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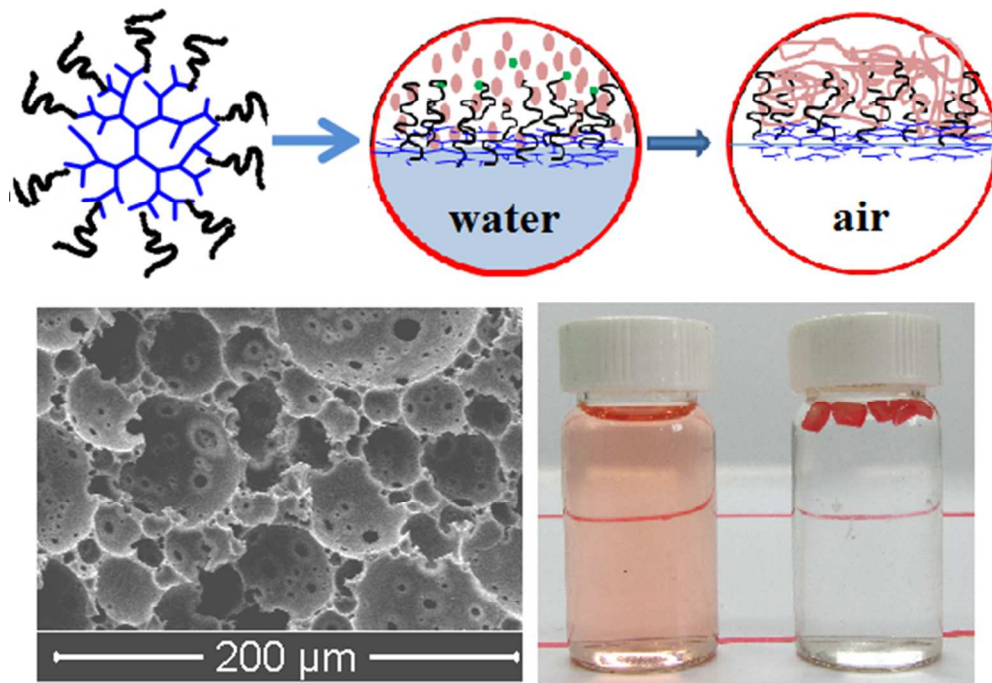


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COMMUNICATION

Dendritic Amphiphile Mediated Porous Monolith for Eliminating Organic Micropollutants from Water

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Few adsorbents can well combine macroscopic size with 3D microscopically well-tailored surface. Here we show that a dendritic amphiphile can directly lead to such an adsorbent, which can simultaneously eliminate anionic dyes, anionic surfactants and hydrophobic polycyclic aromatic hydrocarbons (PAHs) from water.

Water remediation is a globular challenge.^{1, 2} Conventional adsorbents can hardly remove either hydrophilic or hydrophobic micropollutants in water. It is known that a highly hydrophobic organic pollutant is generally of low solubility in water but tends to be biomagnified through aquatic food web and poses negative impacts on a man,³ where a typical example is the toxic, mutagenic, carcinogenic and poorly metabolizable polycyclic aromatic hydrocarbons (PAHs), which are found highly concentrated in fish⁴⁻⁷ but can hardly be eliminated from water.⁸ On the other hand, a hydrophilic pollutant such as a dye, or a partly hydrophilic one such as a surfactant, is ubiquitously found in water and constitutes negative impact on the ecosystem.^{9, 10} Some micro- and nano-scale adsorbents have been reported to efficiently capture trace water pollutants¹¹⁻¹⁴ but are too small to separate from water, while a macroscopic and porous adsorbent can afford ready separation from water but is usually less efficient to capture aqueous micropollutants for the ill-defined microstructure. Much effort has been devoted to macroscopic, porous and well functionalized adsorbents. A typical route for porous and high-surface-area material is the polymerization of the continuous phase of a high internal phase emulsion (termed HIPE and polyHIPE, respectively)¹⁵ with the aid of a large amount of surfactant (5-50% with respect to the monomer), followed by removal of the surfactant and post-synthetic functionalization of the surface. It is found that the surfactant can be replaced by certain stabilizers such as inorganic particles,¹⁶⁻²² and organic polymers.²³⁻²⁷ Unlike small surfactants, such stabilizers can afford quasi-irreversible adhesion to the water/oil interface,²⁸ and usually a much lower dosage is

enough for the preparation of polyHIPE. Some stabilizers such as certain amphiphilic diblock copolymers can even directly lead to a 3D functionalized polyHIPE.²⁶

Nowadays few adsorbents can facilely combine microscopically well-defined surface with a macroscopic size. Dendritic amphiphiles are known to readily undergo self-assembly to form interesting nanostructures.²⁹⁻³¹ A dendritic amphiphile is also able to exist as molecular nanocapsule to efficiently capture small molecules than a linear counterpart due to the morphological feature³² and a tunable electronic environment¹²⁻¹⁴ of a dendritic amphiphile. In view of the fact that dendritic polymers, except dendrimers, are usually one-pot, large-scale available,³³ they and their derivatives are of potential application in a number of fields. Here we show the first example that a dendritic amphiphile can act as an effective stabilizer of a HIPE to lead to new polyHIPE, with the latter's surface directly 3D functionalized with the dendritic amphiphiles (Fig. 1). With the unique morphological feature and well-tuned electronic environment of the dendritic amphiphiles on the surface, the resulting polyHIPE shows an ability to simultaneously eliminate either hydrophobic PAHs, or hydrophilic dyes, or partly hydrophilic surfactants from water to an unprecedentedly low residual level ever reported for a macroscopic material, which seems to be a unique character by a dendritic stabilizer.

A typical process of dendritic amphiphile mediated preparation of functional polyHIPE is schematically outlined in Fig. 1. The dendritic amphiphile is obtained by alkylation of commercially available hyperbranched polyethylenimine (PEI, $M_n = 10^4$, 232 repeat units on average) with epoxy polystyrenes (PS),¹³ leading to a stabilizer of PEI@PS. The polymerization degree (x) of PS and the functional fraction ($y(\%)$) of PEI are both well controllable, leading to a variety of stabilizers of PEI@PS $_x$ - y (Table S1 and Fig. S1, ESI). A typical HIPE of water-in-oil (W/O) process is conducted with styrene (St), divinylbenzene (DVB), toluene (porogen solvent) and PEI@PS (stabilizer) as the oil phase, and water (4-fold the volume of the oil phase) as the dispersed phase.

The PEI@PS x - y samples ($x = 21$ -520, $y = 3$ -55 (%)) stabilized HIPE systems are generally very stable (most are stable at least within 4 months), especially in case when PS makes up over 85% of the stabilizer. The assembly of PEI@PS along the W/O interface (Fig. 1) should be responsible for the stability. The resulting HIPE is transformed into polyHIPE via radical polymerization to yield a creamy white and rigid solid.

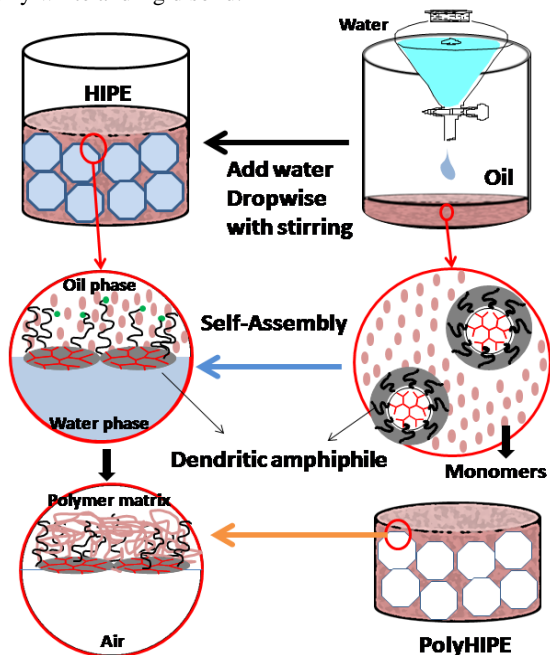


Fig. 1. Schematic representation of dendritic amphiphiles (PEI@PS) mediated preparation of polyHIPE.

Scanning electron micrograph (SEM) shows that for PEI@PS with very long but a few PS chains (PEI@PS520-7), where PEI makes up only 1.0% of the stabilizer, or 0.1% with respect to the oil phase, polyHIPE is readily available with clearly open-cell structure (Fig. 2a). In sharp contrast to the case of a small surfactant, where an open-cell structure is usually available only when the amount of surfactant is over 5%.³⁵ A stabilizer bearing short but more PS chains (PEI@PS22-15, whose PEI makes up 11.1% of the stabilizer) seems to hardly favor the number of pores on the cell (Fig. 2b). However, increasing the amount of toluene (Fig. 2c) or DVB (Fig. 2d) leads to more pores on each cell but the pore sizes are not increased, and in both cases the apparent densities can be decreased, which fall within 0.20 to around 0.12 g m⁻¹. The surface areas of the porous polyHIPE typically fall within 4-16 m² g⁻¹, and porosity within 53-86% (a typical one is shown in Fig. S2, ESI).

The PEI@PS functionalized polyHIPE shows high affinity to a variety of aqueous micropollutants. Any polyHIPE mediated with different PEI@PS (Table 1) can remove anionic dyes in water, and dyes with different rigidities and sizes (Chart S1, ESI) are tested. It is found the dye-eliminating ability of the polyHIPE depends on the morphology of the PEI@PS rather than on the pores. When polyHIPE of S1 (Table 1) is dropped into water, it floats on the water and gradually discolors the methyl orange (MO)-contaminated water. A cutting slice of the polyHIPE shows a color gradient decreasing from the surface to the center, indicating the cellular pores are throughout interconnected and accessible to the water. If the polyHIPE is ground into rough powder and packed in a hydrophilic Teflon bag, the adsorption

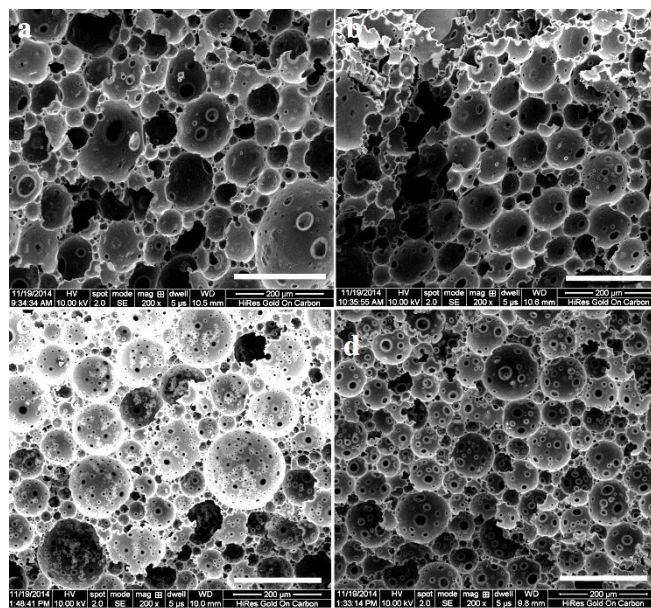


Fig. 2. Scanning electron micrographs of polyHIPE mediated with (a) PEI@PS520-7, at volume ratio of the oil phase St/DVB/toluene = 48/12/30, (b) PEI@PS21-15, St/DVB/toluene = 48/12/30, (c) PEI@PS21-15, St/DVB/toluene = 32/8/50, and (d) PEI@PS21-15, St/DVB/toluene = 30/30/30. Other conditions: water volume remains 4-fold that of the oil phase; PEI@PS remains 10% with respect to the oil phase; AIBN as initiator; the scale bar is 200 μ m for all micrographs.

can be somewhat accelerated and the adsorbent can be readily separated. The residual MO in water is detected with a UV/vis spectrometer, but is detectable only after concentration of the water sample. As shown in Table 1, the very small-sized MO in water can be reduced to a residual level of 10⁻⁸ M. Eosin Y (EY) and rose Bengal (EB), with larger molecular weights and slightly larger sizes, can be more efficiently removed, which should originate from stronger electrostatic and van de Waals complements between the immobilized PEI@PS and the dyes. However, the rigid and much larger direct blue 80 (DB80) can be poorly removed by S1 and S2 but S4 is very effective. Such a phenomenon can be attributed to a morphological factor. The dendritic amphiphile of PEI@PS undergoes self-assembly along the surface of the polyHIPE, with the hydrophobic PS chains penetrating into the polyHIPE matrix and the hydrophilic core facing the water phase, and the core can pose open, semiclosed and closed states towards the water, depending on the substituting degree by PS chains. In case of S4, the core is open and accessible to the large-sized DB80 while in case of S1 the core is closed. Similar trend is found for direct black 71 (DB71) to DB80. That S1 is more favorable to capture MO than S4 is understandable: the closed core is still accessible to the small-sized MO and meanwhile the hydrophobic shell can shield the MO-PEI complement from the competitive binding by water. Clearly, a linear stabilizer can hardly afford such morphological feature and may be less efficient on eliminating such aqueous pollutants.

Besides the morphology, the electronic environment of PEI@PS is also critical to the ability to remove a dye. Congo red (CR) is also a rigid and rod-like dye but is of smaller size than DB80, however, it is very strange that S4 is inefficient to scavenge CR while S1 is, which cannot be explained from a morphological factor. It is found that if the PEI moiety of S4 is further treated with ethylene oxide so that the residual amino protons are transformed

into hydroxyethyl groups, the resulting S5 is effective to capture CR (Fig. 3). Obviously, here the electronic nature of PEI@PS is important, and the multifunctional PEI provides a unique platform

to tune the electronic environment so that strong guest complement is possible.

Table 1. The structures of PEI@PS_{x-y} on ability of the corresponding polyHIPE to eliminate aqueous micropollutants.^a

Poly HIPE	x-y of PEI@PS _{x-y}	residual pollutants (M)							
		MO/10 ⁻⁷	EY ^b /10 ⁻⁸	RB/10 ⁻⁹	DB80/10 ⁻⁹	DB71/10 ⁻⁹	CR/10 ⁻⁹	pyrene ^b /ppb ^d	SDBS/10 ⁻⁹
S1	21-55	0.8	1.3	<1	× ^c	×	<1	0.6	8.3
S2	21-30	1.0	1.4	<1	×	×	×	0.6	8.8
S3	70-15	1.0	1.5	<1	<1	<1	×	0.7	7.8
S4	310-3	1.2	1.9	<1	<1	<1	×	0.7	7.9
S5 ^e	310-3	1.8	2.3	<1	<1	<1	<1	0.8	7.8
Q _e (S3) (mg/g) ^f		0.3	4.8	26.0	30.1	32.0	11.3	0.2	31.5

^a The polyHIPE is ground into powder and packed in hydrophilic polytetrafluoroethylene bag before immersing into polluted water for 1-10 d with the monitor of a UV-vis spectrometer, and the water sample is buffered at pH 7.4 (phosphate buffer, 0.01 M) and concentrated by at least 100 time after adsorption before UV/vis detection; the measuring errors are within 15%; ^b detected by fluorescence without concentration; ^c ×: poor or less efficient adsorption; ^d ppb: part per billion; ^e the mediator is PEI@PS310-10 but the residual amino protons are transformed into hydroxyethyl with ethylene oxide; ^f saturated adsorbing capacity of S3.

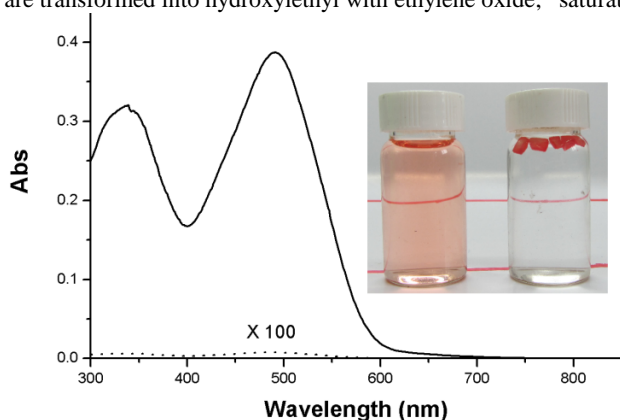


Fig. 3. UV/vis spectra of aqueous CR before (solid line) and after (dot line) the treatment with S5 followed by concentration by 100 times, the inset photo shows a discoloration of CR-contaminated water sample after 5 d.

Interestingly, the highly hydrophobic pyrene, a representative member of the PAH family, can be highly efficiently removed, where fluorescent detection shows a residual concentration below 1 ppb level (Table 1), comparable to the best results ever reported but only from a micromaterial.⁸ The PS domain should be responsible for the efficient adsorption of pyrene because an acidic environment (PEI domain, if protonated, can poorly accommodate pyrene) does not disfavor the efficiency (Fig. S3, ESI). The extraordinary affinity of PS to pyrene may originate from their hydrophobic complement as well as π - π complement. Moreover, as shown in Table 1, anionic surfactant of sodium dodecylbenzenesulfonate (SDBS) can also be effectively removed from water, with a residual concentration at the order of 10⁻⁹ M. A further test shows that contaminants of EY, pyrene and SDBS can be simultaneously removed by S1, and a combined use of S1 and S5 can best remove MO and CR. It is also noticed when the dye- and surfactant-loaded polyHIPE is immersed in alkali water, a fraction of them can be released, for example, in case of S5, 81% released for MO, and 37%, 60% and 18% for RB, DB70 and CR, respectively. And for SDBS, it is 48-90% (dependent on the amount of water). The inefficient release of CR may imply hydrogen-bonding complement besides electrostatic complement. The regenerated polyHIPE can be used for water treatment again with almost identical ability to reduce dyes and surfactants.

The saturated adsorbing capacity of a polyHIPE sample is also tested. As shown in Table 1, the adsorbing capacities are dependent on species of the micropollutants, but are usually rather high.

Conclusions

In conclusion, dendritic amphiphile of PEI@PS can well stabilize a HIPE of St/DVB in water, further leading to one-pot production of polyHIPE with radical polymerization, and the resulting polyHIPE is 3D surface functionalized by PEI@PS. The functional fraction of PEI by PS can be designed as desired, allowing the morphology of the immobilized PEI@PS to pose open, semiclosed or closed states towards differently sized aqueous pollutants. The open state ensures the core kinetically accessible to large-sized pollutants, while the closed state allows the access to small-sized pollutants and meanwhile shields the competitive binding by water, which is favorable to a stronger guest binding. Additionally, the large amount of residual functional groups on PEI provides a unique platform to tune the electronic environment to match a guest. With the well-tuned morphology and electronic environment, sufficient host-guest complement is possible to eliminate micropollutants in water. Within our knowledge, this is for first time that a dendritic amphiphile is used as a stabilizer to mediate the synthesis of polyHIPE, and directly confers the resulting polyHIPE an ability to reduce a wide spectrum of aqueous micropollutants to an unprecedentedly low level ever reported for a macroscopic adsorbent, where other stabilizer can poorly afford. This adsorbent is recyclable and favors the production of quality drinking water. Effort to improve the mechanical property of polyHIPE is ongoing.

Acknowledgements

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Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details, synthesis and characterization of PEI@PS, structure of dyes, fluorescent detection of pyrene. See DOI: 10.1039/c000000x/

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