Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Thermo-responsive Photoluminescent Silver Clusters/Hydrogel Nanocomposites for Highly Sensitive and Selective Detection of Cr(VI)

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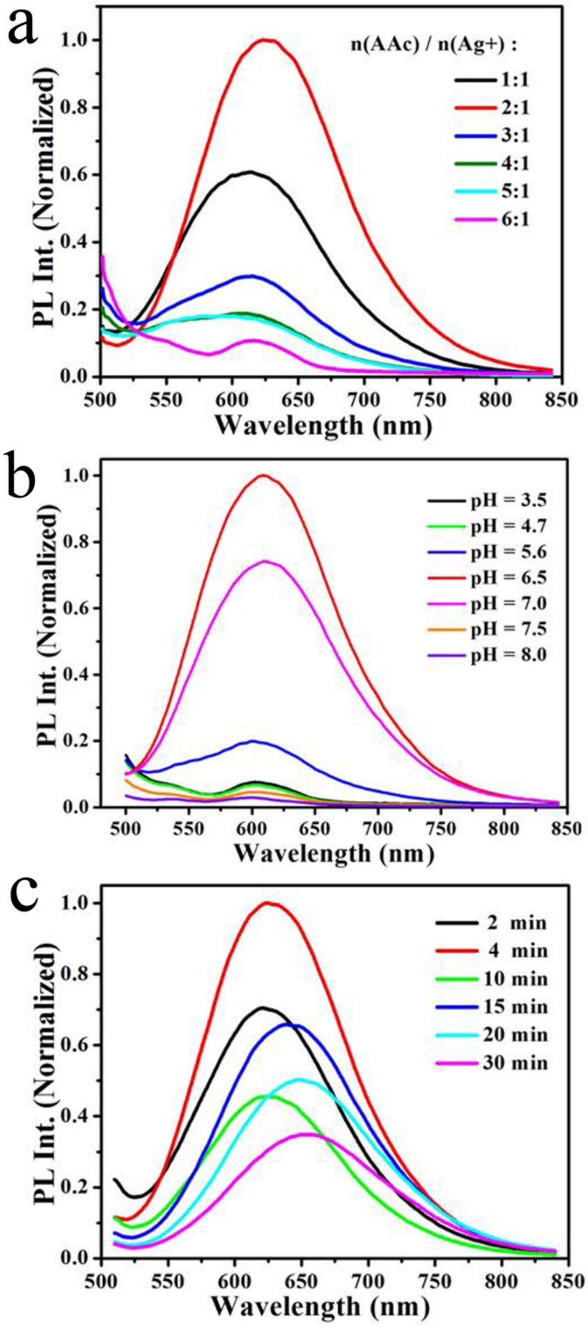

Figure S1. a) The PL spectra of the Ag clusters/p(NIPAM-*co*-AAc) hydrogel composites changes with the ratio of the molar ratios of $[AA]:[Ag^+]$. b) The PL spectra of the Ag clusters/p(NIPAM-*co*-AAc) hydrogel composites changes with the different pH values. c) The PL spectra of the Ag clusters/p(NIPAM-*co*-AAc) hydrogel composites changes with different UV illumination time. We can see, the optimized conditions for the synthesis of Ag clusters/p(NIPAM-*co*-AAc) hydrogel composites is the molar ratios of $[AA]:[Ag^+]$ is ～2:1, the pH value of solution is ～6.5 and the UV illumination time is ～4 minutes.

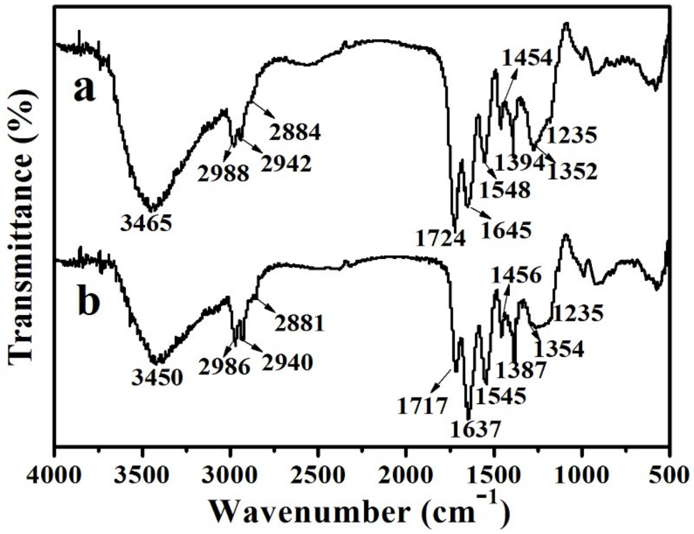

Figure S2. The FT-IR spectra of p(NIPAM-*co*-AAc) hydrogel submicron particles (a) and Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites (b).

As shown in Fig. S2a, the peaks at 2988 cm^{-1}, 2942 cm^{-1} and 2884 cm^{-1} are attaributed to the C-H stretching vibrations of methyl and ethyl, and the asymmetry and symmetry bending vibrations of $-CH_3$ appear at 1454 cm^{-1}, 1394 cm^{-1} and 1352 cm^{-1}, respectively. The bands of amide I at 1645 cm^{-1} and amide II at 1548 cm^{-1} are considered to be from the C=O stretching and the N-H in plane bending, respectively, while the peak at 1235 cm^{-1} corresponds to the C-N stretching vibration of amide. The carbonyl stretching bond attributed to the carboxylic acid group of AAc units is observed at 1724 cm^{-1} in the hydrogel particles. The FT-IR spectra of Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites (Fig. S2b) looks very similar with the FT-IR spectra of p(NIPAM-*co*-AAc) hydrogel submicron particles (Fig. S2a), indicating that the embedded Ag nanoclusters in hydrogel polymer networks do not have much effect on the surface structure of p(NIPAM-*co*-AAc).

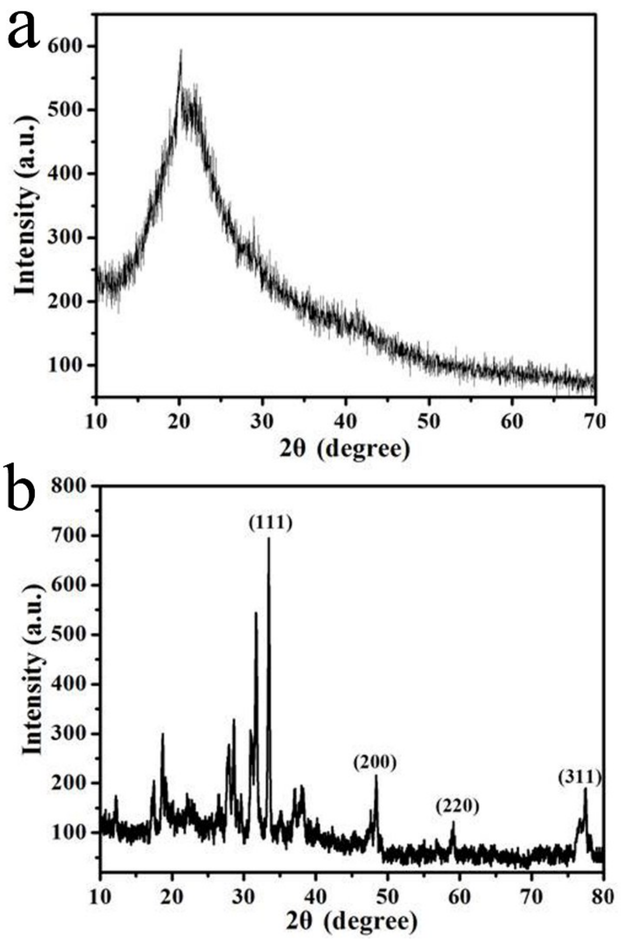

Figure S3. The XRD pattern of p(NIPAM-co-AAc) hydrogel submicron particles (a) and Ag clusters/p(NIPAM-co-AAc) hydrogel nanocomposites (b).

As shown in Fig. S3a, the hydrogel particles exhibit a board peak located at 22.7^{o} of the X-ray diffraction (XRD) pattern, indicating disordered microstructure. In Fig. S3b, the XRD pattern of the Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites also show the board diffraction peaks at 22.7^{o}. Moreover, another four diffraction peaks at $2\theta = 38.1^{o}$, 44.3^{o}, 64.6^{o}, and 77.3^{o} have been detected in composites samples, which are corresponding to (111), (200), (220) and (311) bragg reflections of silver, respectively. These results are in accord well with the previous reports (Advanced Materials, 2005, 17(19): 2336-2340; Chemistry: A European Journal, 2010, 16(46):13698-13705).

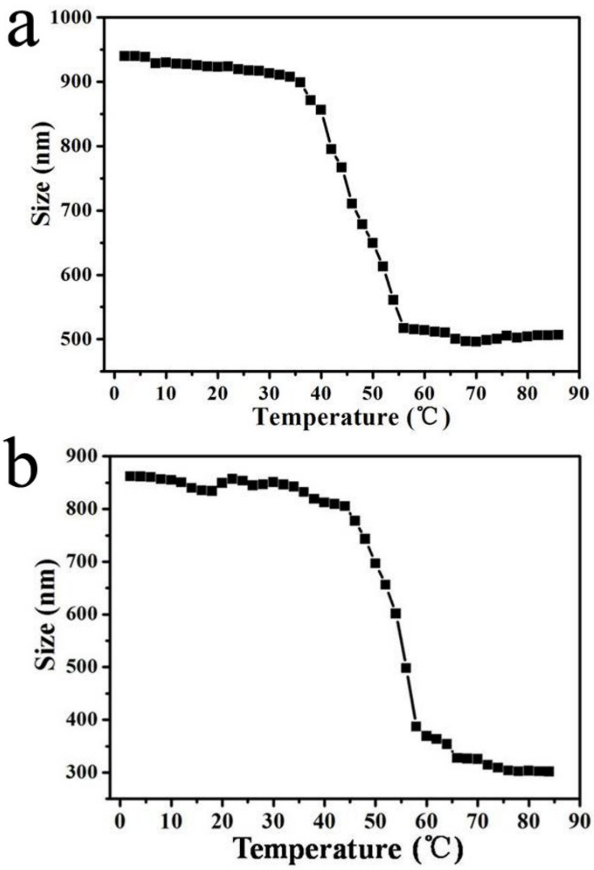

Figure S4. DLS measurements of the p(NIPAM-co-AAc) hydrogel submicron particles (a) and Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites (b) in water, collected during the increase in temperature.

Dynamic light scattering was used to examine particle sizes at different temperatures. During the temperature increase in the range of 2−85 °C, both p(NIPAM-*co*-AAc) hydrogel submicron particles and Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites exhibited a noticeable decrease in size. The size of p(NIPAM-*co*-AAc) hydrogel submicron particles changed from 947 nm to 520 nm, while the Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites changed from 872 nm to 520 nm and 336 nm. The lower critical solution temperature (LCST) of the two particles was in the range of 40−55 °C.

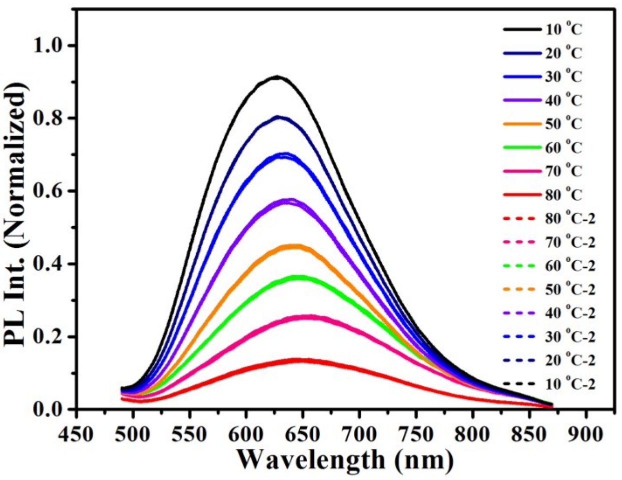

Figure S5. Normalized PL spectra of the Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites with the temperature increasing from 10 to 80 °C, and subsequently decreasing from 80 to 10 °C.

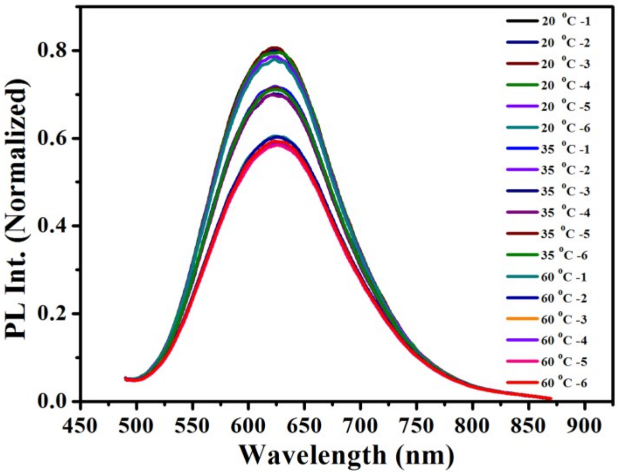

Figure S6. Normalized PL spectra of Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites at different temperatures (20, 35 and 60 °C) for six cycles. The PL spectra were obtained with the excitation at 500 nm.

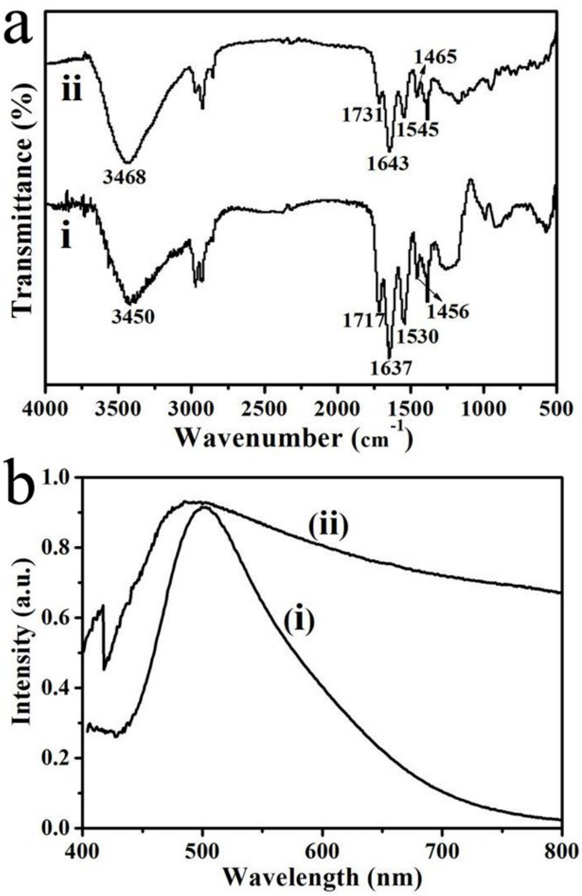

Figure S7. (a) The FT-IR spectra of Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites (i) and the nanocomposites binding with Cr(VI) (ii). (b) The UV-vis absorption spectra of Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites (i) and the nanocomposites binding with Cr(VI) (50 ppm) (ii).

As shown in Fig. S7a, in the spectrum i, the characteristic peaks at 3450 cm^{-1} and 1530 cm^{-1}, correspond to the N-H. Note that the characteristic peaks at 3450 cm^{-1} and 1530 cm^{-1} (in spectrum i) moved to 3468 cm^{-1} and 1545 cm^{-1} (in spectrum ii), respectively. In spectrum i, the characteristic peak at 1637 cm^{-1} corresponds to the C=O. Note that the characteristic peak at 1637 cm^{-1} (in spectrum a) moved to 1643 cm^{-1} (in spectrum ii). In the spectrum i, the characteristic peaks at 1717 cm^{-1} corresponds to the –COOH. Note that the characteristic peak at 1717 cm^{-1} (in spectrum i) moved to 1731 cm^{-1} (in spectrum ii). All movements of the characteristic peaks suggest the Cr(VI) ions have been binding with the Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites.

As shown in Fig. S7b, the UV-vis absorption peak of Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites was focused on 500 nm (spectrum i). After the Cr(VI) aqueous solution added, the UV-vis absorption spectrum existed blue shift phenomena with absorption peak at 482 nm (spectrum ii). It suggested that the Cr(VI) ions have been binding with the Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites and the electrons transfer from the Ag clusters to Cr(VI) ions.

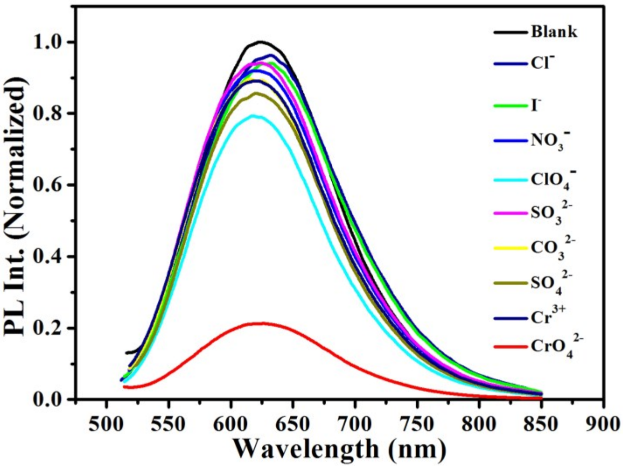

Figure S8. Normalized PL emission spectra of the Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites in the presence of different ions (Cl^-, I^-, NO_3^-, ClO_4^-, SO_3^{2-}, CO_3^{2-}, SO_4^{2-}, Cr^{3+} and CrO_4^{2-}) in aqueous solution at the same concentration of 50 ppm.

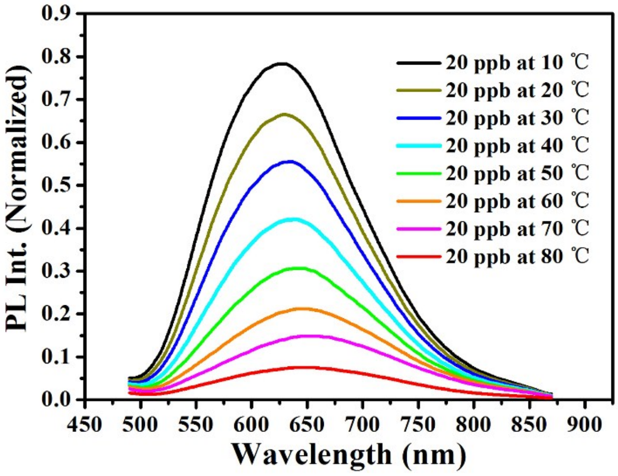

Figure S9. The normalized PL spectra (λ_{ex} = 500 nm) of Ag clusters/p(NIPAM-*co*-AAc) hydrogel nanocomposites in the presence of 20 ppb Cr(VI) at different temperature (10 - 80 ^{o}C).