Synthesis of Highly Fluorescent Metal (Ag, Au, Pt, and Cu) Nanoclusters by Electrostatically Induced Reversible Phase Transfer

Xun Yuan,[†] Zhentao Luo,[†] Qingbo Zhang,[†] Xinhai Zhang,[‡] Yuangang Zheng,[‡] Jim Yang Lee,[†] and Jianping Xie

 Department of Chemical and Biomolecular Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260
Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602



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Introduction

• Noble metal nanoclusters : ultrafine size, excellent photostability, and low toxicity.

Phase transfer

Phase-transfer methods employ a system consisting of two mutually-insoluble phases, either liquid-liquid or solid-liquid, in which inorganic ions are transported into the organic phase by formation of a complex soluble in organic solvents.



Quaternary ammonium and phosphonium salts are commonly used as phase transfer agents

• Purity and Stability of clusters - for diverse applications

In this paper:

• Highly fluorescent Ag, Au, Pt, and Cu NCs synthesised using a mild etching environment by the electrostatically induced phase transfer of thiol-protected metal NCs from an aqueous solution to an organic phase.

 Using Ag as a model metal, a simple and fast (total synthesis time < 3 h) phase transfer cycle (aqueous to organic (2 h incubation) to aqueous) can process originally polydisperse, nonfluorescent, and unstable Ag NCs into monodisperse, highly fluorescent, and extremely stable Ag NCs in the same phase (aqueous) and protected by the same thiol ligand.

Schematic illustration of the process to generate highly fluorescent metal NCs by a phase transfer cycle (aqueous → organic (incubation) → aqueous).





Excitation (dotted lines) and emission (solid lines) spectra of the fluorescent Ag (a), Au (b), Pt (c), and Cu (d) NCs in toluene. The insets show photographs of original NCs in water and in toluene. TEM images of the fluorescent Ag (a), Au (b), Pt (c), and Cu (d) NCs in toluene

Photographs of fluorescent Ag NCs synthesized in 500 mL bottle under normal (a) and UV (b) light.







(a) Optical absorption (solid lines) and emission (dotted lines) spectra of the orginal GSH-protected Ag NCs (black lines) and the returned fluorescent GSH-protected Ag NCs (red lines) in the aqueous phase. The inset shows photographs of the returned fluorescent GSH-protected Ag NCs in the aqueous phase under visible and UV light. (b) XPS spectrum of the returned fluorescent GSH-protected Ag NCs (red line) and GSH Agl complex intermediates (black line). (c) Time-resolved fluorescence lifetime analysis of the returned fluorescent GSH-protected Ag NCs (red line) and GSH Agl fluorescent GSH-protected Ag NCs (black line). The red line is a biexponential fit of the experimental data.



FTIR spectra of original non-fluorescent GSHprotected Ag NCs in water (black line), fluorescent CTAB-coated GSH-protected Ag NCs in toluene (red line), and the final product of fluorescent GSH-protected Ag NCs in water (blue line).

TEM images and size histograms (insets) of the returned fluorescent Ag NCs (a) and original non-fluorescent Ag NCs (b) in the aqueous phase. The inset in (a) shows a STEM image of the returned fluorescent Ag NCs.



Ag:SG ratio



Stability



Photoexcitation (dotted lines) and photoemission (solid lines) of the final fluorescent Ag NCs in the aqueous phase freshly prepared (black lines) and after 6 months storage (red lines) at 4 °C without N_2 protection.

Time-resolved evolution of optical absorption spectra of the original Ag NCs (a) in water and in toluene (c). (b) Photographs of the original Ag NCs in water immediately after preparation (item 1) and after incubation for 2.5 h at room temperature (item 2); Ag NCs tranfered to toluene immediately after preparation (item 3) and after incubation in toluene for 2 h at room temperature (item 4).



A bromide free phase transfer agent (dodecylamine (DDA) can also be used



(a) Optical absorption spectrum of the GSH-protected Ag NCs in toluene immediately after transfer by DDA. The inset shows photos of DDA-coated GSH-protected Ag NCs in toluene immediately after preparation. (b) Excitation (dotted line) emission (solid line) spectra of the fluorescent DDA-coated GSH-protected Ag NCs in toluene (after 2 h of incubation). The inset shows photos of the fluorescent Ag NCs in toluene under visible (item 1) and UV (item 2) light.

Versatility – designer clusters

Thiol ligands can be designed to introduce additional functionalities to the fluorescent metal NC surface - for biolabeling and bioimaging applications.

- glutathione (GSH) is a tripeptide with glutamic acid, cysteine, and glycine residues.
- Several Ag NCs with simple tripeptides, X cysteine X (X indicates any natural amino acid) was synthesized.
- Three types of residues were used for X:
- (a) X = aspartic and glutamic acid torepresent negatively charged carboxylside groups
- (b) X = serine to represent neutral hydroxyl side groups
- c) X = lysine to represent positively charged amine side groups
- Replacement of cysteine with serine in glutathione tripeptide resulted in nanoparticles

Excitation (dotted lines) and emission (solid lines) spectra of fluorescent Ag Ncs synthesized using different peptides.



Conclusion

•A new method for generating highly fluorescent Ag, Au, Pt, and Cu NCs in a mild etching environment made possible by phase transfer via electrostatic interactions.

•Using Ag as a model metal, we demonstrated a simple and fast (total synthesis time < 3 h) phase transfer cycle (aqueous \longrightarrow organic (2 h incubation) \longrightarrow aqueous) whereby polydisperse, nonfluorescent, and unstable Ag NCs in aqueous solution could be transformed into monodisperse, highly fluorescent, and extremely stable Ag NCs in aqueous solution protected by the same original thiol ligand (GSH).

•The synthetic protocol was then extended to fabricate highly fluorescent Ag NCs protected by custom-designed peptides with different functionalities (e.g., carboxyl, hydroxyl, and amine).

•The attractive features of these metal (Ag, Au, Pt, and Cu) NCs, such as an ultrasmall hydrodynamic diameter, high stability, biocompatible protecting ligands, and excellent fluorescence properties, are likely to promote their acceptance in bioimaging and biosensing applications.

Fluorescence visual gel-separation of dansylated BSA-protected gold-nanoclusters

An efficient, rapid, and fluorescence visual method for column separation of BSA-protected gold-nanoclusters was proposed based on the dansylation of BSA. After optimization, this procedure can be extended to the separation of any other macromolecule-protected noble metal bioconjugates.



Hong-Wei Li, Kelong Ai and Yuqing Wu, Chem. Commun., 2011, 47, 9852–9854

600

500

400

300

Au NCs@dBSA

550

600

Isolated Au NCs@dBSA

650

Thank you