Supporting information

In situ Thermal Fabrication of Copper Sulfide-Polymer Hybrid Nanostructures for Tunable Plasmon Resonance

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1. Methods

1.1 Materials

N-vinyl caprolactam (VCL) was purchased from Sigma Co. Ltd and used after the purification through recrystallization in *n*-hexane. Copper dibromide, sodium sulfide, and *N*,*N*-methylene bisacrylamide (MBA), sodium dodecylsulphate (SDS), sodium bicarbonate ($NaHCO_3$), potassium persulfate (KPS), methacrylic acid, sodium hydroxide,were all analytically pure and purchased from Aladdin Co., Ltd.

1.2 Synthesis of poly(VCL-*co*-MAA) microgels

The poly(VCL-*co*-MAA) microgels were synthesized through the modified precipitation polymerization, described as followed. Firstly, 0.873 g of *N*-vinyl caprolactam, 21 mg of *N,N*-methylene bisacrylamide, 15 mg of sodium dodecylsulphate, 40 mg of sodium bicarbonate ($NaHCO_3$) were added into a round-bottom flask with a magnetic stirrer and dissolved in 60 mL of ultrapure water. Then the solution was heated to 70 ^oC under stirring and a degassing process was performed through purging nitrogen for 30 mins to remove oxygen. After that, potassium persulfate dissolved in 5 mL of ultrapure water was injected to initiate the polymerization. Then 29 mg of MAA monomers (the feed ratios of VCL: MAA: MBA were 93: 5: 2) was dissolved in 1 mL ultrapure water and injected into the solution after 5 mins of initiating the polymerization. After 6 hours, the reaction was ended by exposing into airs and stopping heating. The products were purified through dialysis for 4 days with a dialysis bag (8000 - 12 000 kDa) and dried as solid samples for further use.

1.3 Synthesis of poly(VCL-*co*-MAA)@CuS hybrid microgels

General synthesis protocol for hybrid microgels was described below. Firstly, 24 mg of poly(VCL-*co*-MAA) microgels was dispersed in 4mL of ultrapure water and neutralized by 87 μL of NaOH (0.1 mol/L) aqueous solution. Then 1 mL of $CuCl_2$ aqueous solution was added at a series of -COOH/Cu^{2+} molar ratios, and the detail were shown in Table S1. The solution was stirred overnight to promote ion exchange between Na^+ and Cu^{2+} ions, followed by the addition of 6 mL of ethanol. After that, 1 mL of Na_2S aqueous solution at a Cu^{2+}/S^{2-} molar ratio of 1:1 was dropwise added into the dispersion at room temperature, and stirred for another 30 mins. Finally, the dispersion was treated at 70 ^oC under stirring for about 12 hours. The samples were kept as synthesized for further different purposes.
CuS powder was synthesized through similar procedure except the use of microgels for the comparison analysis of XRD.

1.4 Potentiometric measurements

Potentiometric titration was performed at room temperature using a Sartorius PB-10 pH meter equipped with a conventional glass pH electrode, according to the method by Khokhlov *et al*[1]. Briefly, 50 mg of microgels were dispersed in 50 mL of 10^{-3} KCl basic solution. Quantitative data were recorded using slow acid-into-base titrations at a speed of 3 hrs/times to ensure complete equilibration between the aqueous solution and microgels. The concentration of used HCl solution was 0.01 mol/L. The potentiometric titration data were analyzed using the reported method[2]. The degree of ionization α was calculated by subtracting the amount of HCl for the titration curves in the experiment of microgels dispersion and those for blank titration curves.

1.5Photothermal performance

To investigate the photothermal performance of the hybrid microgels, a typical approach similar to the previous report by Liu *et al.*[3]was used. Specially, 1 mL poly(VCL-*co*-MAA)@CuS10 dispersed in aqueous solution at the varying CuS concentration was continuously irradiated with an 980 nm NIR laser at a constant power density of 0.67 W/cm^2. The temperatures were recorded by the imaging thermal imager each thirty seconds.

1.6 Characterization

Microstructures of hybrid microgels were observed by transmission electron microscopy (TEM, FEI Tecnai G2 F30, USA). And the compositions were recorded by the energy-dispersive X-ray spectroscopy (EDX) attachment of the TEM (FEI Tecnai G2 F30, USA). The change of hydrodynamic diameters for the microgels dispersion was recorded by dynamic light scattering measurements (Zetasizernano ZS90, Malvern, UN). X-ray photoelectron spectroscopy (XPS, ThermoFisher ESCALAB 250Xi, USA) was utilized to identify the surface elemental composition of the hybrid microgels. XRD patterns were recorded by the

X-Ray diffraction (XRD, Panalytical Empyrean, Netherlands). The UV-vis spectra for the disperse solution at each step in the synthesis process were recorded by the UV–vis spectrometer (760CRT, INEASA, CN). The cloud points were performed by recording the transmittance of microgels or hybrid microgels dispersion at 550 nm using the mentioned UV-vis spectrometer, equipped with an external heater. The UV-vis-NIR spectra were recorded by UV-vis-NIR spectrophotometer (Agilent Technologies, Cary 5000 UV-Vis-NIR, USA). The digital photographs of the samples solution were taken by MI 5 mobile phone, and used without further treatment.

2. Supporting figures

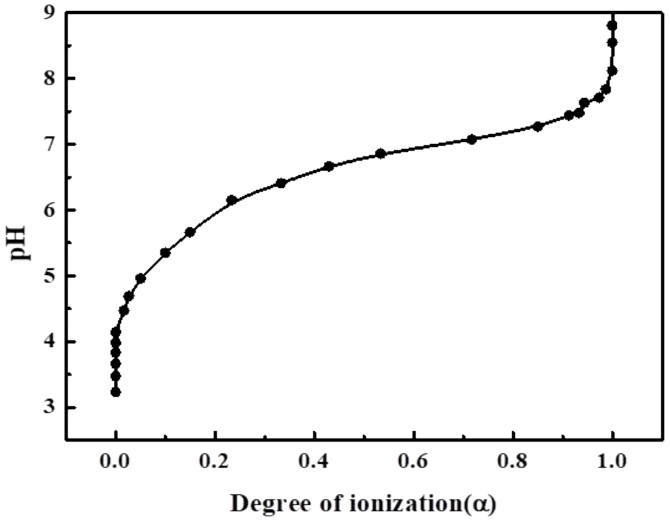


Figure S1 Degree of ionization of poly(VCL-*co*-MAA) microgels as a function of pH.

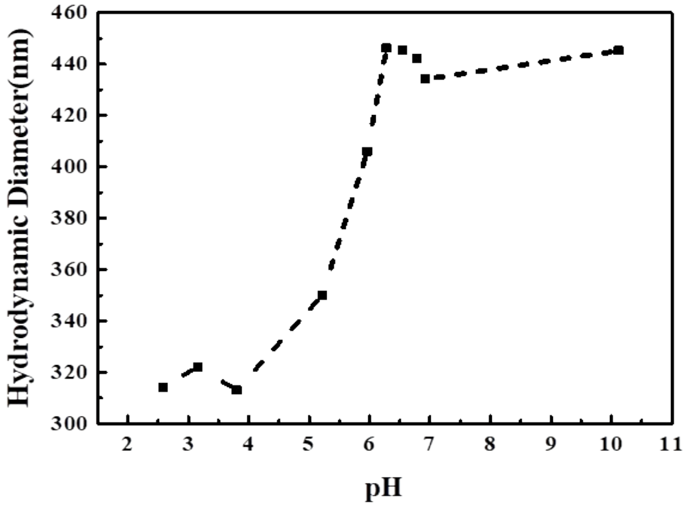


Figure S2 PH dependence of the average hydrodynamic diameters of poly(VCL-*co*-MAA) microgels at the concentration of 0.1 mg/mL.

The degree of ionization results (Figure S1) indicated the full ionization of carboxyl groups over pH 7.50. Near that pH value, the maximum hydrodynamic diameter was measured by dynamic light scattering (DLS, shown in Figure S2) the maximum swelling ratio (($d_{pH}/d_{pH\ 2.5}$)) was obtained as 1.4.

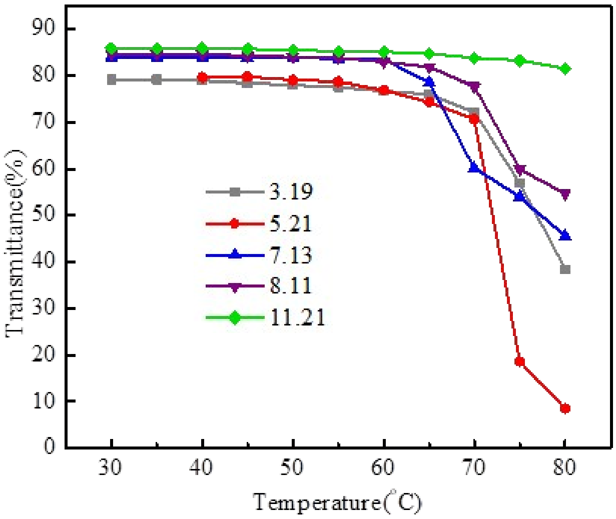


Figure S3 The thermal response of the transmittances of the poly(VCL-*co*-MAA) microgels dispersed in mixed solution of ethanol and water (V_{EtoH}: V_{H20} = 1:1) at constant concentration of 1 mg/mL under various pH values.

The temperature responsivities of microgels at varying pH were investigated in mixed solvents of ethanol and water, as shown in Figure S3. The obtained result showed both phase transition temperatures were higher than 70°C with pH ranging from 3.19 to 11.21, due to the absence of H-bond donor units and the higher solubility in ethanol than that in water. However, in our practical experiments, the phase separation occurred during the heating process between the water and ethanol caused the collapse of the microgels and the transmittance change. To avoid that, the strategy of stirring was introduced during the *in situ* synthesis process.

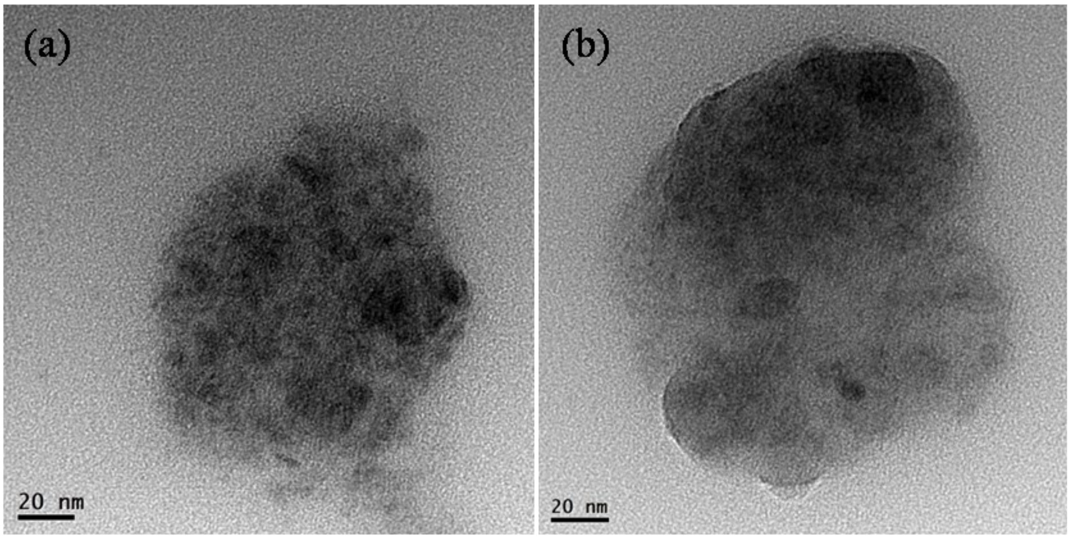


Figure S4 TEM images for poly(VCL-*co*-MAA)@CuS1 hybrid microgels under magnification size of 20nm.

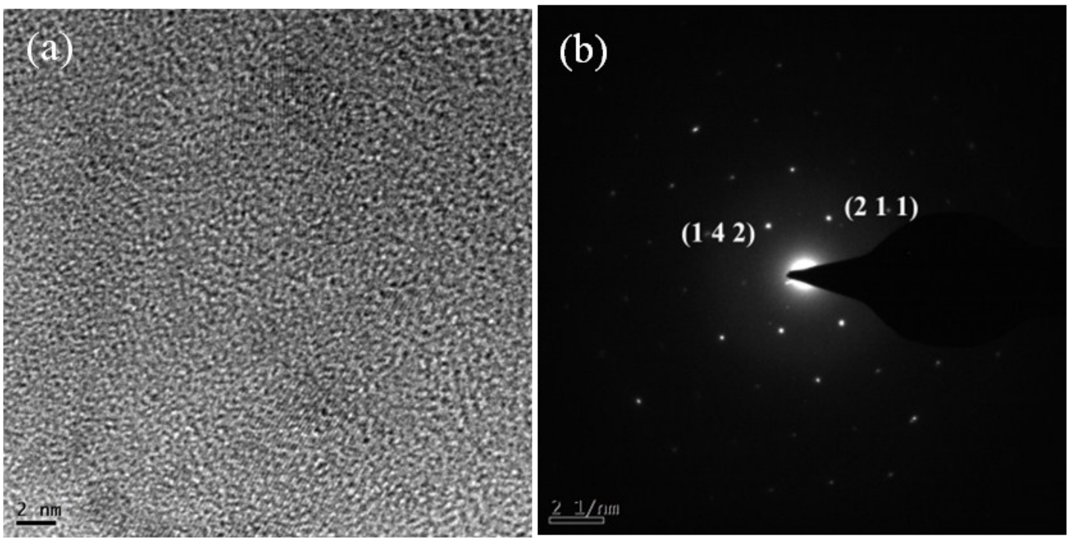
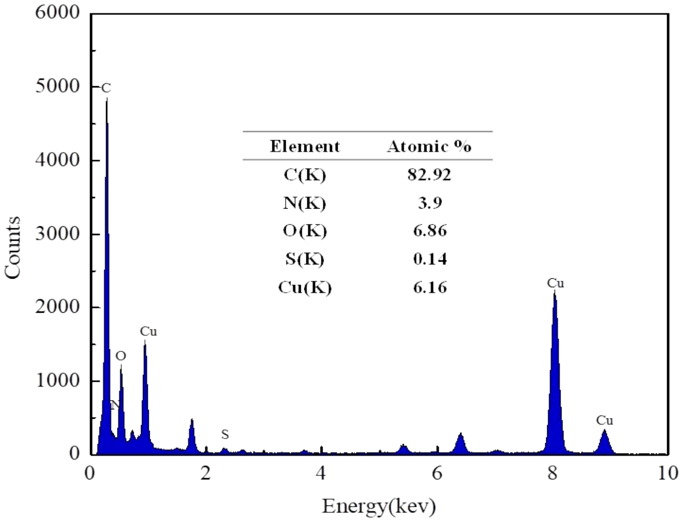


Figure S5 High magnification TEM image(a) and selected area electron diffraction (b) for poly(VCL-*co*-MAA)@CuS1 hybrid microgels.



Element	Atomic %
C(K)	82.92
N(K)	3.9
O(K)	6.86
S(K)	0.14
Cu(K)	6.16

Figure S6 The energy-dispersive X-ray spectroscopy of poly(VCL-*co*-MAA)@CuS10 hybrid microgels.

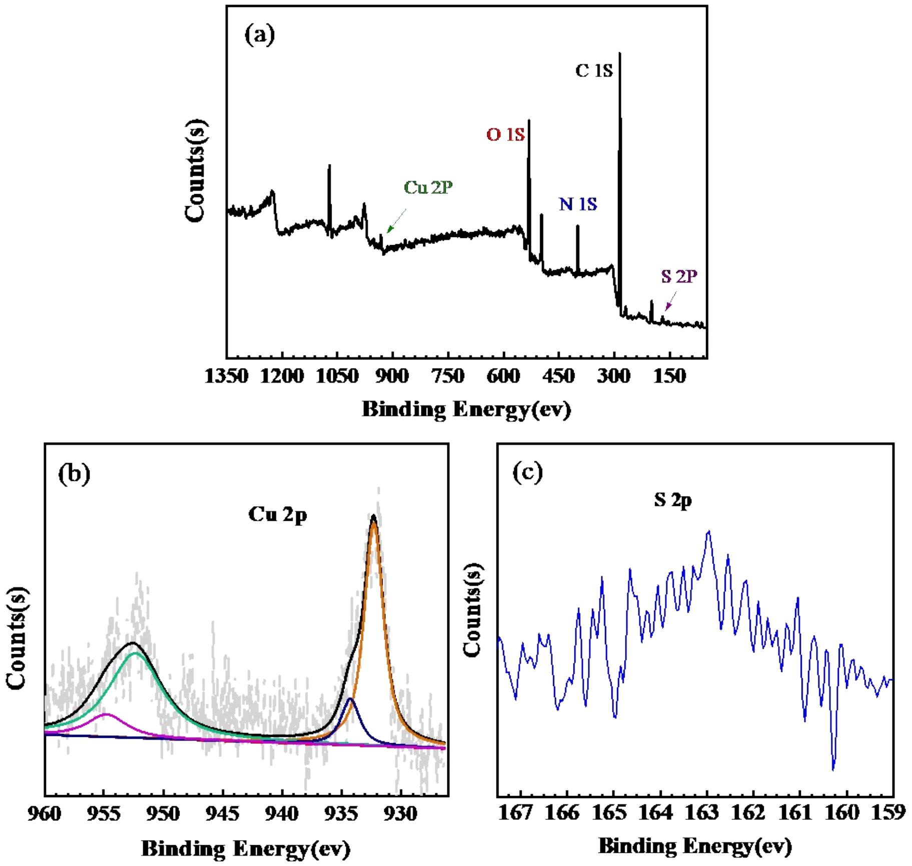


Figure S7 XPS survey spectrum (a), high resolution pectrum of Cu2p (b) and S2p (c) for poly(VCL-*co*-MAA)@CuS10 hyrbid microgels.

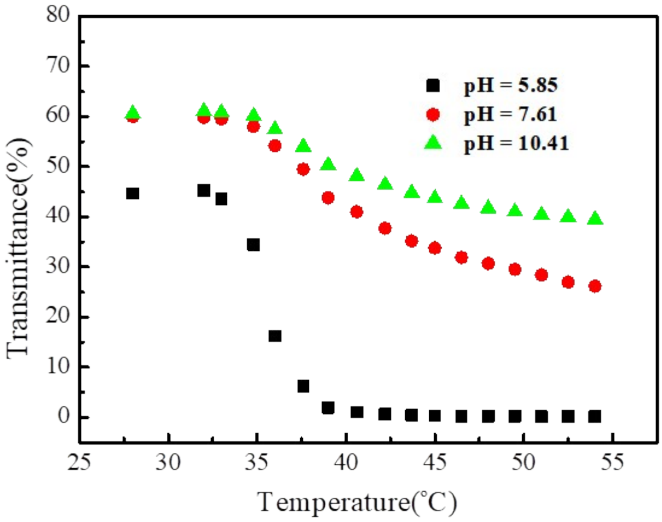


Figure S8 Curves of normalized transmittance *vs* temperature for the aqueous solution of poly(VCL-*co*-MAA)@CuS10 at pH 5.85, 7.61 and 10.41 with constant concentration of 1 mg/mL.

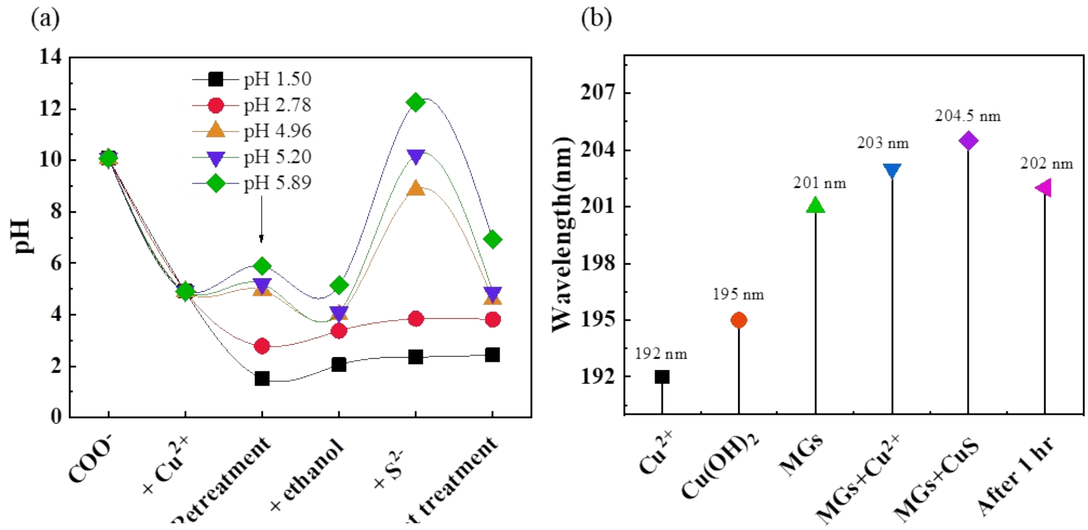


Figure S9 (a) the absorbance spectrum of the solution at different stages of feeding; (b) the absorbance spectrum of Cu atoms in different forms of ions, hydroxide, and sulfide in aqueous solution. The pH was adjusted at the step after adding Cu^{2+} ions to discuss the pH variation in the synthesis process.

The pH variation and the UV-vis absorption as each made step in the synthesis process were recorded in Figure 1b and 1c, respectively. As Cu^{2+} ions were added, the pH decreased and the absorption peak red-shifted, indicating the formation of complex between Cu^{2+} ions and carboxyl groups. And when no more acid or base was added, the addition of ethanol caused lower pH value due to its lower dielectric constant than that of water. Adding S^{2-} caused the increase of pH and the change of absorption, demonstrating that the form of CuS precursor resulted in releasing carboxyl groups from the complex with Cu^{2+} ions. We found that both excess acid and base (500 µL) would cause the fail in synthesizing nanocrystals. When acid or base were added after adding Cu^{2+} ions, the pH values varied in a similar pattern but ended with different final pH value. Only at the pH ranging from 3.81 to 5.87, the solutions were found dark green.

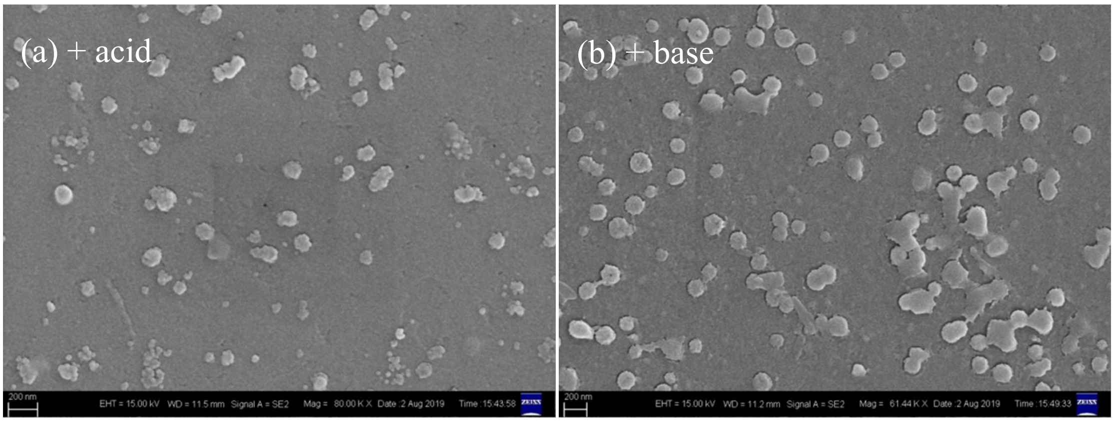


Figure S10 SEM images for the poly(VCL-*co*-MAA)@CuS10a (a) and poly(VCL-*co*-MAA)@CuS10b (b) hybrid microgels.

From Figure S8(a), abundant nanocrystals could be observed outside microgels, indicating the formation of nanocrystals occured outside microgels, instead of the inside of micorgels. Contrast to that, after the addition of base, bare nanocrystals could be found outside microgels while parts of microgels aggregated, indicating the relatively poorer colloidal stability.

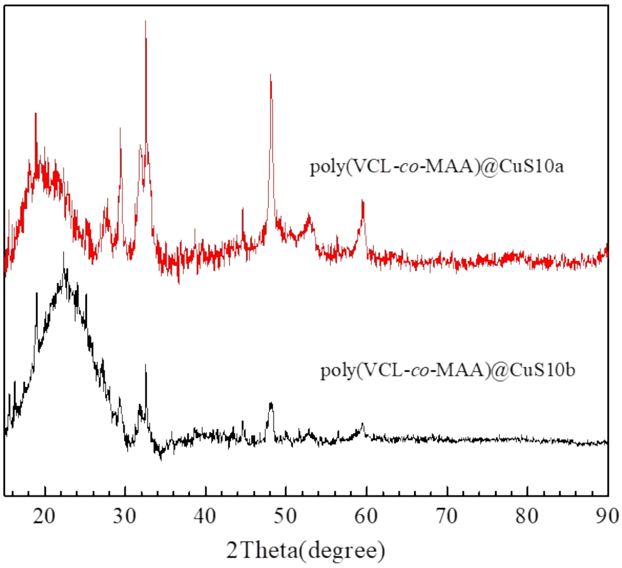


Figure S11 XRD patterns of the poly(VCL-*co*-MAA)@CuS10a (a) and poly(VCL-*co*-MAA)@CuS10b (b) hybrid microgels.

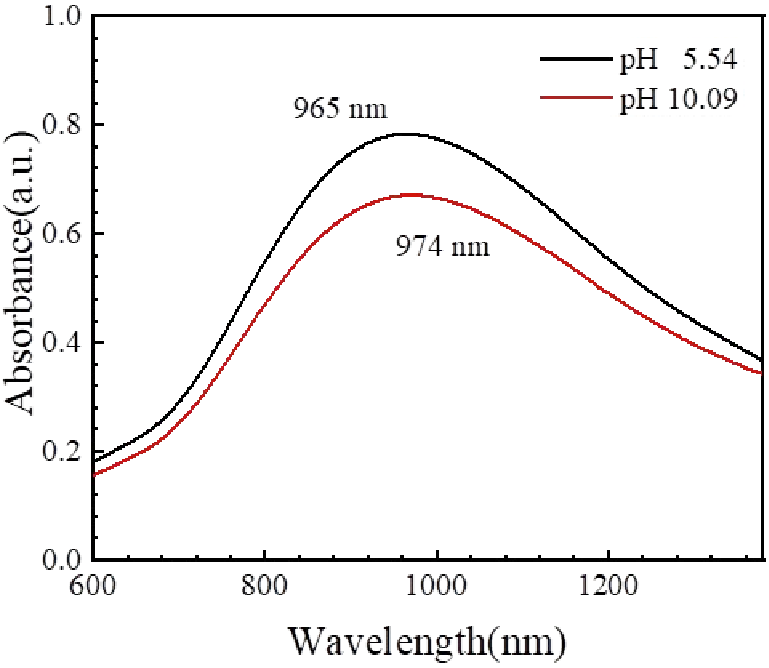


Figure S12 UV-vis-NIR spectra for poly(VCL-*co*-MAA)@CuS10 at the constant concentration of 0.2 mg/mL and different pH values of 5.54 and 10.09.

3. Table

Table S1 The experimental parameters in the preparation of hybrid microgels[*]

Name	poly(VCL-*co*-MAA)@CuS 1	poly(VCL-*co*-MAA)@CuS 3	poly(VCL-*co*-MAA)@CuS 5	poly(VCL-*co*-MAA)@CuS 10	poly(VCL-*co*-MAA)@CuS 10a	poly(VCL-*co*-MAA)@CuS 10b	poly(VCL-*co*-MAA)@CuS 10aa	poly(VCL-*co*-MAA)@CuS 10bb
$CuCl_2$(mg)	0.7245	2.1735	3.6225	7.2450	7.2450	7.2450	7.2450	7.2450
Vol$_{(acid)}$(μL)	0	0	0	0	50	0	500	0
Vol$_{(base)}$(μL)	0	0	0	0	0	50	0	500
Na^{2}S(mg)	1.0205	3.0615	5.1025	10.2050	10.2050	10.2050	10.2050	10.2050

[*] All samples were prepared with 24 mg pure microgels in the mixed solution of ethanol and water (12 mL, the volume ratio of ethanol and water 1:1) at 70°C for 12 hrs under stirring. The extra acid or base was added after adding Cu^{2+} ions to adjust the pH of the solutions. The added acid was adjusted to pH 1 with HCl; and the added base was adjusted to pH 13 with sodium hydroxide.

Reference

1. E. E. Makhaeva, H. Tenhu and A. R. Khokhlov, *Macromolecules*, 2002, **35**, 1870-1876.
2. S. M. Tehrani, W. Lin, S. Rosenfeld, G. Guerin, Y. Lu, Y. Liang, M. Drechsler, S. Foerster and M. A. Winnik, *Chemistry of Materials*, 2016, **28**, 501-510.
3. Q. W. Tian, J. Q. Hu, Y. H. Zhu, R. J. Zou, Z. G. Chen, S. P. Yang, R. W. Li, Q. Q. Su, Y. Han and X. G. Liu, *J Am Chem Soc*, 2013, **135**, 8571-8577.