larger sizes (78, 102 and 112 nm) and thicker shells (10, 13 and 20 nm) were also made and visualized in Figure 2 (for experimental details, see SI). From the TEM images it is clear that all these nanospheres contain a PIL core and a mesoporous silica shell with radial cylindrical mesopores (~2 nm in diameter), which provide the shortest way for mass transport across the silica shell.

It was demonstrated previously that PILs are excellent supports and stabilizers for noble MNPs.^{37,40} The complexing ability (also partially the anion exchange) of the PIL was used in our study to bind Pd ions onto the surface of PIL nano-spheres in the hollow silica, which were subsequently reduced by NaBH₄ to generate Pd NPs.^{41,42} As shown in Figure 1E, the Pd NPs are mainly located around the PIL core of the nano-reacotor, with uniform size (~2 nm in diameter) and are highly dispersed (denoted as PIL@SiO₂-Pd).

The catalytic performance of the fabricated PIL@SiO₂-Pd nanoreactor was investigated by a model reaction, the selective oxidation of primary aromatic alcohols to the corresponding aldehydes in water. To illustrate the advantages of our nanoreactor design, two additional catalysts were synthesized and adopted as control experiments: a reference mesoporous silica material (MCM41 particles with pore size 2.4 nm) and PIL nanospheres (without silica shell) loaded with Pd NPs (denoted as MCM41-Pd and PIL-Pd, respectively). Their TEM images are displayed in Figure S1. The MCM41-Pd catalyst showed a spherical mesoporous nanostructure (~100 nm in diameter) with Pd NPs (3-10 nm) deposited on the sphere surface (due to its small pore size). The PIL-Pd is composed of aggregated PIL spheres with Pd NPs of 2-4 nm.

The nitrogen sorption isotherms of MCM41-Pd and PIL@SiO₂-Pd display typical type-IV isotherms with a capillary condensation in the relative pressure range P/P_0 of 0.4-0.6 and 0.4-0.9, respectively (Figure S2). The Brunauer-Emmett-Teller (BET) specific surface area for MCM41-Pd is 542 m² g⁻ ¹. In comparison, the PIL-Pd as a soft matter structure is poorly porous (18 m² g⁻¹). The PIL@SiO₂-Pd bears a medium BET surface area of 110 m² g⁻¹ (Table S1), underlining the combination of the two sides as a building principle. According to Density Functional Theory (DFT) method, MCM41-Pd and PIL@SiO₂-Pd showed peaks at 2-3 nm in their pore size distribution curves, which correspond to the mesopores in the silica nanospheres (for MCM41-Pd) or the shells (for PIL@SiO₂-Pd), respectively. These results are also in good agreement with the TEM characterization. The chemical composition of these three catalysts was verified by Fourier transform infrared (FTIR) spectroscopy, as shown in Figure S3.

In the next step, the surface nature and hydrophobic/hydrophilic behavior of these three catalysts were studied. The surface character was first investigated according to their dispersity in different solvents. Toluene and water were chosen as hydrophobic and hydrophilic models, respectively. The three catalysts (same weight) were individually placed into the same amount of water. After slightly shaking, it is seen from the photographs (Figure 3A) that a uniform dispersion of the

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PIL@SiO₂-Pd nanospheres in water was found, meanwhile a large part of the MCM41-Pd catalyst deposited at the bottom of the bottle. This completely opposite appearance stems from the structural difference of these two catalysts: one is hollow and smaller while the other is denser and larger. In the case of PIL-Pd, it fails to be dispersed (floating on the surface of water) due to the aforementioned intrinsic hydrophobic nature of the PIL polymer.



Figure 3. Photographs illustrating the solution behavior of PIL@SiO₂-Pd, MCM41-Pd and PIL-Pd catalysts. The three catalysts in water (A), toluene + water (B) and water + benzyl alcohol (C). The photographs were taken 30 s and 2 min after shaking the mixture strongly in B and C, respectively.

The central construction philosophy of our nanoreactor lies in providing a flexible, adjustable hydrophobicity to bind the substrates around the Pd NPs inside the hydrophilic silica shell. Therefore, the same amount of toluene was added into these three aqueous bottles, and the mixture was shaken vigorously. After 30 seconds, it is interesting to observe that the PIL@SiO₂-Pd catalyst was suspended as a foamy emulsion at the interface of toluene and water, meanwhile the MCM41-Pd catalyst remained in the aqueous phase (Figure 3B). This foam-like suspension formed by PIL@SiO2-Pd at the liquid interface is very stable, without any significant change even after 5-day storage (Figure S4). This tells that the PIL@SiO₂-Pd acts as a Pickering stabilizer, *i.e.* it is turning amphiphilic in this situation. Coincidently, the PIL-Pd catalyst stays at the interface too, however due to the non-dispersity of PIL in neither water nor toluene.

The dispersity of these solid catalysts in the mixture of water and benzyl alcohol was investigated similarly. It is interesting to find that 2 min after shaking the mixture strongly, the PIL@SiO₂-Pd catalyst was transferred from the up water phase to the bottom benzyl alcohol phase (density 1.04 g/mL), while the MCM41-Pd catalyst was still trapped in water (Figure 3C). This is exciting and very unconventional, as the PILphase is essentially trapped within the exoskeleton of the silica shell. Speculatively, the van der Waals interactions seem to be able to "reach-through" the shell. For the PIL-Pd catalyst, its aggregates became soft and sticky due to its partial swelling and attached on the bottle wall. Combining the above phenomenon, it is obvious that the PIL@SiO₂-Pd displays an amphiphilic behavior, well dispersed in water while keeping high affinity toward benzyl alcohol molecules.



Figure 4. STEM-HAADF images of a PIL@SiO₂ nanosphere (A) after the platinum(II) acetylacetonate (dissolved in benzyl alcohol) adsorption experiment and the corresponding STEM-EDXS maps of the Pt (B), Si (C), O (D) and N (E) signals. F is the combined image of (B) to (E) and additionally F1 is the signal of fluorine, to show the background, since the material does not contain fluorine.

This unconventional "reach-through" van der Waals interaction between the hydrophobic substrate and PIL core is very probably facilitated by the "bridge" function of the CTAB residue in the silica mesopores. To prove this effect, dye adsorption experiments (Nile-red dissolved in benzyl alcohol, 0.5 mg/mL) of PIL@SiO2, MCM41-Ext (without CTAB) and MCM41-As (with CTAB) were designed for a visual detection (Figure S5-6, Experiment details in SI). The rapid color change of PIL@SiO2 and MCM41-As compared to MCM41-Ext after a short dye adsorption time indicates the difference in adsorption rate indeed stems from CTAB. It is well-known that micelles can transfer and enrich hydrophobic molecules into their hydrophobic core in water. According to the adsorption experiments mentioned above, the CTAB residue confined in the thin porous silica shell showed similar solubilization function of free micelles in water. Since the nanoreactor resembles and behaviors as micelle (the amphiphilicity and high affinity towards hydrophobic molecules in water) with the assistance of residue CTAB inside silica shell, a quick transmission of the hydrophobic substrates through the silica mesopores to the hydrophobic PIL core is expected.

To further prove the enrichment of the hydrophobic molecules inside the PIL@SiO₂ nanospheres in water, another hydrophobic molecule platinum(II) acetylacetonate (soluble in benzyl alcohol) was used instead of Nile-red to render a detectable signal-to-noise ratio in Scanning Transmission Electron Microscopy (STEM) and Energy Dispersed X-ray Spectroscopy (EDXS) measurements (details see SI). The results are shown in Figure 4. Assisted by the mapping technique, the distribution of Pt, Si, O and N elements (Figure 4) is the same, thus proving the location of Pt inside the PIL@SiO₂ nanosphere. Since the sample is free of fluorine, the map of fluorine element was made as a contrast to show the background. Therefore combining the results of adsorption experiments and STEM-EDXS, it is clear that the PIL@SiO₂ nanosphere 1

showed strong affinity towards hydrophobic molecules in water with the assistance of the residual CTAB inside the mesopores of silica shell. This high affinity has accelerated the mass transport of the hydrophobic substrates and led to an enriched substrate concentration inside the PIL@SiO₂ nanospheres.

 Table 1. Catalytic performance of different catalysts on the selective oxidation of aromatic alcohols.

R	ОН <u>1 ma</u> 6	ol% Pd, H 5 °C, 5 h	20 ►		+ R 3	Он
Entry	Catalyst	R in 1	Conv. (%) ^[b]	Sel. of $2(\%)^{[b]}$	Pd (wt%) ^[c]	$\begin{array}{c} TOF \\ (h^{-1})^{[d]} \end{array}$
1	MCM41-Pd	MeO	34	100	1.39	21
2	PIL@SiO2-Pd	MeO	> 99	100	0.41	60
3	PIL-Pd	MeO	trace	n.d.	0.85	n.d.
4	MCM41-Pd	Н	28	100	1.39	32
5	PIL@SiO2-Pd	Н	> 99	100	0.41	414
6	PIL-Pd	Н	trace	n.d.	0.85	n.d.

^[a] Reaction conditions: aromatic alcohol/Pd (mmol) /H₂O (mL): 0.5/0.0048/1.3, oxygen balloon (~2 atm), 65 °C, 5 h. ^[b] The conversion and selectivity were determined by GC-MS. ^[c] Pd content was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). ^[d] TOF = (The converted number of substrate molecules)/(total amount of Pd atom)/(reaction time, h), Figure 5.



Figure 5. The reaction profiles of PIL@SiO₂-Pd and MCM41-Pd towards benzyl alcohol (a and d) and 4-methoxybenzyl alcohol (b and c) respectively.

The selective oxidation of aromatic alcohols, especially benzyl alcohol to benzaldehyde, is a key reaction for the synthesis of many high value-added fine chemicals, such as pharmaceuticals, agrochemicals, and perfumery industries. The well-designed nanoreactor was tested in the selective oxidation of primary aromatic alcohols to aromatic aldehydes, whose catalytic performance was compared with that of MCM41-Pd and PIL-Pd. The results were summarized in

Table 1. The reaction kinetic profiles (conversions as a function of time) of PIL@SiO₂-Pd and MCM41-Pd towards both substrates were recorded to provide more reaction details. It is clearly seen that PIL@SiO2-Pd showed much higher activity than MCM41-Pd catalysts towards both substrates (Figure 5). The MCM41-Pd catalyst presents a turnover frequency (TOF) of 21 and 32 h⁻¹ for benzyl alcohol and 4-methoxybenzyl alcohol (entries 1 and 4, Table 1), respectively. This catalytic activity is comparable to other values reported in literature towards both substrates.⁴³⁻⁴⁴ In contrast, the PIL@SiO₂-Pd catalyst delivers a much higher catalytic activity here, for example, a TOF of 2.9, 12.9 times (entries 2 and 5, Table 1) of that for the MCM41-Pd catalyst. This catalytic activity is unusually high with regard to the literature results.⁴⁵⁻⁴⁶ Moreover, it can be seen from the table that both PIL@SiO₂-Pd and MCM41-Pd catalysed the reaction to form aldehydes at a high selectivity (100%), but for PIL@SiO₂-Pd at a conversion of 100%. In comparison, the PIL-Pd catalyst showed, as expected, negligible activity towards both substrates (entries 3 and 6, Table 1), which is mainly caused by its poor dispersity in water.

As a typical advantage of heterogeneous catalysts, the PIL@SiO₂-Pd catalyst can be reused by simple centrifugation and washing. The reusability was tested by using benzyl alcohol as a model substrate. As shown in Figure 6, this novel amphiphilic nanoreactor can be recycled for at least 4 sequential runs, with slight loss of activity in the fourth run, which stems from the loss of the catalyst during the catalyst recycling procedure *via* centrifugation. There is no obvious CTAB loss after recycling experiment (Figure S7). It is worth mentioning that the selectivity towards benzaldehyde is constantly above 99%, which is quite good for such a long-run recycling experiment.



Figure 6. The conversion of benzyl alcohol and selectivity of benzaldehyde in recycle tests. Time for the last two recycles is 10 h.

The reason for the dramatic enhancement in catalytic activity and recyclability of the PIL@SiO₂-Pd catalyst in our opinion a natural outcome of its exquisite nanostructure configuration, *i.e.* an incompatible, but adaptive hydrophobic core and a hydrophilic shell coupled in a hybrid nanoreactor to work synergistically. Specifically, the PIL@SiO₂-Pd catalyst is highly dispersible in water through the assistance of the hydrophilic silica layer. The hydrophobic substrates can be accumulated in the PIL core through the van der Waals interactions as proven by dye adsorption experiments (Figure S5-6, Figure 4). This provides a local enrichment and close proximity of the substrates to the Pd NPs, leading to a significantly boosted catalytic activity.

4. CONCLUSIONS

In summary, a hydrophobic@hydrophilic hybrid nanoreactor was built up and functioned as a robust, highly efficient and easily reusable catalyst for the selective oxidation of primary aromatic alcohols in an eco-friendly way. The tailormade structural design benefits from the unusual solution properties of poly(ionic liquid) and features a targeted, sitespecific enrichment of the hydrophobic substrate in the nanoreactor in aqueous environment, overcoming the common accessibility problem between substrate and catalytically active sites. This advancement leads to outstanding catalytic activity and selectivity, pointing out a new methodology in nanostructure design to conduct the catalytic conversion of many hydrophobic aromatic substrates to valuable organics in aqueous phase in a cost-effective manner.

ASSOCIATED CONTENT

Supporting Information.

TEM images, N₂ sorption isotherms, FT-IR spectra and photos of substrates adsorption results in different solvents. 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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