Supporting Information

Layer-by-Layer Assembly of Polyelectrolytes on Hydrophobic Particles in Aqueous Milieu for Efficient Dye Removal

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1. Experimental Section

1.1 Materials

PDADMAC (Mw 200 000 - 350 000), PSS (Mw about 70 000), NaCl, R6G$^+$ (log P = 6.36 [S1]) and SF$^-$ (log P = 2.64 [S2]), were purchased from Sigma-Aldrich (Shanghai, China) and absolute ethanol (>99%) from China Sinopharm Chemical Reagent Co., Ltd. All the chemicals were used as received without purification. Water with a resistivity of 18 MΩ·cm^{-1} was prepared using a Millipore Milli-Q system and used in all experiments. Hydrophobic particles of PE, PTFE, PVC, and PP with mean particle sizes in the range of 20 - 30 μm were purchased from Dongguan Shuangfu Plastic Raw Materials Co. Ltd.

Aqueous solutions of polyelectrolytes – PDADMAC and PSS – were prepared at a concentration of 1 mg·mL^{-1}. The dissolved gas in water and aqueous solutions of polyelectrolytes was removed by repetition of freezing the solutions in liquid nitrogen, pumping and thawing according to the procedures reported in literature[S3]. Firstly, the glass tube bearing a given aqueous milieu – water or aqueous polyelectrolyte solutions – was frozen by slow immersion into liquid nitrogen to prevent ice expansion. After pumping the gas from the space above it, the frozen aqueous milieu in the glass tube was warmed to room temperature, which allowed the gases dissolved therein to be pulled into and the fill the space above it. The freezing/pumping/thawing process was repeated for five times to ensure the complete removal of the gas dissolved in the aqueous milieu, evidenced by the fact that oil could be readily emulsified in the resulting degassed aqueous milieu.

1.2 Methods

1.2.1 Dispersion of hydrophobic particles in degassed saline water in the presence of PDADMAC.
Firstly, hydrophobic particles of PE, PP, PVC, and PTFE were thoroughly cleaned using ethanol and water to remove impurities from their surfaces. After being dried in air under ambient conditions, a given amount of the particle powder were placed in degassed water in the absence and presence of PDADMAC and/or NaCl, followed by 20 min vigorous mixing with the aid of a homogenizer. Subsequently, the hydrophobic particles were filtered out from the aqueous media, followed by thorough washing with fresh water to remove the excess PDADMAC and/NaCl. The resulting PDADMAC-coated particles were dried in air under ambient conditions.

1.2.2 PDADMAC/PSS LbL assembly on PDADMAC-coated hydrophobic particles.
Taking advantage of their reasonable dispersibility and colloidal stability in degassed saline water, as-prepared PDADMAC-coated hydrophobic particles were submitted to LbL assembly of PSS and PDADMAC according to conventional protocol reported in literature[S4]. Firstly, the PDADMAC-coated hydrophobic particles were immersed in the degassed aqueous solution of PSS (1.0 mg·mL^{-1}) in the presence of 1 M NaCl, followed by 20 min incubation. After being thoroughly washed with water to remove the excess of PSS from their surfaces, secondly, the resulting particles were submitted to 20 min incubation in the degassed aqueous solution of PDADMAC (1.0 mg·mL^{-1}) in the presence of 1 M NaCl, followed by removal of excess PDADMAC by

means of thorough water washing from their surfaces. Thirdly, the cycle of alternating deposition of PSS and PDADMAC on the PDADMAC-coated hydrophobic particles were repeated to grow (PDADMAC/PSS)$_m$ shells on targeted hydrophobic particles, leading to hydrophobic core/hydrophilic shell particles .

1.2.3 Preparation of hydrophobic particle yolk /PEM shell particles (YSPs). After the (PDADMAC/PSS)$_m$ shells with a given bilayer number (m) were formed, the resulting hydrophobic polymer/PEM, core/shell particles (CSPs) were submitted to successive 6 h incubation in ethanol/water mixtures with ethanol-to-water volume ratios of 2:8, 5:5 and 8:2. Subsequently, the resulting particles were dispersed in anhydrous ethanol for 6 h incubation, followed by filtering out the particles and redispersing them in anhydrous ethanol. The cycle comprising incubation in anhydrous ethanol, filtration, and redispersion in anhydrous ethanol was repeated for 5 times to remove the remaining water in the PEM shells, which caused complete cleavage of the hydrophobic interactions between the PEM shells and the hydrophobic cores and liberated the hydrophobic cores, thus leading to hydrophobic polymer/PEM, yolk/shell particles (YSPs).

1.2.4 Spectroscopic assessment of the dispersibility of hydrophobic polymer particles coated with and without PDADMAC in degassed water. The scattering and absorption of light by suspended and colloidal particles dispersed in aqueous media results in noticeable loss in transmission of the aqueous media, which is known as turbidity and can be quantitatively assessed by means of transmission spectroscopy according to the relationship between the transmittance intensity (I_{trans}) of aqueous dispersion of colloidal particles and the particle content therein (Equation S1):

$$I_{trans} = I_0^{-k \times C} \qquad \textbf{S1}$$

where I_0 is the transmittance intensity of water in the absence of colloidal particles and k is a proportionality constant dependent on particle size, shape, refractive index, and sample path length. After we carried out vigorous mixing of hydrophobic particles with targeted aqueous media, therefore, here we assessed the ratio of transmission intensity of the aqueous media before (X_{water}) and after ($X_{particles}$) being subject to dispersion of hydrophobic particles in the visible light wavelength range (400 – 800 nm), defined as percentage transmittance (Equation S2):

$$\text{Percentage transmittance} = \frac{\int_{400}^{800} X_{particles}\, dx}{\int_{400}^{800} X_{water}\, dx} \times 100\% \qquad \textbf{S2}$$

The resulting percentage transmittance values were used to quantitatively compare the dispersibility of hydrophobic particles in different types of aqueous media, including aerated water, degassed water, and degassed aqueous solutions of polyelectrolytes (PDADMAC or PSS) in the presence of NaCl.

1.2.5 Surface wettability-assisted assessment of the surface coverage of polyelectrolyte coatings deposited on hydrophobic particles in degassed waster. According to Cassie-Baxter equation,[S5] the contact angles of water on as-prepared PEM-coated hydrophobic particles in air ($\theta_{w/a}^{PEM-HP}$) can be decomposed into the component of the PEM shells ($\theta_{w/a}^{PEM}$) and that of the uncoated (PEM-free) surfaces of the hydrophobic particles ($\theta_{w/a}^{HP}$), described by Equation S3 and S4:

$$cos\theta_{w/a}^{PEM-HP} = f_{PEM}cos\theta_{w/a}^{PEM} + f_{HP}cos\theta_{w/a}^{HP} + f_{air}cos\theta_{w/a}^{air} \qquad \textbf{S3}$$

$$f_{PEM} + f_{HP} + f_{air} = 1 \qquad \textbf{S4}$$

where f_{PEM} and f_{HP} are the surface coverage of the PEM shells and the fraction of the uncoated (PEM-free) surfaces of the hydrophobic particles, respectively, and the term of the right-hand side in Equation S3 reflects the fact that when PEM-coated particles are pressed into plates, the contribution of air trapped in the interstices between the particles to the surface wettability of water on the resulting particle plates. The water contact angles of PDADMAC or PSS-capped PEM shells deposited on planer substrates can be used as $\theta_{w/a}^{PEM}$ and those of planer hydrophobic polymer substrates as $\theta_{w/a}^{HP}$. While $\theta_{w/a}^{air}$ can be safely assumed to be 180° [S6], the f_{air} values can be derived from corresponding pristine particle plates.

Since direct measurement of water contact angles on micron-sized particles is a colossal technical challenge, 0.1 g of the powder of as-prepared PEM-coated hydrophobic particles were pressed under pressure of 2 MPa for 2 min to thin plates, which were used for contact angle measurement. After the $\theta_{w/a}^{PEM-HP}$ values were obtained by means of sessile droplet technique, the corresponding f_{PEM} values were readily calculated according to Equations S3 and S4.

1.2.6 Quantitative assessment of the adsorption kinetics of as-prepared hydrophobic /hydrophilic CSPs and YSPs towards organic dyes in water. A series of batch equilibrium adsorption experiments were conducted at room temperature to evaluate the adsorption performance of as-prepared hydrophobic polymer/(PDADMAC/PSS)ₘ CSPs or YSPs particles towards negatively charged dye – SF⁻ – and positively charged dye – R6G⁺ – in water, respectively, with the aid of absorption spectroscopy. After the CSPs or YSPs particles were introduced into aqueous solutions of the ionic dyes at a given initial concentration (C_0, mg·L^{-1}), the dye concentrations (C_t, mg·L^{-1}) in water at a particular adsorption time (t_a, min) were monitored by means of UV-vis absorption spectroscopy. The adsorption uptake of the ionic organic dyes (q_t, mg·g^{-1}, with respect to the adsorbent mass) after incubation of a given amount (m) of the CSPs and YSPs particles for t_a was calculated according to Equations S5:

$$q_t = (C_0 - C_t) \times V_a/m \qquad \textbf{S5}$$

where V_a is the total volume of the aqueous dye solutions used for adsorption (10 mL). When the adsorption equilibrium was established, the equilibrium adsorption uptake (q_e, mg·g^{-1}) of the CSPs or YSPs (with respect to the adsorbent mass) were calculated according to Equation S6:

$$q_e = (C_0 - C_e) \times V_a/m \qquad \textbf{S6}$$

where C_e is the dye concentration in water obtained at the adsorption equilibrium.

The experimentally measured adsorption kinetics data were fitted by both pseudo-first-order and pseudo-second-order models, respectively, as described in Equations S7 and S8:

$$\ln(q_e - q_t) = \ln q_e - k_1 t_a \qquad \textbf{S7}$$
$$t_a/q_t = 1/k_2(q_e)^2 + t_a/q_e \qquad \textbf{S8}$$

where k_1 is the rate constant of the pseudo-first-order kinetics model and k_2 is the rate constant of the pseudo-second-order kinetics model.

In current work, the special attention was paid on the adsorption performance of

as-prepared hydrophobic polymer/(PDADMAC/PSS)$_m$ CSPs or YSPs towards organic dyes in water via hydrophobic interactions. In the case, the targeted dyes and the outermost layer of the (PDADMAC/PSS)$_m$ shells of the CSPs or YSPs were identically charged and the adsorption efficiency of the CSPs or YSPs were measured by the residual percentage (*Re* %) of the targeted dyes in water according to Equation S9:

$$Re = C_e/C_0 \times 100\% \qquad \qquad \textbf{S9}$$

1.3 Characterization

Absorption/transmittance spectra were obtained in the wavelength range of 400–800 nm using a Shimadzu UV-2700 UV-vis spectrometer (Japan). The zeta potential values of PEM-coated hydrophobic particles in degassed were measured using a Brookhaven 90 Plus Zeta apparatus, during which care was taken to ensure there were no air bubbles in the cell as they can affect the results. Each sample was measured five times to minimize error. Confocal microscopic images were obtained using Nikon C2 confocal fluorescence microscopes. The static contact angle values ($\theta_{w/a}$) on as-prepared PEM-coated hydrophobic particles at ambient temperature were measured with the aid of a drop shape analyzer-DSA100 system (Krüss GmbH, Germany).

1.4. References

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S4 F. Caruso, H. Lichtenfeld, E. Donath, H. Möhwald, *Macrmolecules* 1999, **32**, 2317

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2. Supplementary data

2.1 Spectroscopic assessment of the dispersibility of hydrophobic particles in degassed water with the aid of PDADMAC and NaCl.

Figure S1. Transmission spectra of aqueous dispersions of PE particles in aerated water and degassed water in the absence and presence of 1 mg·mL^{-1} PSS and PDADMAC.
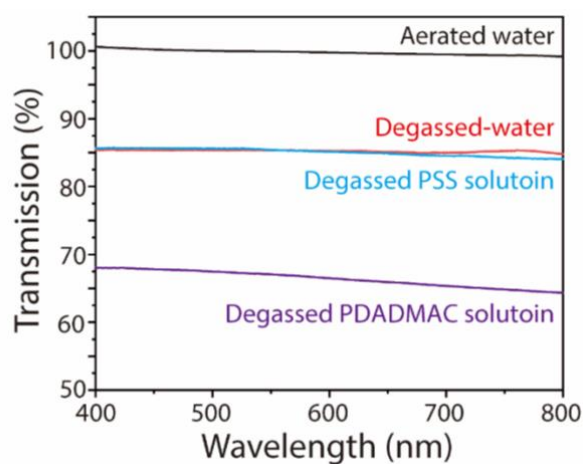

Figure S2. Transmission spectra of aqueous dispersions of PE (a) and PTFE (b) particles dispersed in degassed water in the presence of PDADMAC at concentration of 1 mg·mL^{-1} PDADMAC and NaCl at concentration ranging from 0 M to 0.25, 0.5, 1.0, 2.0, and 3.0 M.
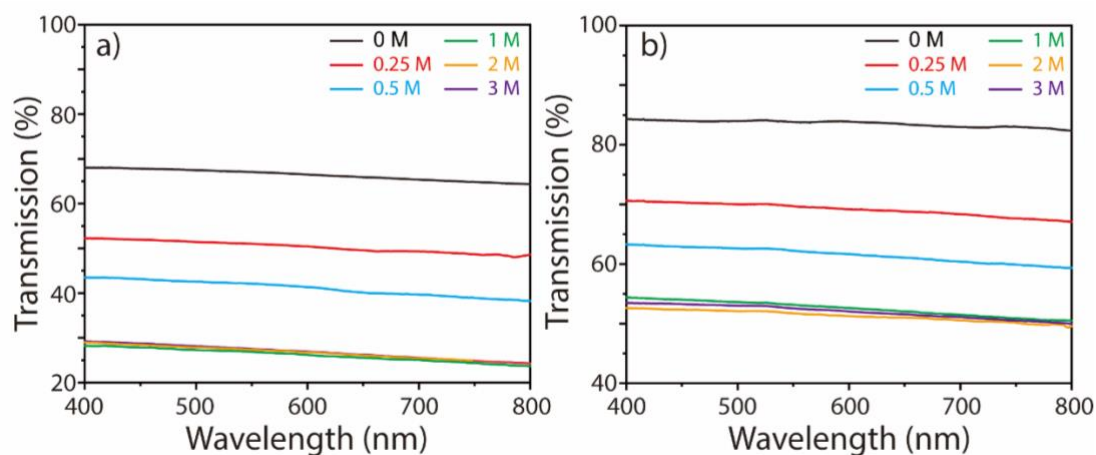
2.2 Visualization of dispersion of PVC and PP particles in degassed water with the aid of PDADMAC and NaCl.

Figure S3. Photos of glass vials containing the dispersions of PVC (a) and PP particles (b) dispersed in degassed water in the presence of PDADMAC at concentration of 1 mg·mL^{-1} PDADMAC and NaCl at concentration (C) in the range of 0.25 - 3.0 M. The insets show the photos show water droplets (2 µL) on the resulting particles in air with corresponding $\theta_{w/a}$ and $f_{PDADMAC}$ values marked.
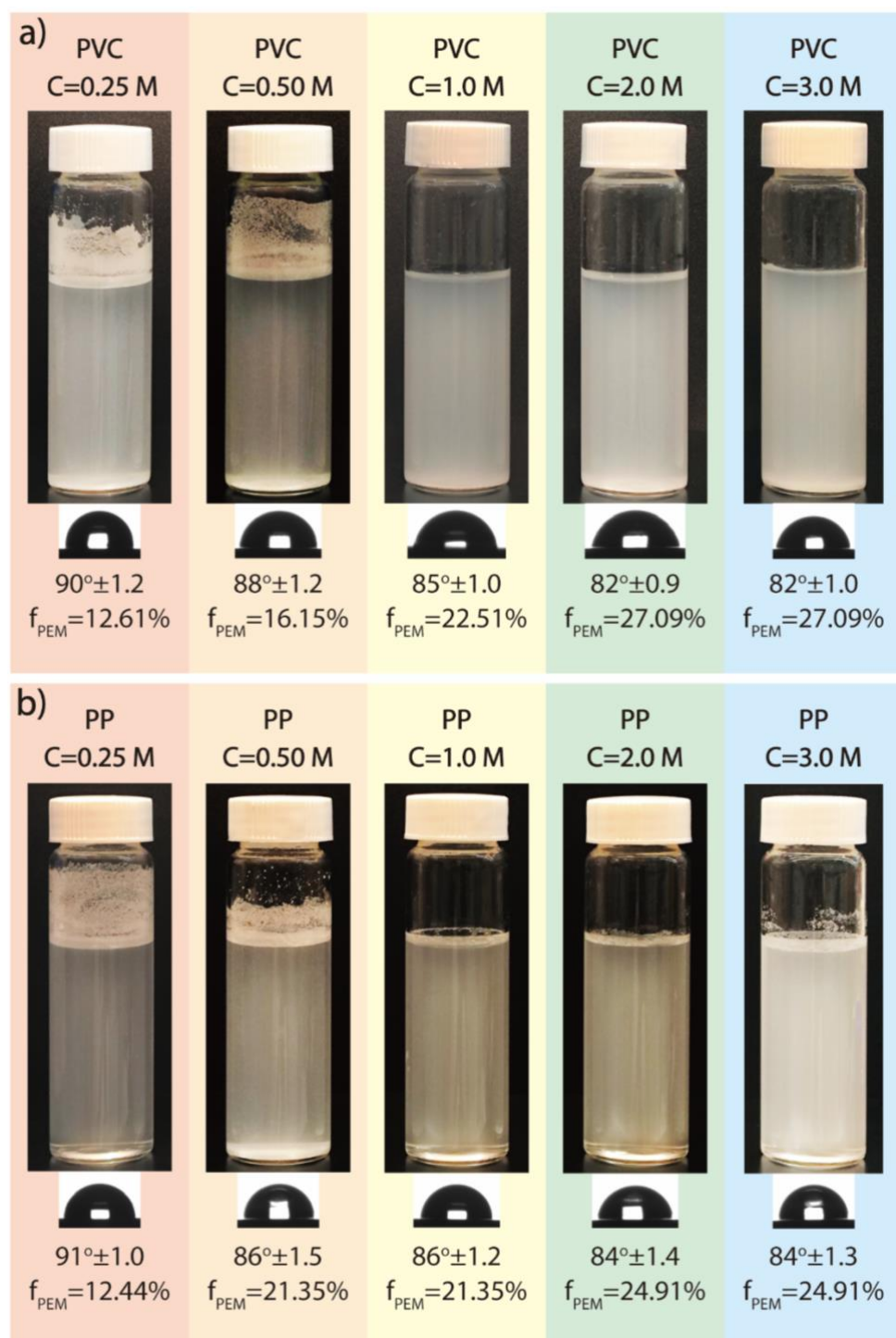
2.3 Summary of the zeta-potential values of hydrophobic particles dispersed in degassed water with and without the aid of PDADMAC and NaCl.

Figure S4. Summary of the zeta-potential values of pristine (circles) and PDADMAC-coated hydrophobic particles (squares) in degassed water. The PDADMAC-coated hydrophobic particles are obtained by dispersing pristine particles in degassed water in the presence of 1 mg·mL^{-1} PDADMAC and 1.0 M NaCl.
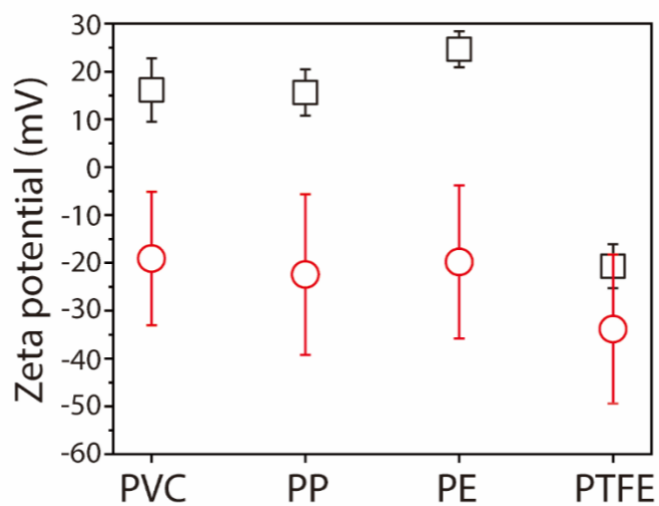
2.4 Evolution of the $\theta_{w/a}$ and f_{PEM} of PEM coatings deposited on hydrophobic particles during PDADMAC/PSS LbL assembly

Figure S5. Plots of the values of $\Delta\theta_{w/a}$ (squares) and Δf_{PEM} (circles) of as-prepared PEM-coated PVC (a), PP (b) and PTFE (c) particles versus the values of N_{PSL}.
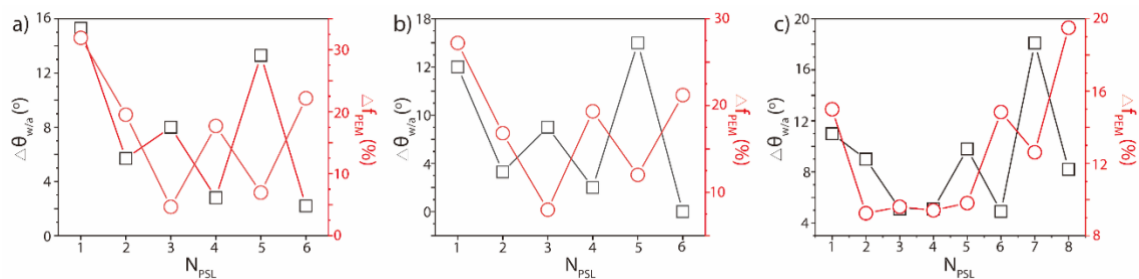

Figure S6 Plots of the values of $\theta_{w/a}$ (black symbols) and f_{PEM} (red symbols) of as-prepared PEM-coated PVC (squares), PP (circles) PE (upper triangles) and PTFE particles (down triangles) versus the values of N_{PSL}.
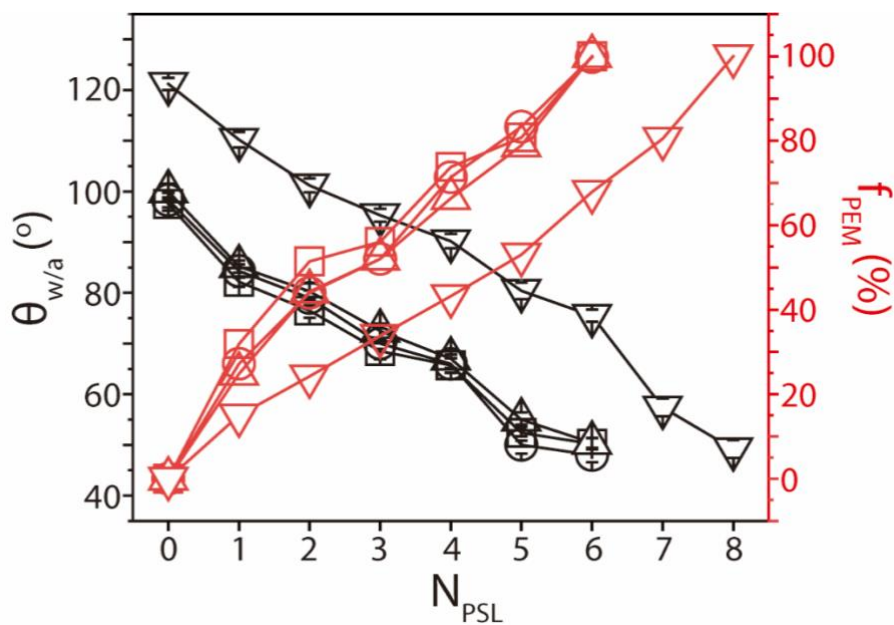
2.4 Quantitative assessment of the adsorption performance of PE/(PDADMAC /PSS)$_{7.5}$ and PE/(PDADMAC/PSS)$_{8.0}$ YSPs and their corresponding CSP precursors against organic dyes in aqueous solutions of SF$^-$ and R6G$^+$, respectively.

Figure S7. UV-vis absorption spectra of the aqueous solutions of SF$^-$ (a) and R6G$^+$ (b) before (black curves) and after 12h incubation of as-prepared, respectively, in which the YSP content is varied from 0 to1, 2, 3, 6, 8, 10, 12, 15, and 18 mg·mL^{-1} (from the top to the bottom) and the dye concentration is 20 μM·L^{-1}.
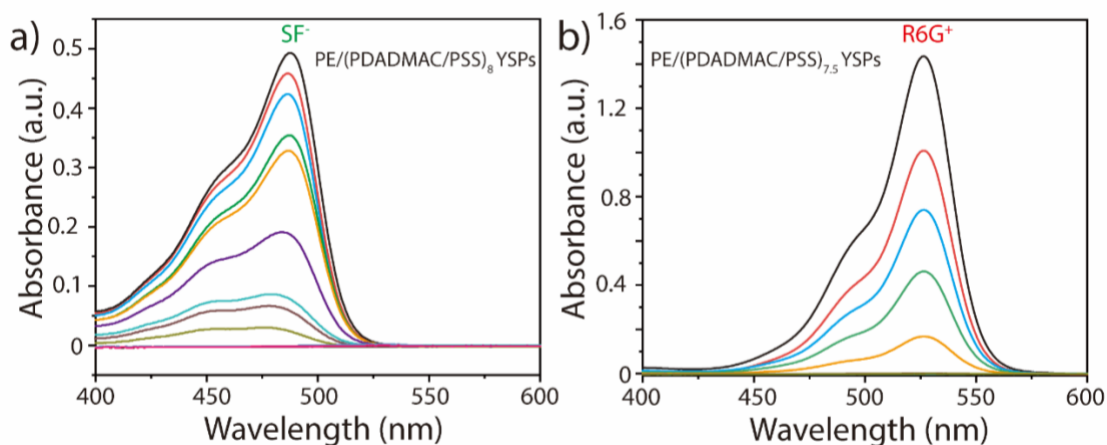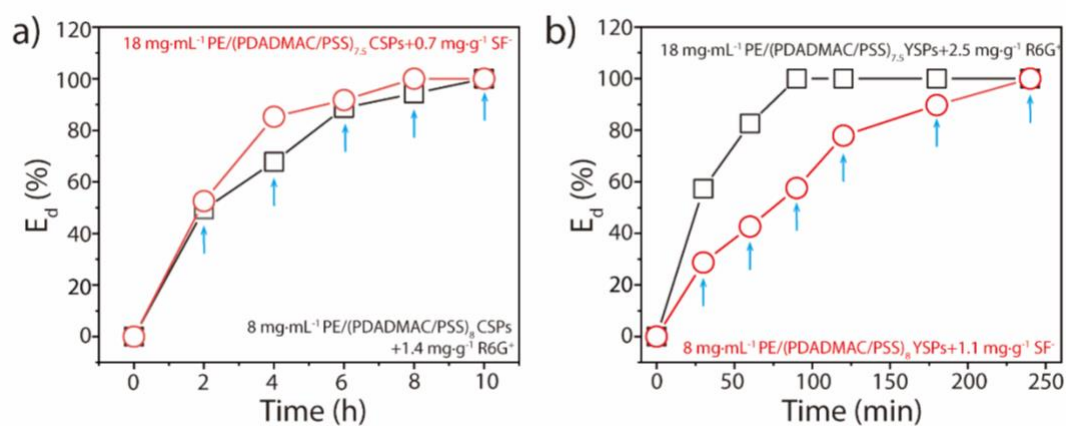

Figure S8. Temporal evolution of UV-vis absorption spectra of the aqueous solutions of organic dye during 12 h incubation of YSPs through hydrophobic interactions. The dye concentration is 20 μM·L^{-1}.
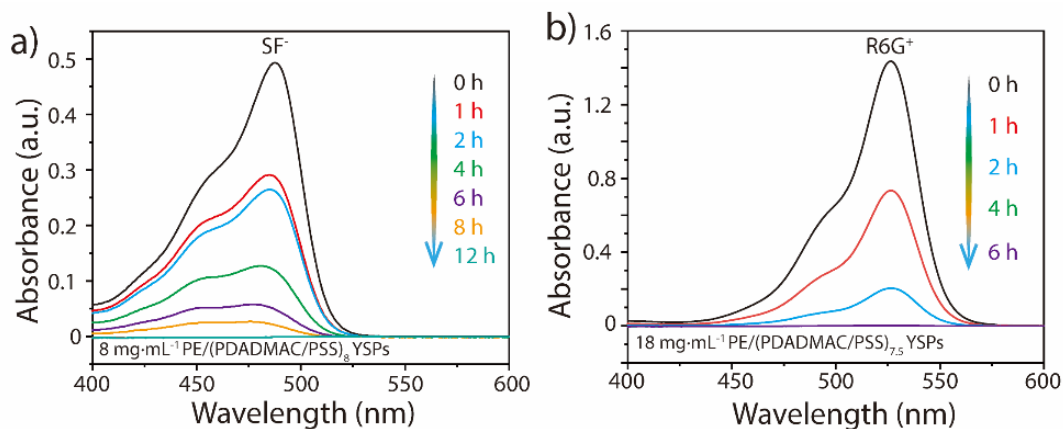
Figure S9. Temporal evolution of UV-vis absorption spectra of the aqueous solutions of organic dye during 12 h incubation of CSPs through electrostatic interactions. The dye concentration is 20 $\mu M \cdot L^{-1}$
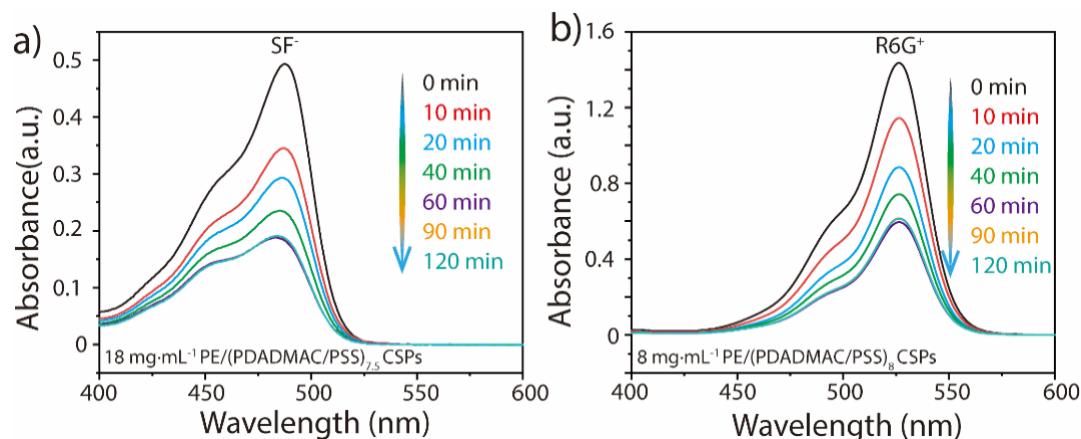
Figure S10. Plots of the organic dye desorption efficiency (E_d %) versus desorption time. To release the adsorbed organic molecules adsorbed through electrostatic interactions (a) and hydrophobic interactions(b), the CSPs (a) and YSPs (b) are consecutively incubated in aqueous solution of NaCl and fresh ethanol, respectively. When comparing the use of ethanol to shield hydrophobic forces, desorbing the adsorbed organic dyes on the surface of hydrophobic particles through YSPs hydrophobic interactions takes only 250 minutes (around 4 hours). In contrast, desorbing the organic dyes adsorbed onto the surface shell of CSPs particles through electrostatic forces requires 10 hours. This indicates the high efficiency of hydrophobic interactions in dye adsorption. The blue arrows in Figures indicate the time when the CSPs or YSPs are bought into fresh NaCl solution or ethanol, respectively.

Figure S11 Temporal evolution of the electrostatic interaction-driven adsorption effici
ency (q, micromoles of adsorbed dyes per microgram of CSPs) of PE/(PDADMAC/PS
S)$_{7.5}$ CSPs (8 mg·mL^{-1}, circles) towards SF$^-$ and PE/(PDADMAC/PSS)$_{8.0}$ CSPs (18 mg
·mL^{-1}, squares) toward R6G$^+$ molecules in aqueous solutions through, respectively, wh
ere the initial dye concentration is 20 μM·L^{-1}.
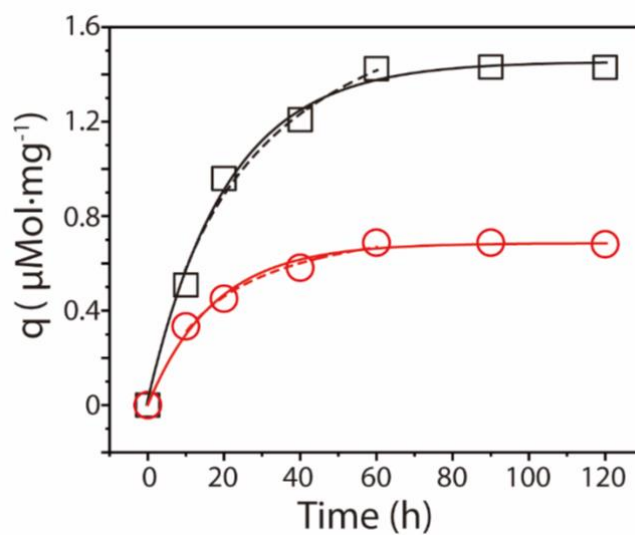
Table S1. Summary of the q_e values of 18 mg·mL^{-1} PE/(PDADMAC/PSS)$_{7.5}$ YSPs against SF$^-$ and those of 8 mg·mL^{-1} PE/(PDADMAC/PSS)$_{8.0}$ YSPs against R6G$^+$ in water via hydrophobic interaction driven. The experimental values of q_e (Exp. q_e) are obtained by 24 h incubation of the YSPs in the aqueous dye solutions at the initial concentration of 20 μM·L^{-1}. The q_e values (Cal. q_e) are derived from the corresponding adsorption kinetics data, shown in Figure 3c, by fitting the data according to pseudo-first-order and pseudo-second-order models, respectively. The fitting details, listed in Table S1, reveal the pseudo-first-order model gives better fitting of the adsorption kinetics of the present YSPs against organic dyes via hydrophobic interactions, which provide the values of Cal. q_e are comparable to the values of Exp. q_e.

Dyes	Exp. q_e /mg·g^{-1}	Pseudo-first-order model			Pseudo-second-order model		
		Cal. q_e /mg·g^{-1}	k_1 /min^{-1}	r^2	Cal. q_e /mg·g^{-1}	k_2 /min^{-1}	r^2
R6G$^+$	2.5	2.526	0.789	0.990	3.683	0.576	0.885
SF$^-$	1.1	1.115	0.351	0.991	1.399	0.355	0.975

Table S2. Summary of the q_e values of 18 mg·mL^{-1} PE/(PDADMAC/PSS)$_8$ CPSs against SF$^-$ and those of 8 mg·mL^{-1} PE/(PDADMAC/PSS)$_{7.5}$ CPSs against R6G$^+$ in water via electrostatic interaction-driven. The experimental values of q_e (Exp. q_e) are obtained by 12 h incubation of the CPSs in the aqueous dye solutions at the initial concentration of 20 μM·L^{-1} for SF$^-$ and 20 μM·L^{-1} for R6G$^+$. The q_e values (Cal. q_e) are derived from the corresponding adsorption kinetics data, shown in Figure S9, by fitting the data according to pseudo-first-order and pseudo-second-order models, respectively. The fitting details, listed in Table S1, reveal the pseudo-first-order model gives better fitting of the adsorption kinetics of the present YSPs against organic dyes via hydrophobic interactions, which provide the values of Cal. q_e are comparable to the values of Exp. q_e.

Dyes	Exp. q_e /mg·g^{-1}	Pseudo-first-order model			Pseudo-second-order model		
		Cal. q_e /mg·g^{-1}	k_1 /min^{-1}	r^2	Cal. q_e /mg·g^{-1}	k_2 /min^{-1}	r^2
R6G$^+$	1.4	1.454	0.049	0.994	2.038	0.038	0.969
SF$^-$	0.7	0.685	0.057	0.989	0.862	0.058	0.974