Photogeneration of Fluorescent Silver Nanoclusters in Polymer Microgels**

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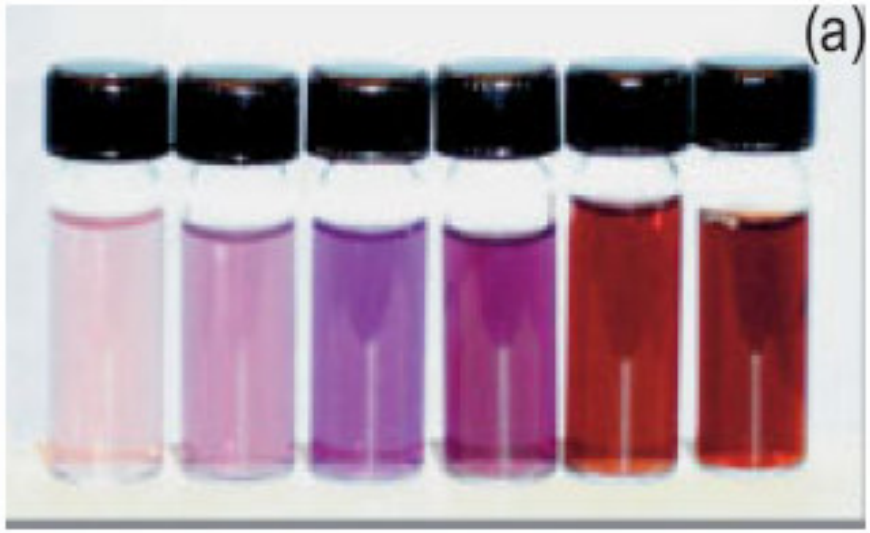
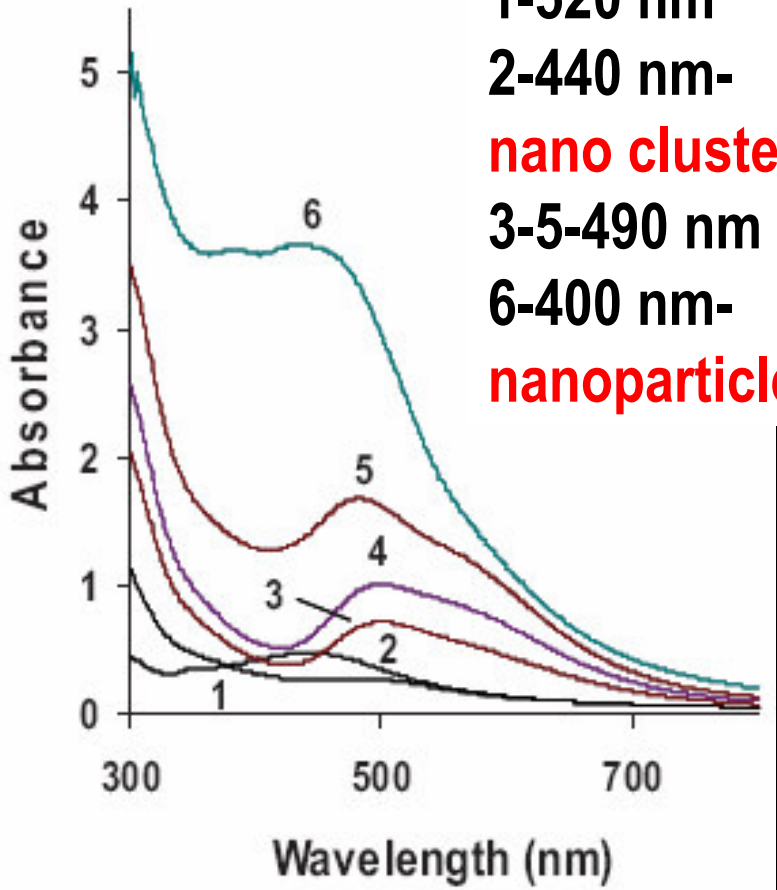
- Small clusters - Dimension equals to the Fermi wavelength of electron.
- Highly fluorescent - Applications as stable chromophores in various fields.
- Non-fluorescent metal nanoparticles were synthesized in polymer templates.
- Polymer microgels – simple synthesis, easy functionalization, tuning dimension from nanometer to micrometers and undergo large volume transitions with pH, temperature, ionic strength etc.
- Reports the synthesis of stable fluorescent silver nanoclusters inside microgel poly(N-isopropylacrylamide-acrilicacid-2-hydroxyethyl acrylate) by uv irradiation.

- Poly(NIPAM-AA-HEA) microgel average diameter-220 nm at 25°C, pH=3.92
- 0.2 M $AgNO_3$ added to microgel-$[Ag^+]$/[COOH] =1:1
- Mixed for 30 minutes, dialysed and subjected to uv radiation (365 nm)

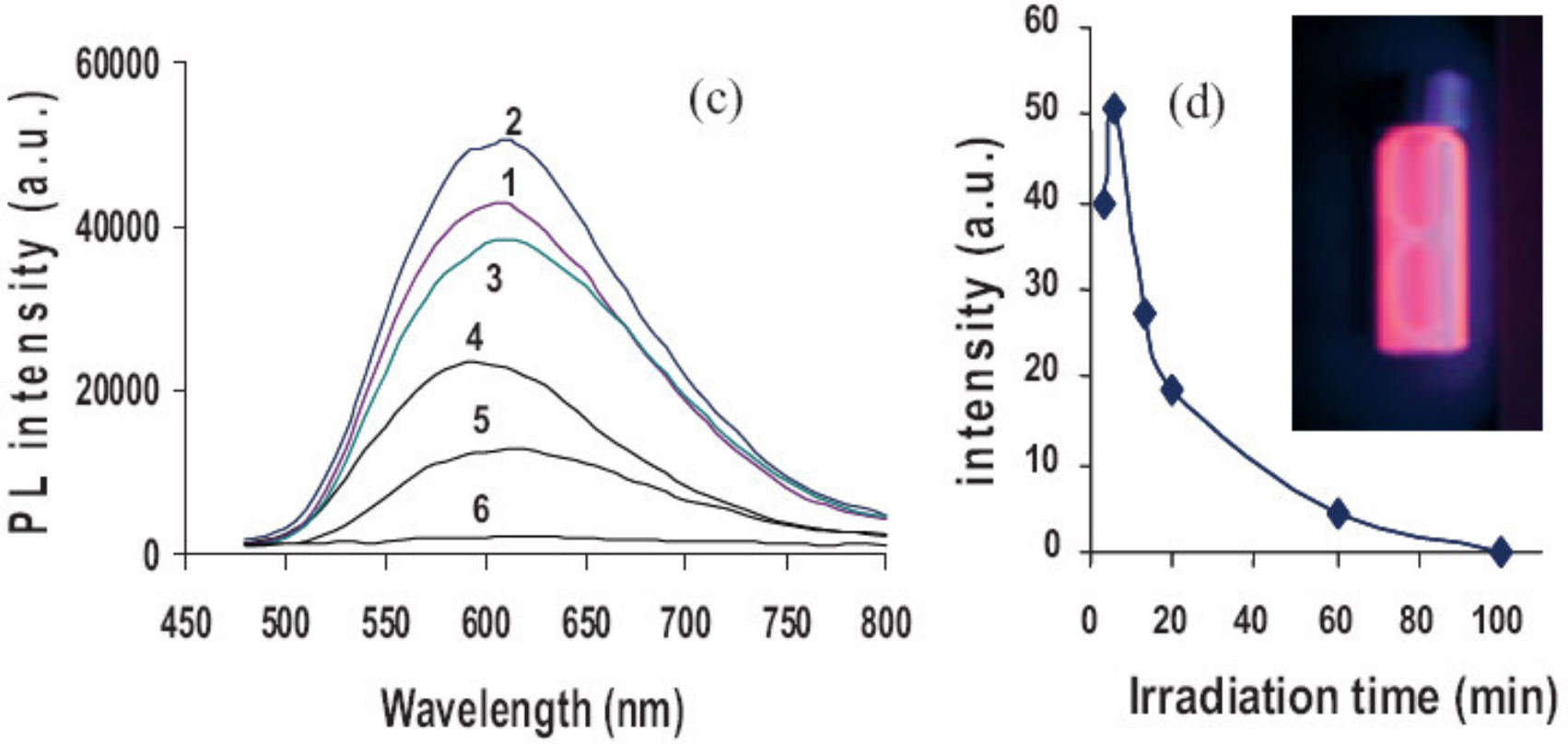


Colourless-pink-purple-dark red



1-520 nm
2-440 nm-
nano cluster
3-5-490 nm
6-400 nm-
nanoparticle

Figure 1. Typical appearance (a) and UV-vis spectra (b) of poly(NIPAM-AA-HEA) microgel dispersions after mixing with Ag^+ ions and UV-irradiating them for different time intervals, in minutes: 1) 3; 2) 6; 3) 13; 4) 20; 5) 40; 6) 100. In (a), dispersions from left to right correspond to spectra 1–6; in (b) λ_{irr} = 365 nm,



pH 8.14. c) Evolution of PL spectra and d) PL intensity of Ag nanoclusters photogenerated in microgels. UV-irradiation time in minutes: 1) 3, 2) 6, 3) 13, 4) 20, 5) 40, 6) 100; pH 8.14, $\lambda_{irr} = 365$ nm, $\lambda_{ex} = 450$ nm. The inset shows a photoluminescent hybrid microgel obtained after 10 min UV irradiation.

- UV irradiation generates H and OH radicals which reduce Ag^{+} to Ag^{0} leading to the formation of silver clusters.

- Prolonged irradiation leads to the formation of non-fluorescent nanoparticle

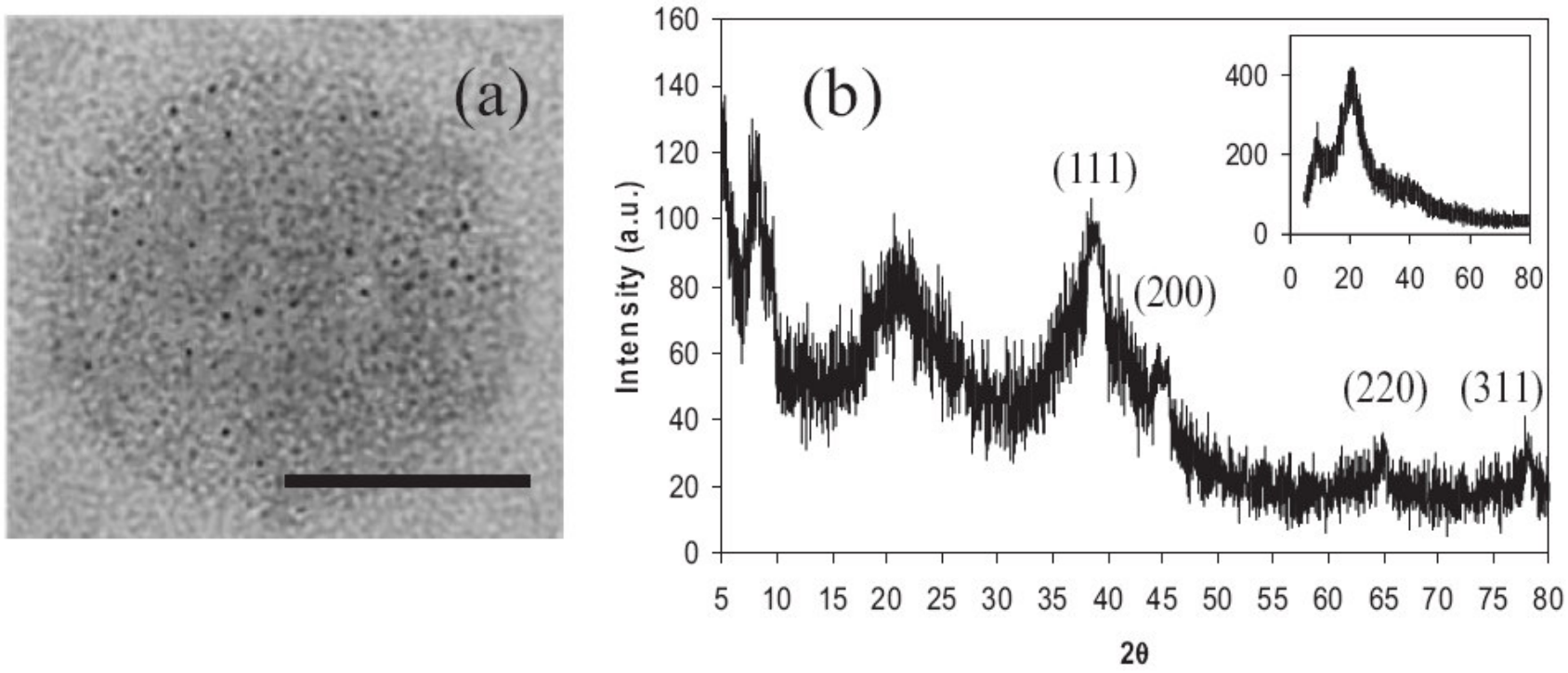


Figure 2. a) Typical TEM image of hybrid microgel obtained after 100 min UV irradiation of Ag^+ ions sequestered by microgels. Scale bar is 100 nm, b) XRD pattern of a hybrid poly(NIPAM-AA-HEA) microgel UV-irradiated for 100 min. The inset in (b) is an XRD pattern of dried poly(NIPAM-AA-HEA) microgel particles used for the synthesis of Ag nanoclusters.

Control experiments

No fluorescence

- Irradiation of $AgNO_3$ solution in the absence of microgel.
- Irradiation of $AgNO_3$ mixed with poly NIPAM and poly (NIPAM-HEA)
- Chemical reduction of $AgNO_3$ inside poly (NIPAM-HEA) by $NaBH_4$.
- Photoreduction of $AgNO_3$ with aq. Solution of poly methacrylic acid and PAA.

Fluorescence

- Irradiation of $AgNO_3$ with poly NIPAM-AA.

Acrylic acid play a crucial role in the generation of silver nanoclusters

- Attraction between Ag^{+} and COO^{-} of AA
- Varying the degree of ionization of AA and size of microgel
- Elecrostatic repulsion between the charged hybrid microgel controlls colloidal stability

Synthesis of nanoclusters at various pH

- pH 3.92-4.41 - low PL of nanocluster-AA not fully deprotonated and microgel did not aquire fully swollen shape

- pH 5.02-8.34 - high PL-AA completely deprotonated and microgel acquired fully swollen shape.

- pH 8.94 -no PL-AgOH pptes.

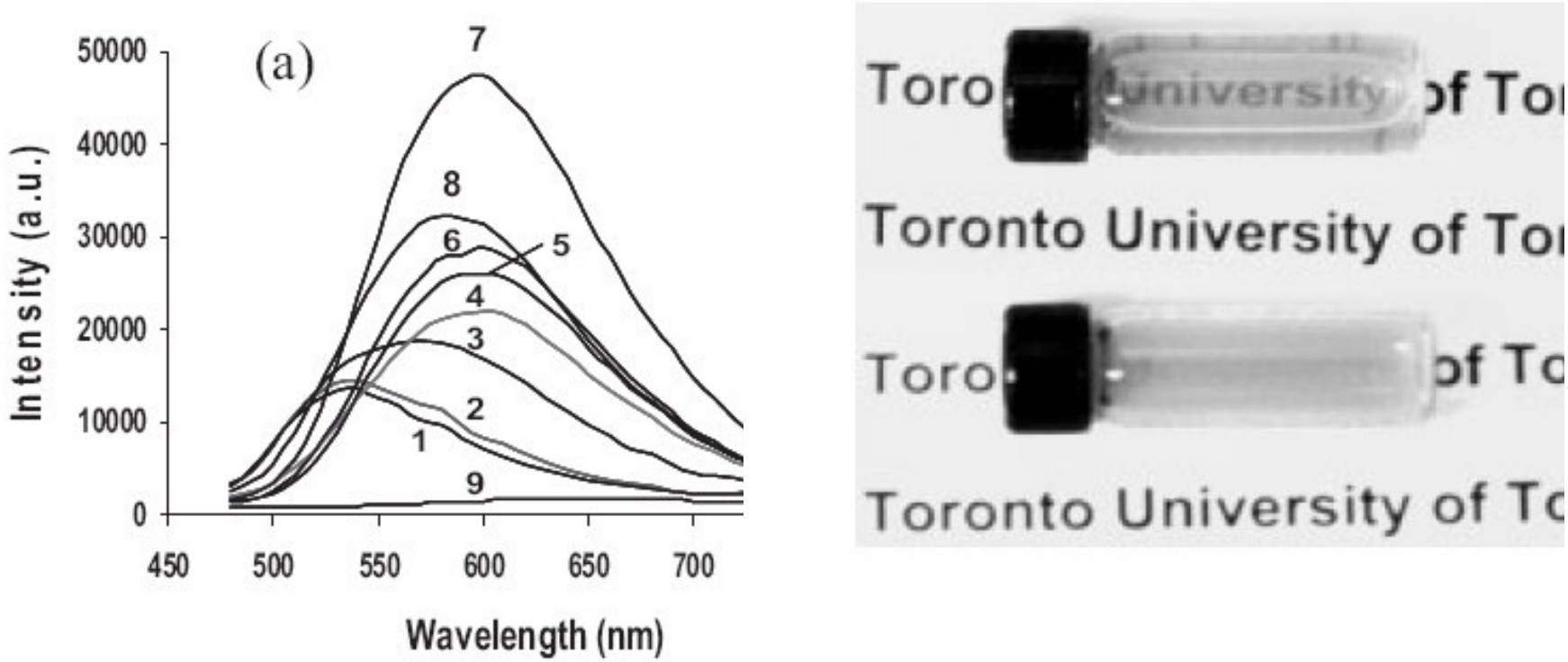


Figure 3. a) PL spectra of Ag nanoclusters photoreduced in the microgel interior at different values of pH: 1) 3.92; 2) 4.41; 3) 5.04; 4) 5.55; 5) 6.21; 6) 7.52; 7) 8.04; 8) 8.34; 9) 8.89. $\lambda_{irr} = 365$ nm; $\lambda_{ex} = 450$ nm. b) Change in microgel transparency prior to (top) and after (bottom) heating from 25 to 38 °C.

Summary

In summary, we described a simple approach to hybrid fluorescent microgels via photoactivated synthesis of Ag nanoclusters in the microgel hosts. The role of microgels was twofold: i) they allowed for the controlled nucleation and growth of very small nanoclusters; and ii) they protected these nanoclusters from interactions with PL quenchers in the bulk dispersion. Fluorescent microgels were produced only in a particular pH window, bound by the value of the solubility product of AgOH and efficient ionization of AA residues. Since hybrid fluorescent microgels remained stimuli responsive, they have potential for all the typical applications of polymer microgels, such as drug delivery,[8,21] fabrication of photonic crystals[9] and chemical and biosensing.[22]