Electronic Supplementary Information file

Synthesis and characterization of thermoresponsive ZIF-8@PNIPAm-co-MAA microgel composites with enhanced performance as adsorption/release platform

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This Supporting Information file contains 9 pages including materials, Synthetic procedures, technical details, experimental data and calculations. This document includes 6 figures, 1 table and this cover page.

1. Experimental Methods

1.2 Synthetic procedures:

1.2.1. Microgel synthesis:

Briefly, based on the procedure reported by Zavgorodnya et al.,[1]1.358 g of NIPAm and 0.043 g of N,N'-methylene-bis-acrylamide (BIS) were dissolved into 100 mL of Milli-Q water (1:0.023 molar ratio) was heated under stirring to 70°C and purged with N_2 in a 250 mL three-neck round-bottom flask. Then, 0.148 g of MAA were added to a final molar ratio of 1:0.143 NIPAm:MAA, keeping the stirring for 5 minutes. 0.046 g of APS were dissolved in 1 mL Milli-Q water at room temperature and added into the mixture (final molar ratio of 1:0.017 NIPAm:APS). After four-hour synthesis, microgels were purified by centrifugation/re-suspension in water three times and finally freeze-dried.

1.2.2. ZIF-8 synthesis:

ZIF-8 particles were obtained by mixing equal volumes of a 25 mM ZnN methanolic solution and 50 mM HmIm methanolic solution at 25 °C. After one-hour synthesis, samples were centrifuged at 7000 rpm for 30 minutes and re-suspended in 5 mM NaCl three times. Final dispersion had a mass concentration of 1.63±0.09 mg/mL, determined by dry weight at TGA.

1.2.3. ZIF-8@microgel synthesis:

Freeze-dried microgels were dispersed in a 25 mM solution of $Zn(NO_3)_2$ -ZnN- (one of the ZIF-8's precursor) to a final concentration of 1 mg/mL for the Zn^{2+} preconcentration to took place. The dispersion was left on the fridge (4 °C) for 1 week to ensure a perfect dispersion. Elapsed the dispersion time, 50 mM methanolic solution of 2-methylimidazole (HmIm) was added over the microgel's methanolic dispersion to a final a 1:2 Zn:HmIm molar ratio. After one hour (ZIF-8's synthesis time, as mentioned above), the sample was centrifugated at 6000 rpm for 30 minutes in a Heraeus Biofuge 22R with an HFA 1494 rotor and re-suspended in NaCl 5 mM three times (the same salt solution was used to prepare 1 mg/mL microgel dispersions, see below). Slight ionic strength (IS) is needed while manipulating microgels in aqueous environments, to have control on its swollen state. By using a 5 mM IS solution, PNIPAm-co-MAA microgels were proved to be swollen at their maximum capacity.[2]

2. Experimental data:

2.1 ZIF-8 growth followed by DLS:

ZIF-8 was synthesized with the conditions described above in a glass cuvette with a fixed temperature (25 °C). Successive single measurements were done in a Backscatter configuration (173°) without delay between them, letting the number and duration of runs to be adjusted automatically by the software. Figure S1 shows the ZIF-8 particle size (Intensity distribution) vs. time at 25 °C. It was found that, after one-hour synthesis, ZIF-8 particles reach a stable size.

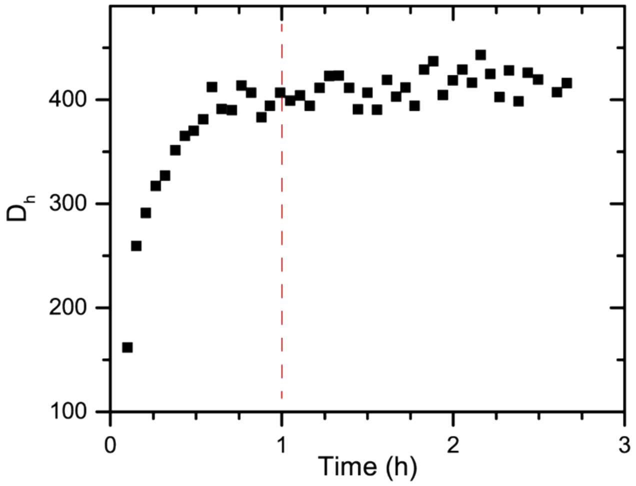

Figure S1. Hydrodynamic Diameter (D_h) increase as a function of time for ZIF-8 growth at 25 °C.

2.3. Nuclear Magnetic Resonance experiments:

The final microgel composition, estimated in 81% NIPAm (F_{NIPAm}=0.81) and 19% MAA (F_{MAA}=0.19), was obtained from ^{1}H NMR spectrum (figure S2 top) using the integration of signal "e" at 3.8 ppm corresponding to NIPAm monomer, respect to the integration of signals between 0.5 and 2.5 ppm corresponding to signals "a, b, c, d and f" using the equation:

$$F_{NIPAm} = {5 \times I^{3.8}} \Big/ {(I^{0.5-2.5} - 4 \times I^{3.8})}$$

Figure S2 down shows the ^{1}H NMR spectrum for ZIF-8@microgel composite. The presence of two new signals at 2.4 ppm and 7.1 ppm confirm the imidazole presence in the synthesized material. Moreover, the absence of a signal around 12 ppm, corresponding H "j" support the bonding formation in ZIF-8 synthesis since HmIm must be deprotonated to form ZIF-8.

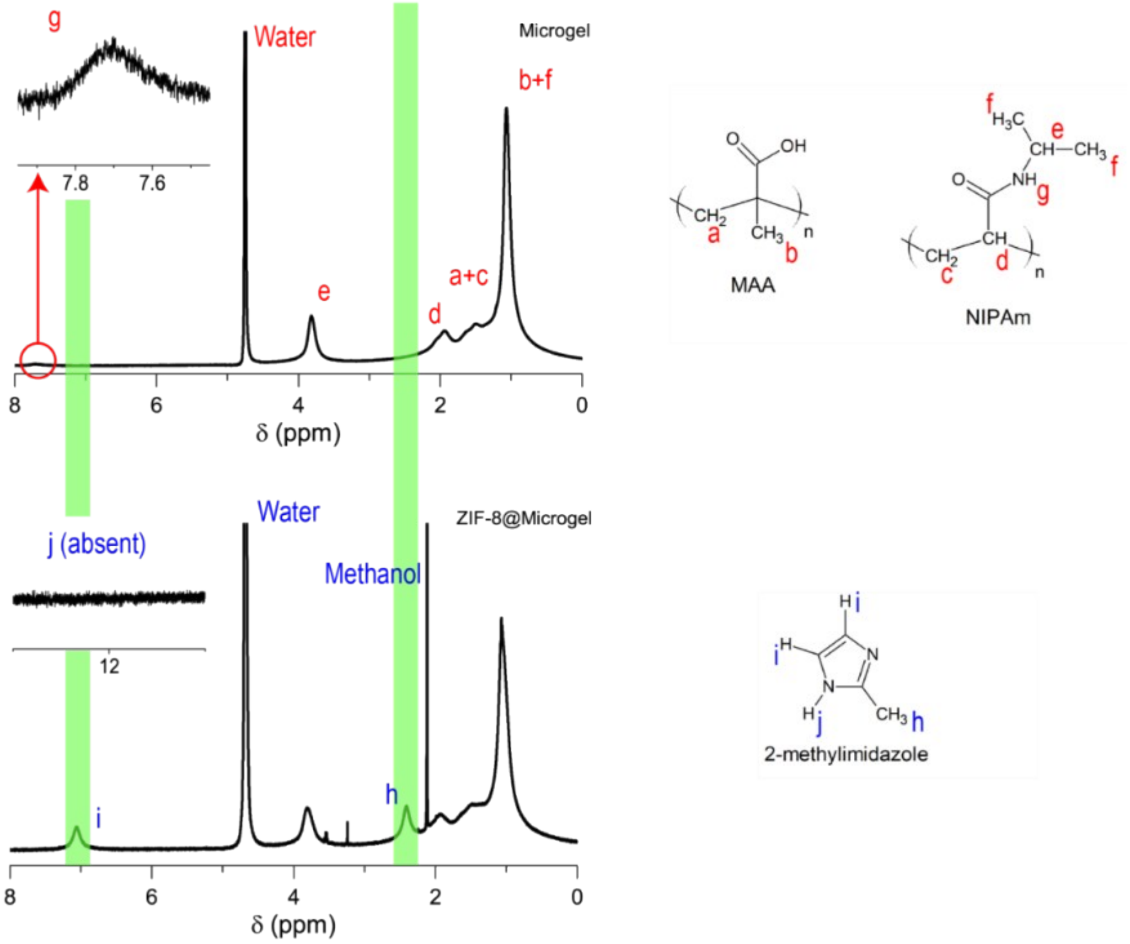

Figure S2. ^{1}H-NMR comparison between PNIPAm-co-MAA microgel (top) and ZIF-8@microgel samples (down). Chemical structures are shown at the right with the corresponding peak assignment.

2.4. Surface Area analysis:

Four isotherms were obtained. Brunauer–Emmett–Teller (BET) analysis was done manually in order to obtain the sample’s Surface Area, as follows:

From the reported volume adsorbed V (cm^3g^{-1}) vs P/P_0 the mass of adsorbed gas W (g_{N2}/g_{ads}) was calculated:

$$W = V \times \frac{M_{N_2}}{V_m}$$

were M_{N2} is the molar mass of N_2 (28.013 $gmol^{-1}$) and V_m it's molar volume at STP (22400 cm^3mol^{-1}).

Then, Rouquerol's plot was done, representing $W(1-P/P_0)$ vs P/P_0 in order to select the range of relative pressure at which the increase is monotonic. The range of P/P0 found by Rouquerol's plot is used to represent the linearized BET equation:

$$\frac{1}{W\left(\frac{P_0}{P}-1\right)}=\frac{1}{C\times W_{monolayer}}+\frac{C-1}{C\times W_{monolayer}}\left(\frac{P}{P_0}\right)$$

Where C is the BET constant, related to the heat adsorption. Finally, the specific surface area of the sample is obtained by:

$$S(m^2g^{-1})=\frac{W_{monolayer}\times N_a\times A_{N_2}\times 1\cdot 10^{-20}}{M_{N_2}}$$

where $W_{monolayer}$ represents the weight of the adsorbed monolayer (at maximum coverage), N_a is Avogadro's number, and A_{N2} is the cross-section of N_2 molecule (16.2 $Å^2$). The values obtained this way for the four isotherms were averaged and its standard error calculated to get a final value of 632±5 m^2g^{-1}.

Langmuir analysis, more suitable for type-1 isotherms as is this case, was done too, by using its linearized expression:

$$\frac{P/P_0}{W}=\frac{1}{K_L\times W_{monolayer}}+\frac{1}{W_{monolayer}}\left(\frac{P}{P_0}\right)$$

Where K_L is the equilibrium constant. Again, by averaging the four isotherms and calculating its standard error, a final value of 666±6 m^2g^{-1} was found.

It must be said that microgel's surface area was impossible to determine due to experimental limitations: preliminary results indicate that the amount of microgel needed to obtain a reliable value, was too high (in weigh). However, it was previously reported that these microgels presents a polymer volume fraction between 0.002 and 0.01 on the swollen and collapsed states respectively, i.e., the fraction of "empty space" is between 0.998 and 0.990 (which explains the above-mentioned limitation).[2]

2.4.1. Pore size distribution analysis:

Barrett-Joyner-Halenda (BJH) method, while developed for mesoporous materials, has proved to be suitable for Metal Organic Frameworks analysis too. It uses the modified Kelvin equation to relate the amount of adsorbate removed from the pores of the material, measured at 77 K, while P/P0 decreases.

2.5. TEM analysis

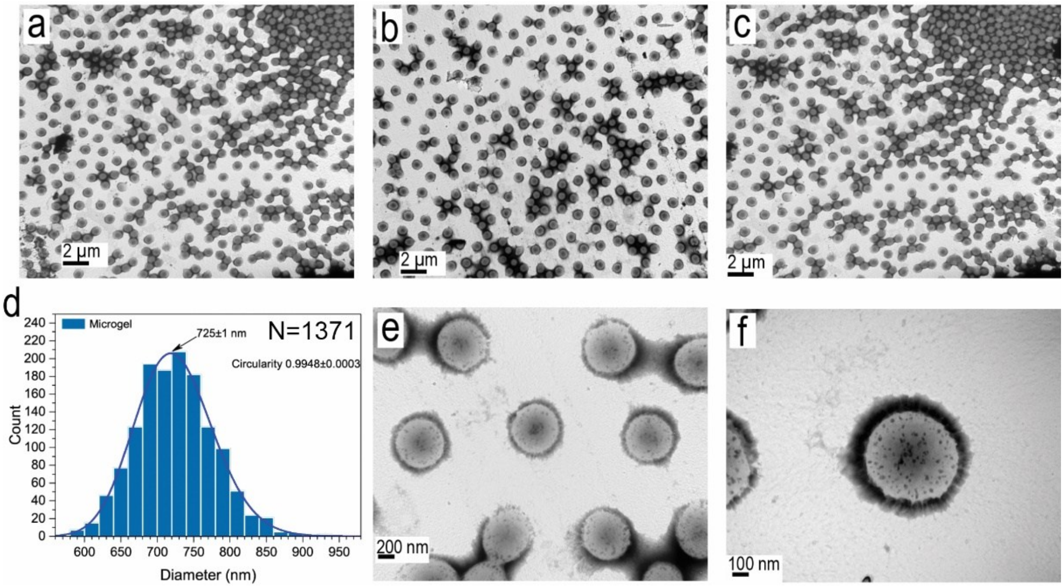

Figure S3. (a-c) TEM images for microgels with negative stain under 8k magnification. (d) Size distribution of microgels from images a-c. (e) 50k and (f) 100k magnification of microgels with negative stain.

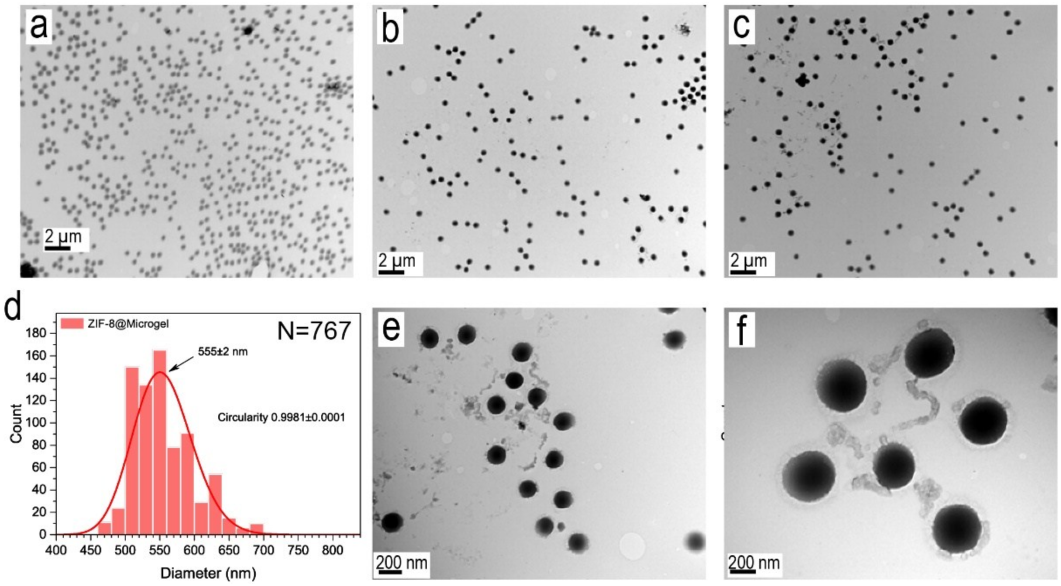

Figure S4. (a-c) TEM images for ZIF-8@microgels without negative stain under 8k magnification. (d) Size distribution of ZIF-8@microgels from images a-c. (e) 30k and (f) 80k magnification of ZIF-8@microgels without negative stain.

2.6. Effect of -COOH and zinc coordination on pH of aqueous suspensions

In order to bring further support to the discussed hypothesis, the resulting pH of suspensions prepared with bare ZIF-8, bare microgel, and ZIF-8@microgel (~1 mg/mL in 5 mM NaCl in all cases) were measured, which can be related to the effect of carboxylic acid moieties present. The pH values obtained for such aqueous suspensions were 8, 5, and 7 respectively. According to NMR experiments and previous reports, it is expected a resulting pH = 5 for poly(NIPAm-co-MAA) bare microgel suspensions, which can be translated into a ≈ 50% of MAA moieties in the network ionized and thus present as methacrylate.[2] The value obtained for ZIF-8@microgel suspensions (pH = 7), suggests that a considerable proportion of MAA moieties are no longer involved in acid-base equilibrium, due to ZIF-8 growth (triggered from previous Zn^{2+} ion coordination), thus inducing a higher pH on the resulting suspension.

2.7. UV-Vis absorption experiments:

Experiments were done on 1.50 mL of ZIF-8 (1.63±0.09 mg/mL), microgel (1.73±0.01 mg/mL), and ZIF-8@microgel (1.7±0.2 mg/mL) dispersions, which were placed into 2 mL Eppendorf tubes and kept at 25 ºC or 45 ºC for 24 h in a water bath. Then, a volume of a stock solution (1.0 mg/mL) of methylene blue in NaCl 5 mM was added as well as a certain volume of NaCl 5 mM solution to a final volume of 1.90 mL, according to Table S1 to get an initial concentration C_0.

V methylene blue stock (µL)	V NaCl 5 mM (µL)	C_0 Methylene Blue (mg/mL)
76	324	0.04
152	248	0.08
228	172	0.12
380	20	0.20

Table S1. Methylene Blue initial concentrations for the uptake experiments

The dispersions were kept at constant temperature for 48 h to reach the equilibrium.[3] Elapsed that time, the samples were centrifugated at 14000 rpm for 5 minutes in an EPF-12 high-speed centrifuge (Presvac) with a CFE-16 rotor. Absorption at 662 nm was measured to determine the equilibrium adsorption of dye (Q_e) according to:

$$Q_e(mg/g) = \frac{MB_0 - MB_f}{w_{ads}}$$

where MB_0 and MB_f correspond to the initial and free amount (in mg) of methylene blue and w_{ads} correspond to the mass of adsorbent (in g, either ZIF-8, microgel or ZIF-8@microgel particles).

The pellets formed during centrifugation were re-dispersed in 1.9 mL of NaCl 5 mM and kept at 25 ºC or 45 ºC for another 48 h. The samples were then centrifugated again at 14 krpm for 5 minutes and supernatant's absorption at 662 nm was measured to calculate the released amount of MB. The Release efficiency was then calculated as:

$$RE = \frac{MB_r}{MB_0 \times w_{ads}}$$

where MB_0, as previously defined, is the initial amount (in mg) of MB in contact with a given mass of the empty adsorbent (w_{ads}), and MB_r corresponds to the released amount (in mg) of MB after 48 h.

A calibration curve for MB absorbance at 662 nm was made (see Figure S5) using MB solutions in NaCl 5 mM with the following concentrations: 0.001-0.002-0.006-0.008 mg/mL. The linear fit was forced to a null intersection, to finally gets the absorbance dependence with the sample's concentration, as:

$$A_{\lambda = 662\ nm} = 159(\pm 5) \times C(mg/mL).$$

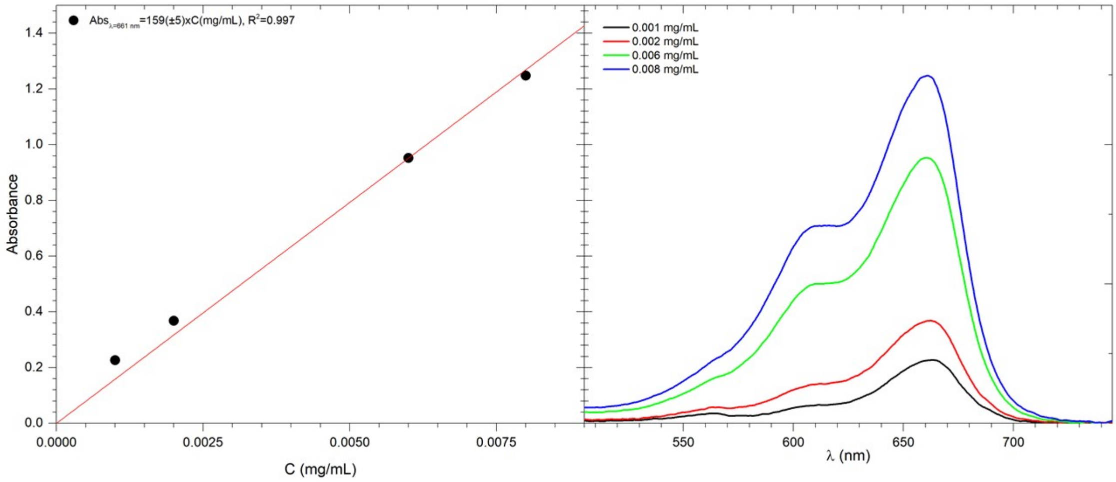

Figure S5. Calibration curve (left) and absorption spectra (right) of Methylene Blue solutions.

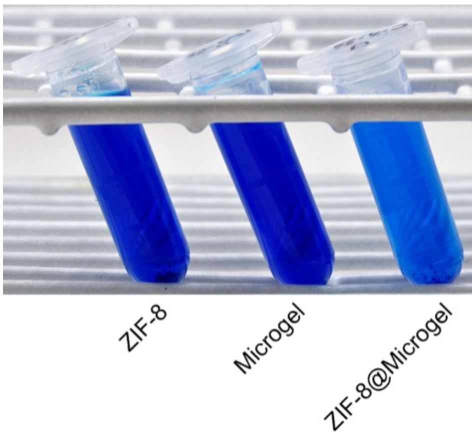

Figure S6. Photography of supernatants after MB adsorption at C_0=0.20 mg/mL.

2.8. Long time exposure of composites and evolution of crystalline structure:

WAXS experiments were performed on ZIF-8, and ZIF-8@microgel composite after five months exposure to NaCl 5 mM. The materials were found to be stable, as can be observed in Figure S7.

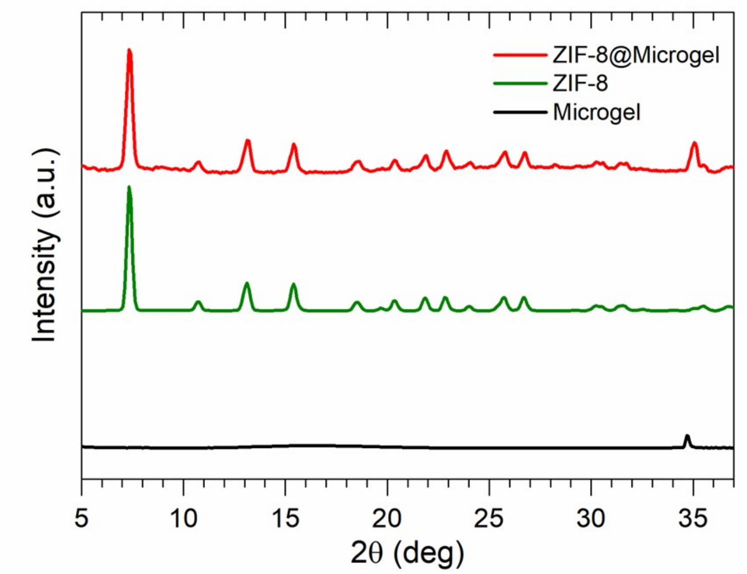

Figure S7. WAXS experiments on the materials exposed to aqueous environments after 5 months.

References:

1 O. Zavgorodnya and M. J. Serpe, Assembly of poly(N-isopropylacrylamide)-co-acrylic acid microgel thin films on polyelectrolyte multilayers: Effects of

polyelectrolyte layer thickness, surface charge, and microgel solution pH, *Colloid Polym. Sci.*, 2011, **289**, 591–602.

2 J. M. Giussi, M. I. Velasco, G. S. Longo, R. H. Acosta and O. Azzaroni, Unusual temperature-induced swelling of ionizable poly(N-isopropylacrylamide)-based microgels: experimental and theoretical insights into its molecular origin, *Soft Matter*, 2015, **11**, 8879–8886.

3 B. Luan Tran, H. Chin, B. K. Chang and A. S. T. Chiang, Dye adsorption in ZIF-8: The importance of external surface area, *Microporous Mesoporous Mater.*, 2019, **277**, 149–153.