Supporting Information

Transition from Nanoparticles to Nanoclusters: Microscopic and Spectroscopic Investigation of Size-Dependent Physicochemical Properties of Polyamine-Functionalized Silver Nanoclusters

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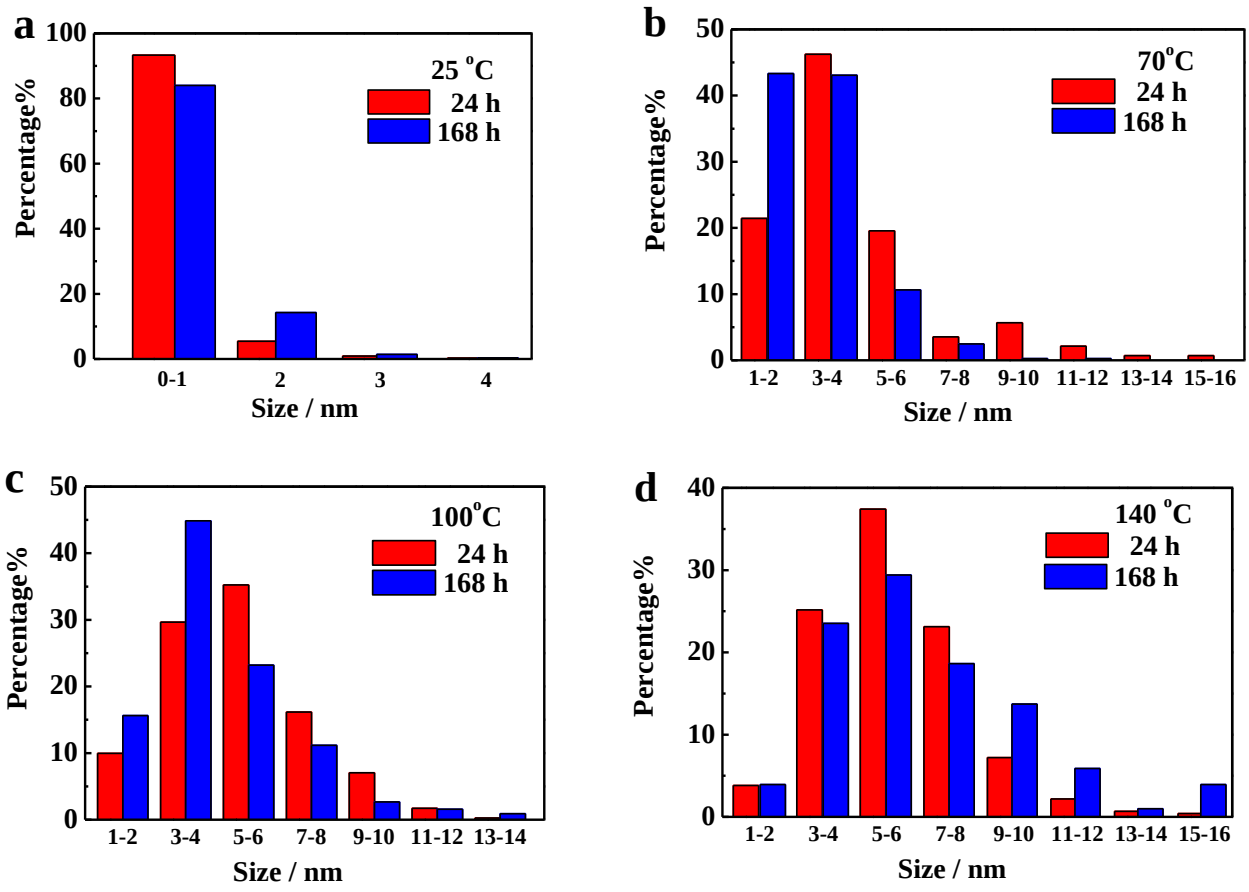

Figure S1. Size transition of PEI-capped Ag particles kept at 25 ℃ (a) and prepared by a heating process at 70 (b), 100 (c), and 140 °C (d) for 10 min and then a cooling process at ambient temperature for 24 and 168 h.

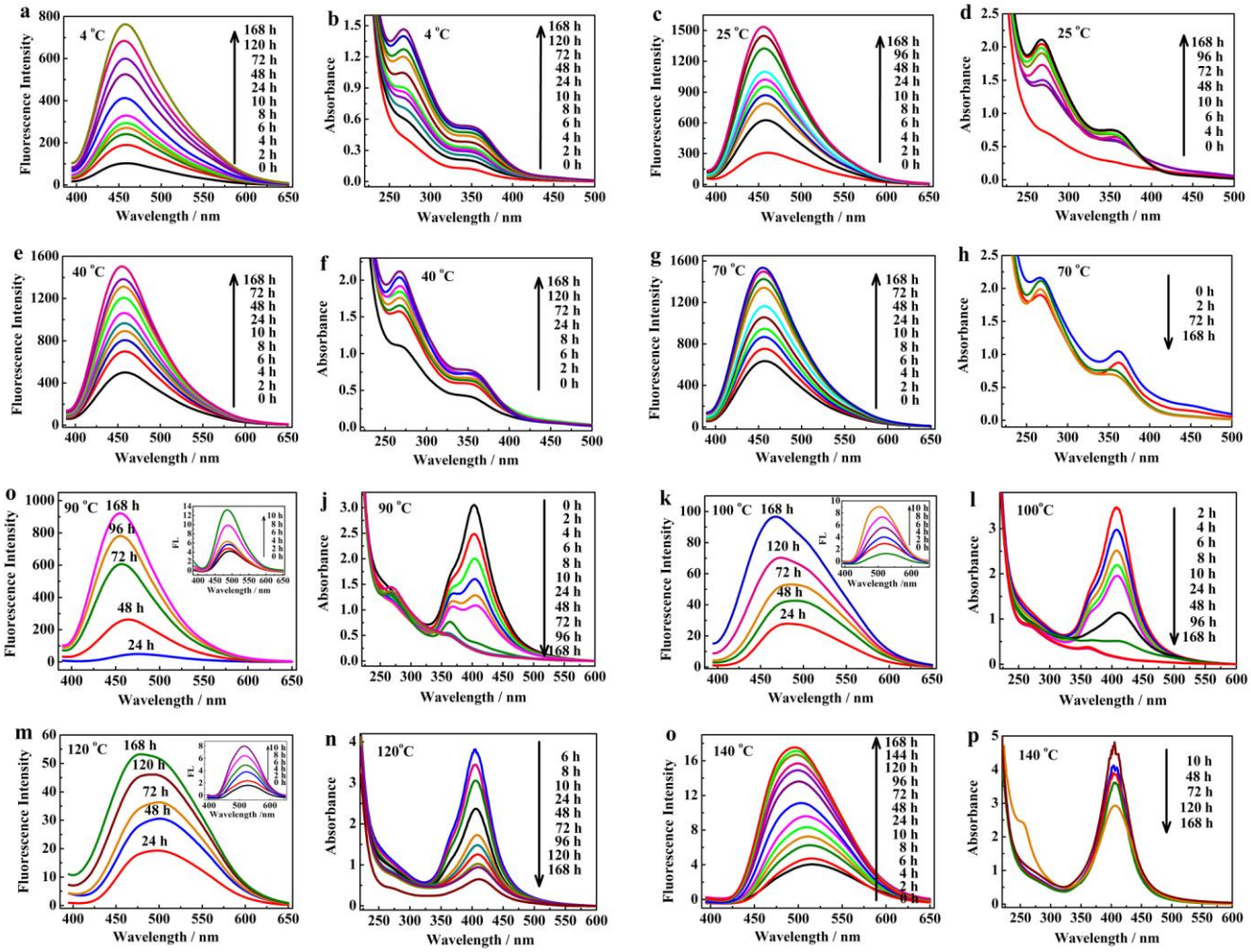

Figure S2. Time evolution of fluorescence and UV–vis spectra of PEI-capped Ag particles kept at 4 (a, b) and 25 ℃ (c, d), and prepared by a heating process at 40 (e, f), 70 (g, h), 90 (i, j), 100 (k, l), 120 (m, n), and 140 ℃ (o, p) for 10 min and then a cooling process to ambient temperature.

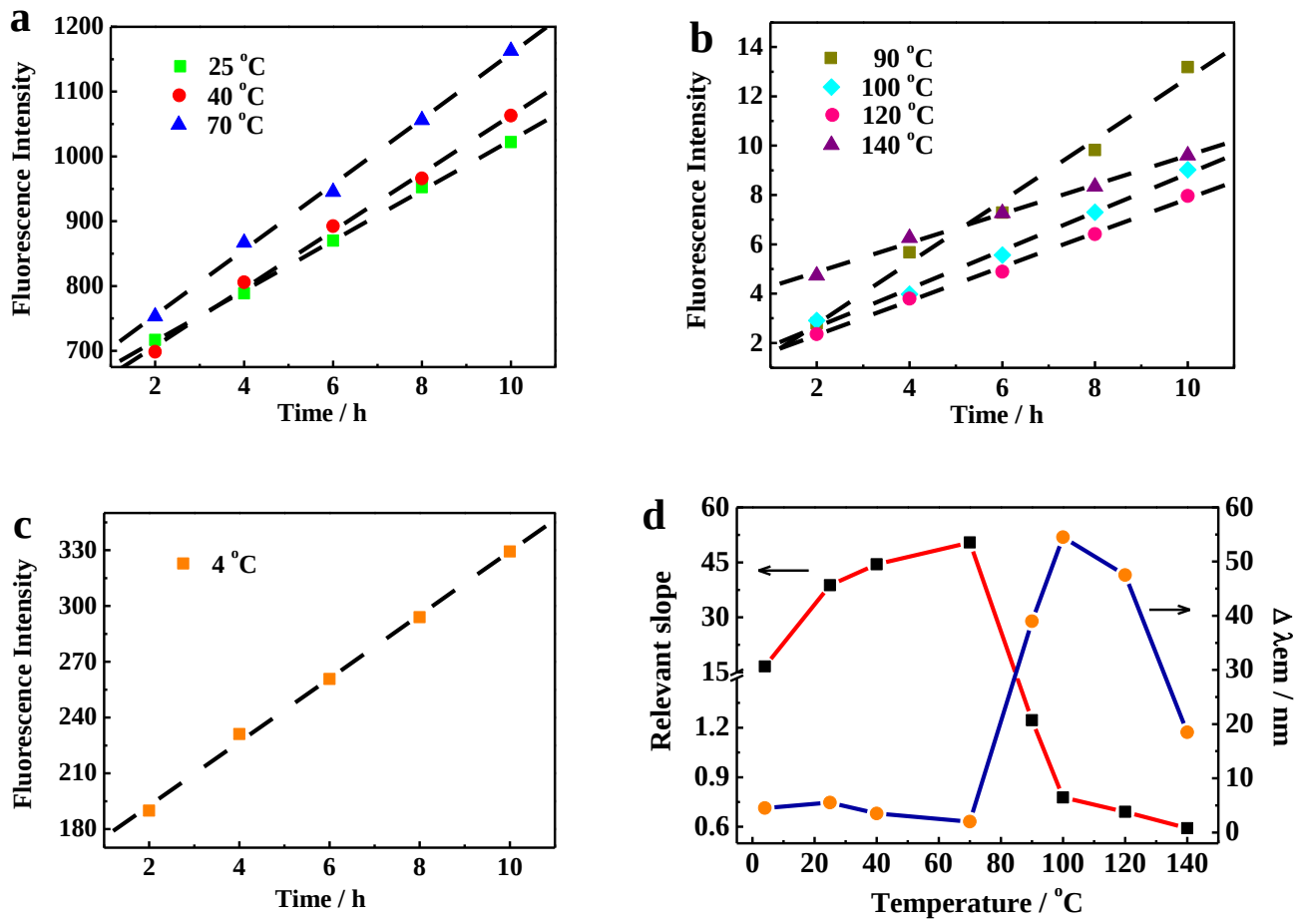

Figure S3. Correlations of fluorescence intensities of PEI-capped Ag particles prepared by a heating process at different temperatures for 10 min and then a cooling process to ambient temperature with time from 2 to 10 h: (a) 25, 40, and 70 °C; (b) 90, 100, 120, and 140 °C; (c) 4 °C; (d) the increase rate of fluorescence intensities (left) (relevant slopes about the linear equations of different temperatures from 2 to 10 h) and the shift degree of the maximum emission wavelength at different temperatures (right) (Δλem expressed as the differences of the maximum emission wavelength between 0 and 168 h).

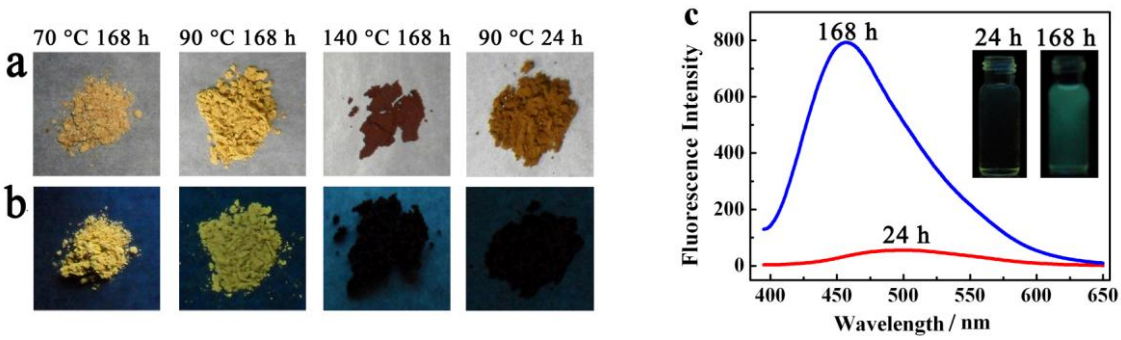

Figure S4. Photographs of PEI-capped Ag particles in solid state synthesized by heating at 70, 90 and 140 °C for 10 min and then kept at ambient temperature for 24 and 168 h: under visible light (a) and UV light (b). Note that the fluorescence intensity in solid state for the sample treated at 90 °C was very low at 24 h, but it recovered gradually over time and expressed yellow color under UV light after 168 h; however, when the powder was dissolved in water, the fluorescence returned to blue color again (c).

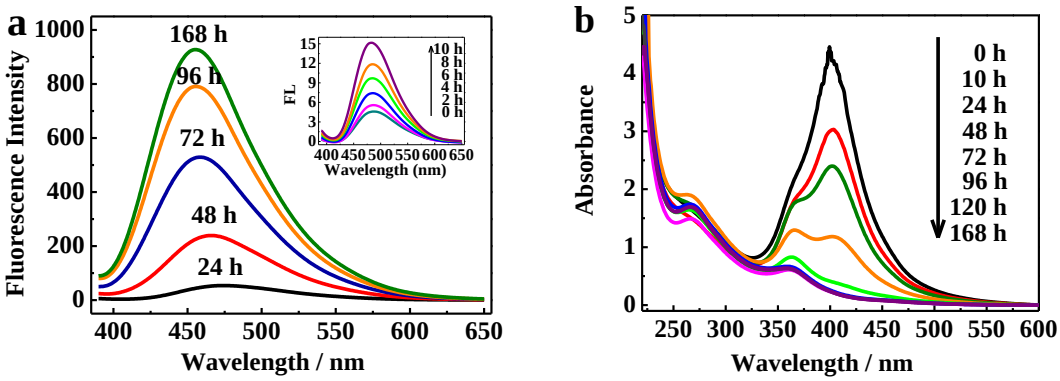

Figure S5. Time evolution of fluorescence (a) and UV–vis spectra (b) of PEI-capped Ag particles prepared by a heating process at 70 °C for 40 min and then a cooling process to ambient temperature.

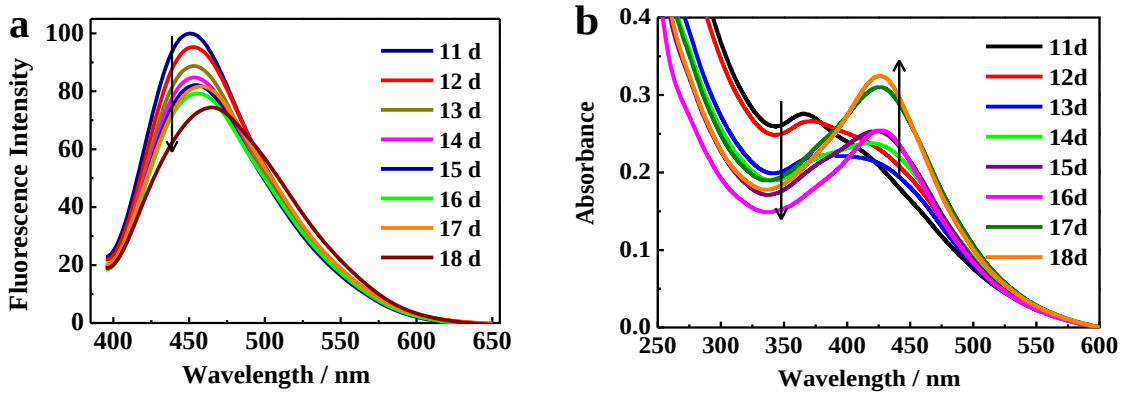

Figure S6. The stability of PEI-capped Ag particles prepared by heating at 100 °C for 10 min and then kept at ambient temperature: the time evolution of fluorescence spectra (a) and UV–vis spectra (b) from 11 to 18 days.

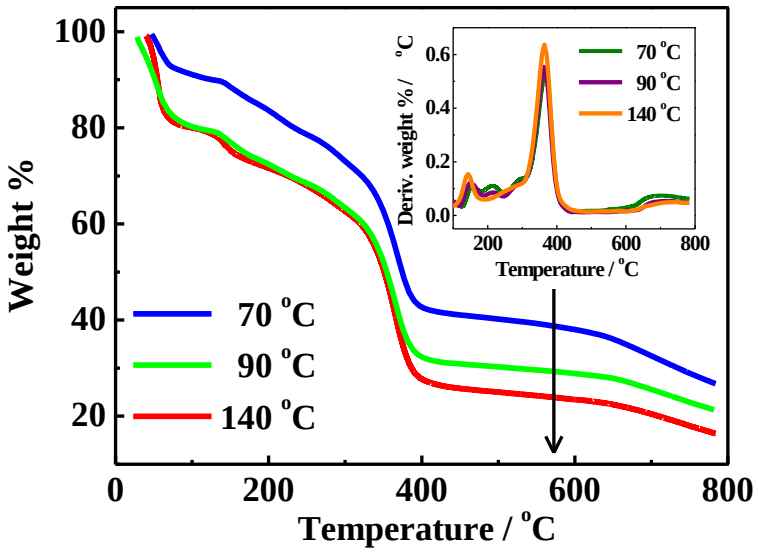

Figure S7. Comparison of TGA curves of PEI-capped Ag particles prepared by a heating process at 70, 90 and 140 °C for 10 min and then a cooling process to ambient temperature for 168 h. The decomposition of PEI occurred at ~350 °C. The slow weight loss before 250 °C can be attributed to the removal of trapped water.[S1]

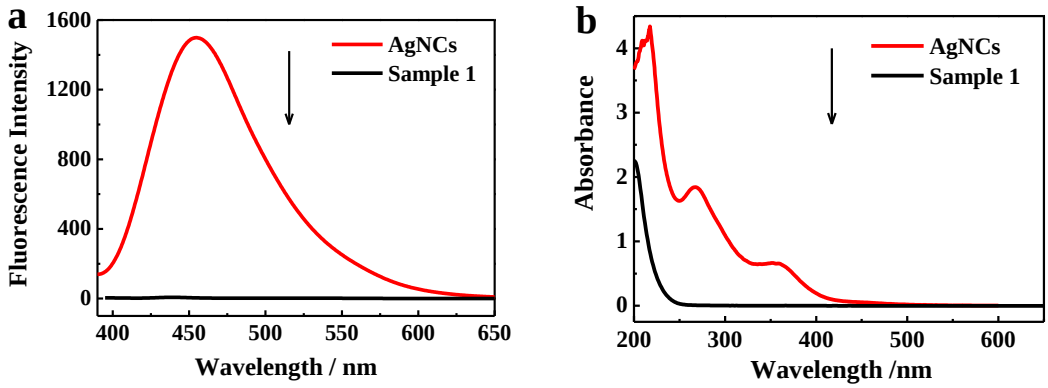

Figure S8. Comparison of fluorescence and UV–vis spectra of sample 1 with PEI-capped Ag nanoclusters (AgNCs). Sample 1 was prepared according to the synthetic method of PEI-capped Ag nanoclusters except for addition of $AgNO_3$.

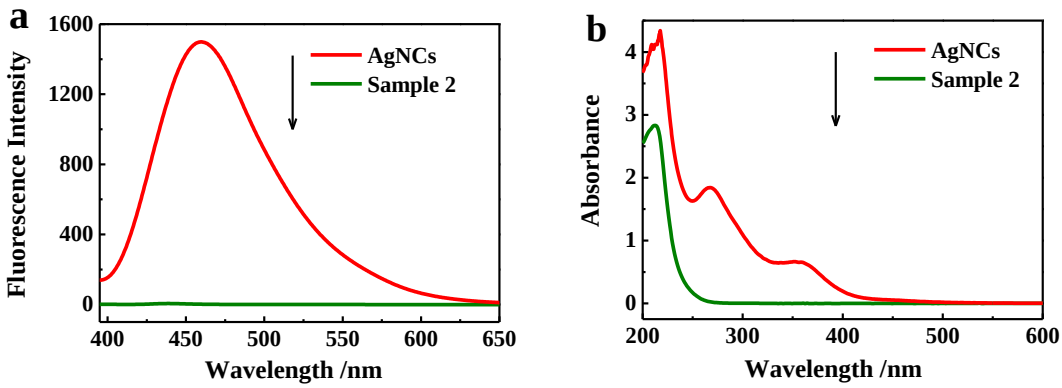

Figure S9. Comparison of fluorescence emission and UV–vis spectra of sample 2 with PEI-capped Ag nanoclusters (AgNCs). Sample 2 was prepared according to the synthetic method of PEI-capped Ag nanoclusters except for addition of formaldehyde.

References

(S1) Zhang, J. X.; Xu, Q.; Ye, F.; Lin, Q. L.; Jiang, D. L.; Iwasa, M. Effect of Citric Acid on the Adsorption Behavior of Polyethyleneimine (PEI) and the Relevant Stability of SiC Slurries. *Colloid. Surface. A* **2006**, *276*, 168–175.