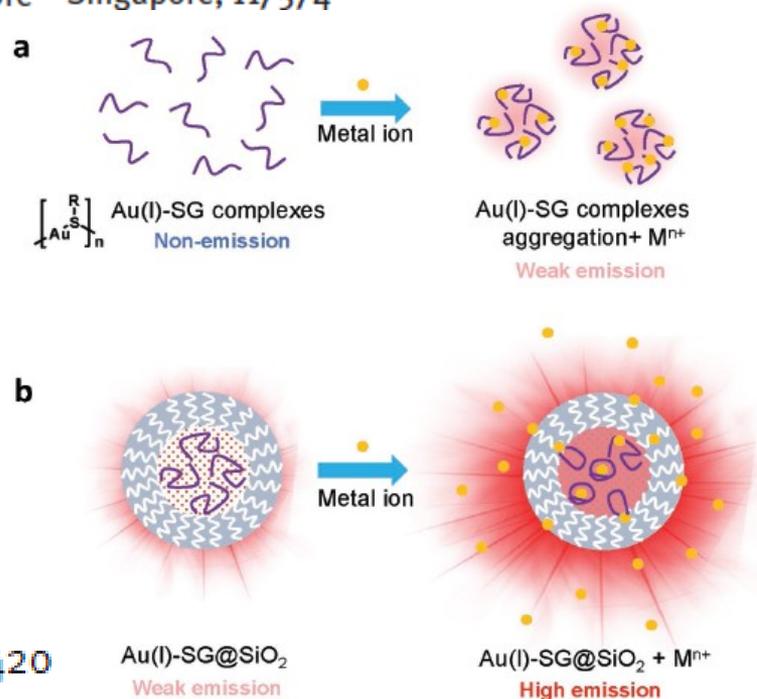


Probing the Microporous Structure of Silica Shell Via Aggregation-Induced Emission in Au(I)-Thiolate@SiO₂ Nanoparticle

Tingting Zhao, Nirmal Goswami, Jingguo Li, Qiaofeng Yao, Yan Zhang, John Wang, Dan Zhao, and Jianping Xie*

Department of Chemical and Biomolecular Engineering National University of Singapore Singapore, 117574 Department of Materials Science & Engineering



From Aggregation-Induced Emission of Au(I)–Thiolate Complexes to Ultrabright Au(0)@Au(I)–Thiolate Core–Shell Nanoclusters

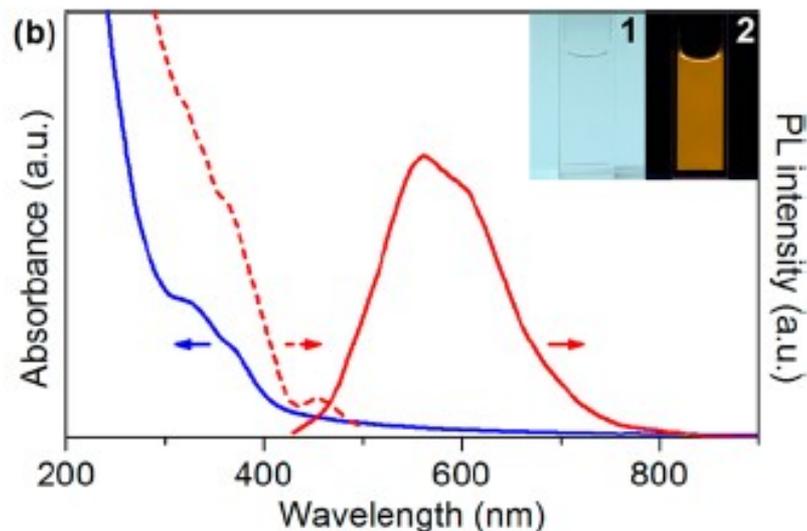
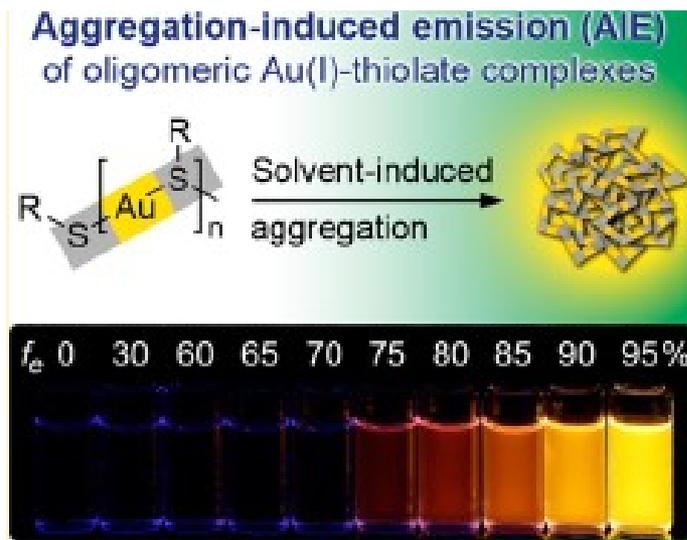
Zhentao Luo,[†] Xun Yuan,[†] Yue Yu,[†] Qingbo Zhang,[‡] David Tai Leong,[†] Jim Yang Lee,[†] and Jianping Xie^{*,†}

[†]Department of Chemical and Biomolecular Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

[‡]Department of Chemistry, Rice University, Houston, Texas 77251-1892, United States

Received: June 25, 2012

Published: September 24, 2012



Introduction

- ❑ Core-shell silica nanoparticles have drawn considerable research interest in diverse fields like catalysis, sensing, controlled drug delivery etc.
- ❑ Stöber method is the most widely used synthetic approach to prepare such nanostructure.
- ❑ A number of techniques such as TEM, electron diffraction have been used for the structural characterization of the microporous material.
- ❑ All the above methods are having drawbacks to characterize the pore size of the material.
- ❑ Therefore it requires to develop an alternative method that could effectively determine the microporous window size of silica shell in a very rapid manner.

In this paper.....

They presented a novel design of core-shell Au(I) SC@SiO₂ NP that

Synthesis

Synthesis of Au(I)-Thiolate Complexes

Aqs. solution of GSH (0.20 mL) + HAuCl_4 (0.50 mL) + 4.30 mL of
Stirred (500 rpm) in pure water $\xrightarrow{25^\circ\text{C}, 5 \text{ min}}$ White ppt $\xrightarrow{\text{NaOH}}$ ppt. dissolved and
reaction was continued for 1 h at 25°C

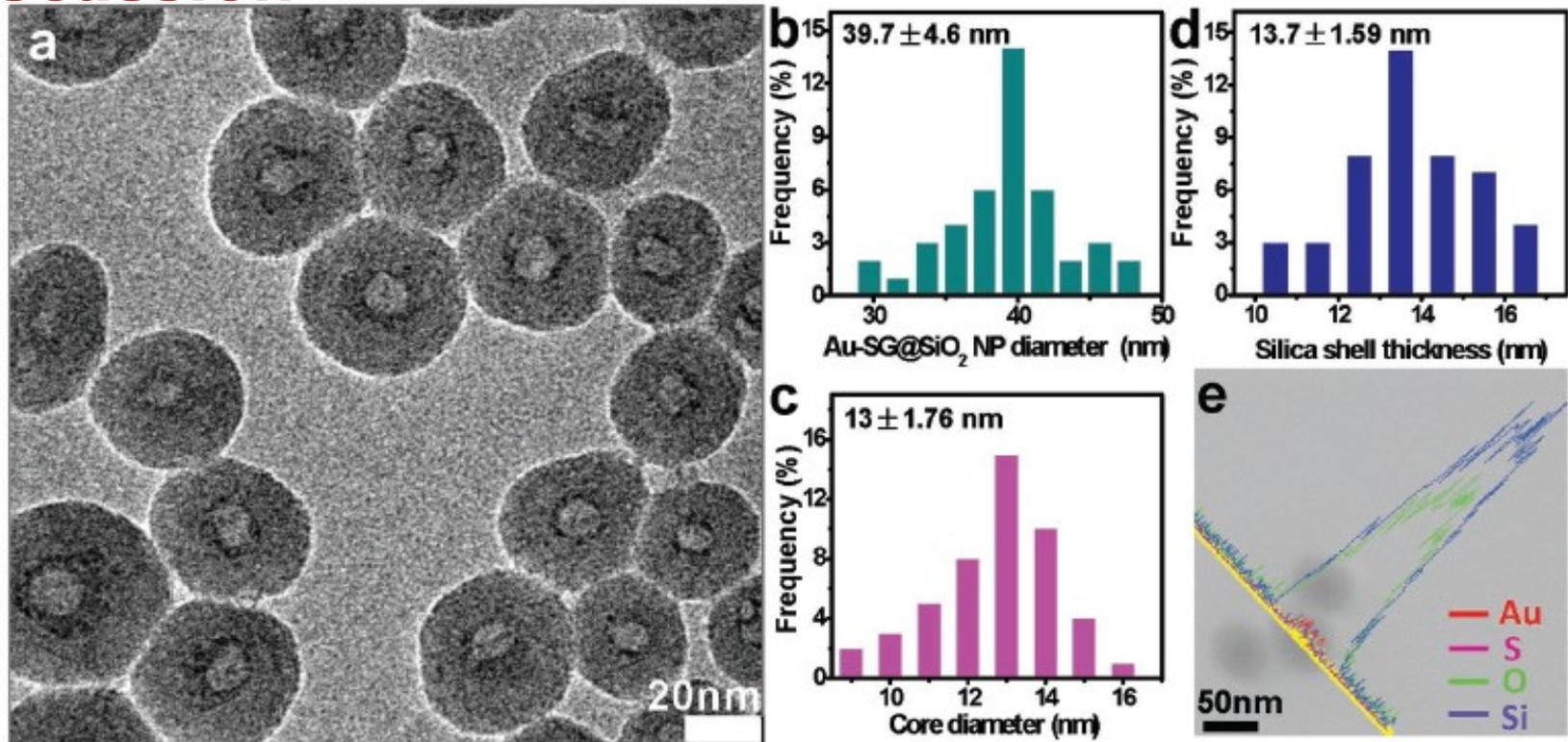
Synthesis of Silica-Coated Au(I)-Thiolate Complexes [Au(I)-SG@SiO₂ NPs]

Au(I)-SG complexes + $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution was added to an ethanol solution kept for 15 min

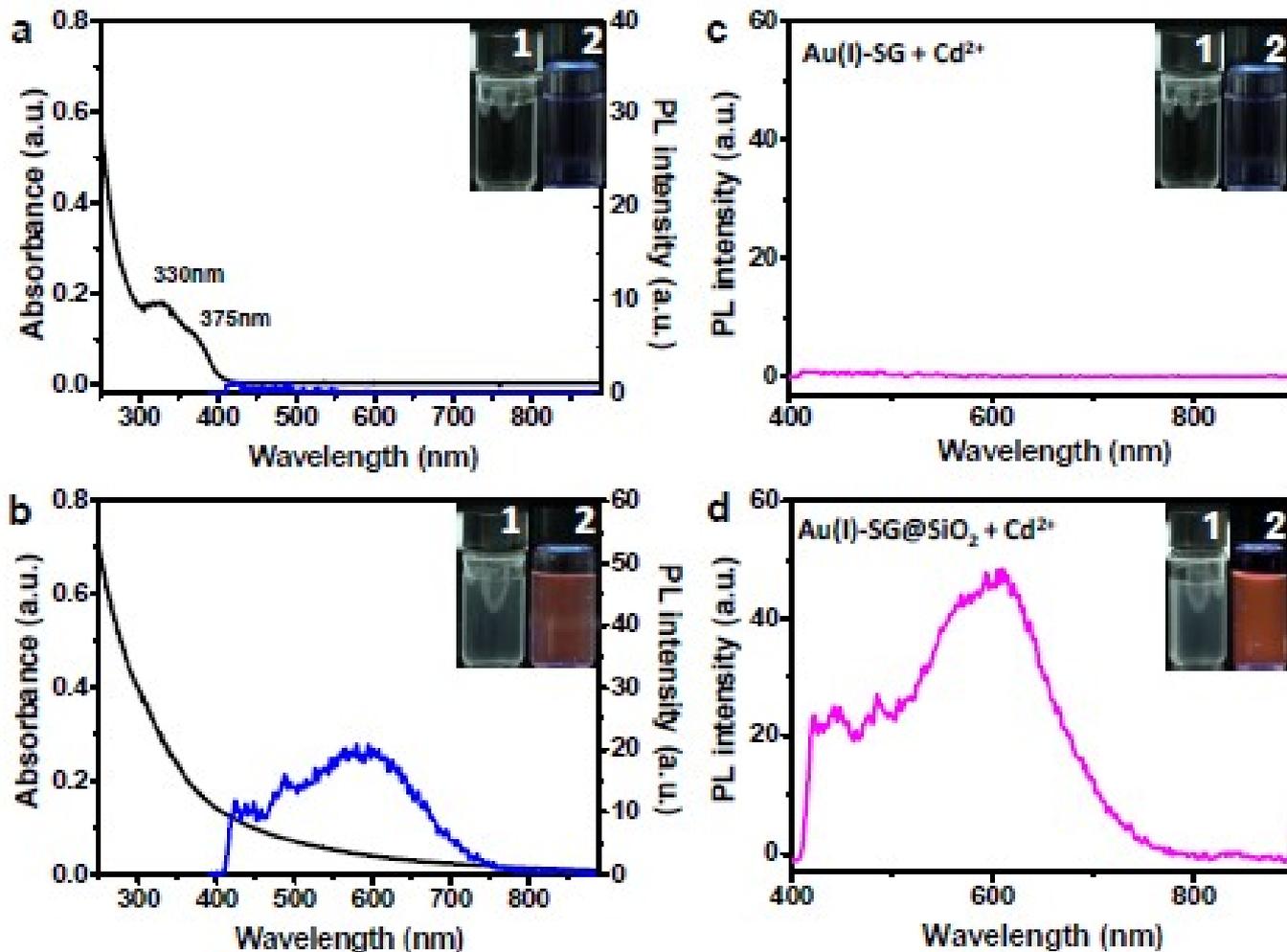
TEOS in ethanol
Stirred for 2 h
RT
500 rpm
Au(I)-SG@SiO₂ NPs

(collected by centrifugation at a speed of 10 000 rpm, washed several times with ethanol and DI H₂O and then dispersed in ultrapure water for further use)

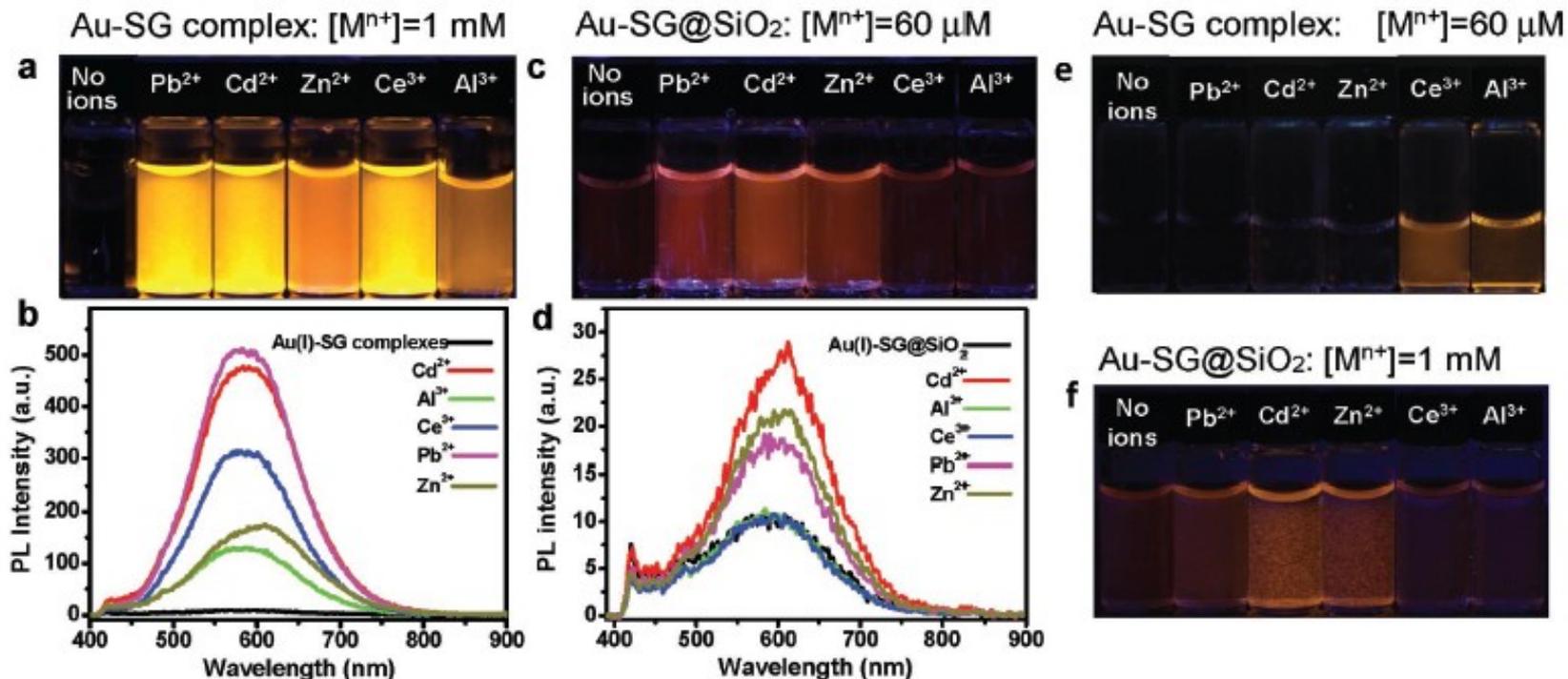
Results and discussion



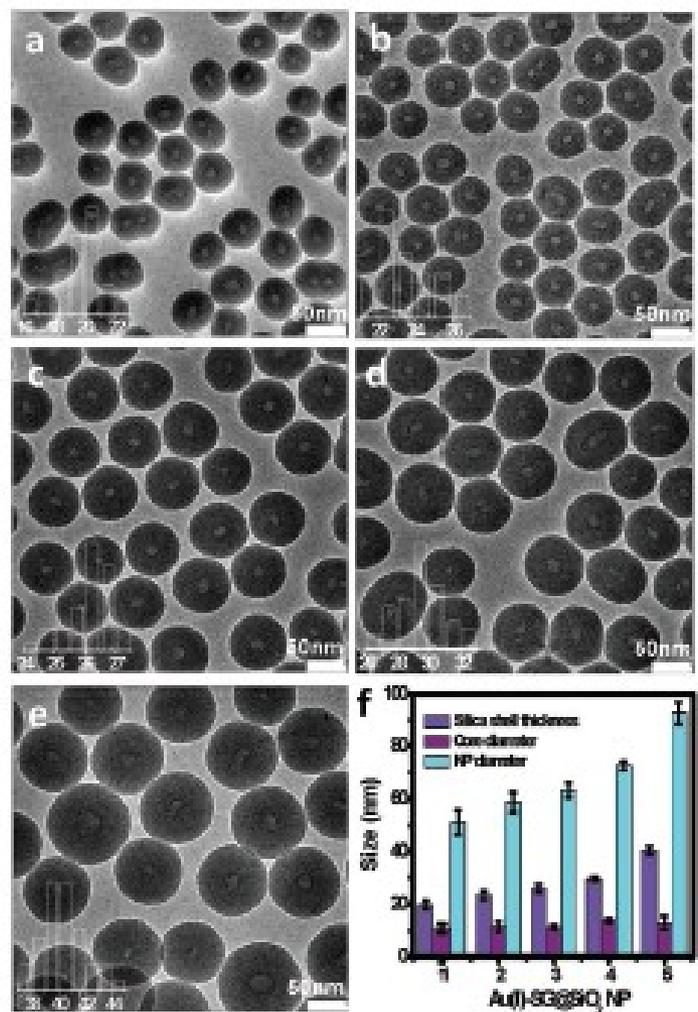
a) TEM image of Au(I)-SG@SiO₂ NPs with a silica shell thickness of ~ 13.7 nm. Size distribution of b) core-shell NP, c) core, and d) silica shell, e) Energy-dispersive X-ray spectroscopy (EDX) line scan across a single Au(I)-SG@SiO₂ NP, and line profiles for elements Au, S, Si, and O.



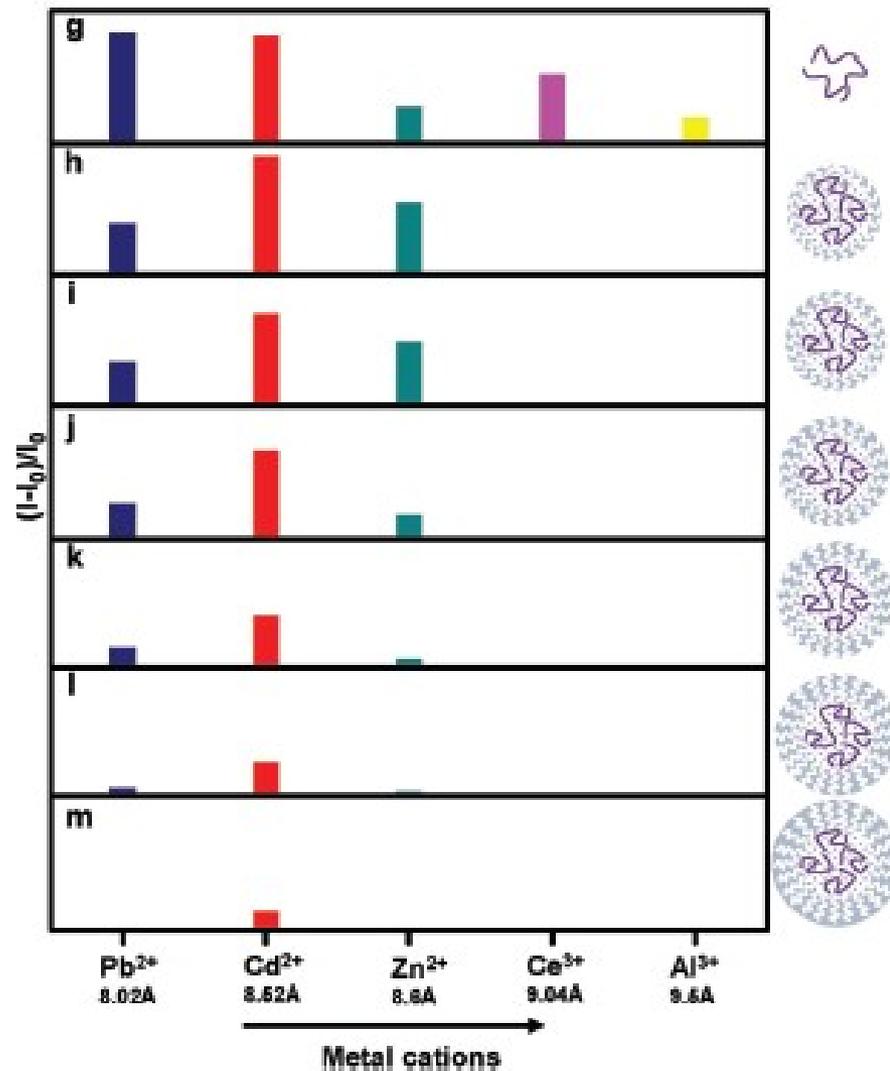
UV-vis absorption spectra and luminescence spectra of a) Au(I)- SG complexes and b) Au(I)- SG@ SiO₂ NPs. (Inset) Digital photographs of the Au(I)-SG complexes and Au(I)- SG@ SiO₂ NPs in aqueous solution under (1) visible and (2) UV light. Luminescence spectra of c) Au(I)- SG complexes and d) Au(I)- SG@ SiO₂ NPs solution upon the addition of Cd²⁺ (60 μM). (Inset) Digital photographs of the Au(I)-SG complexes or Au(I)- SG@ SiO₂ NPs with



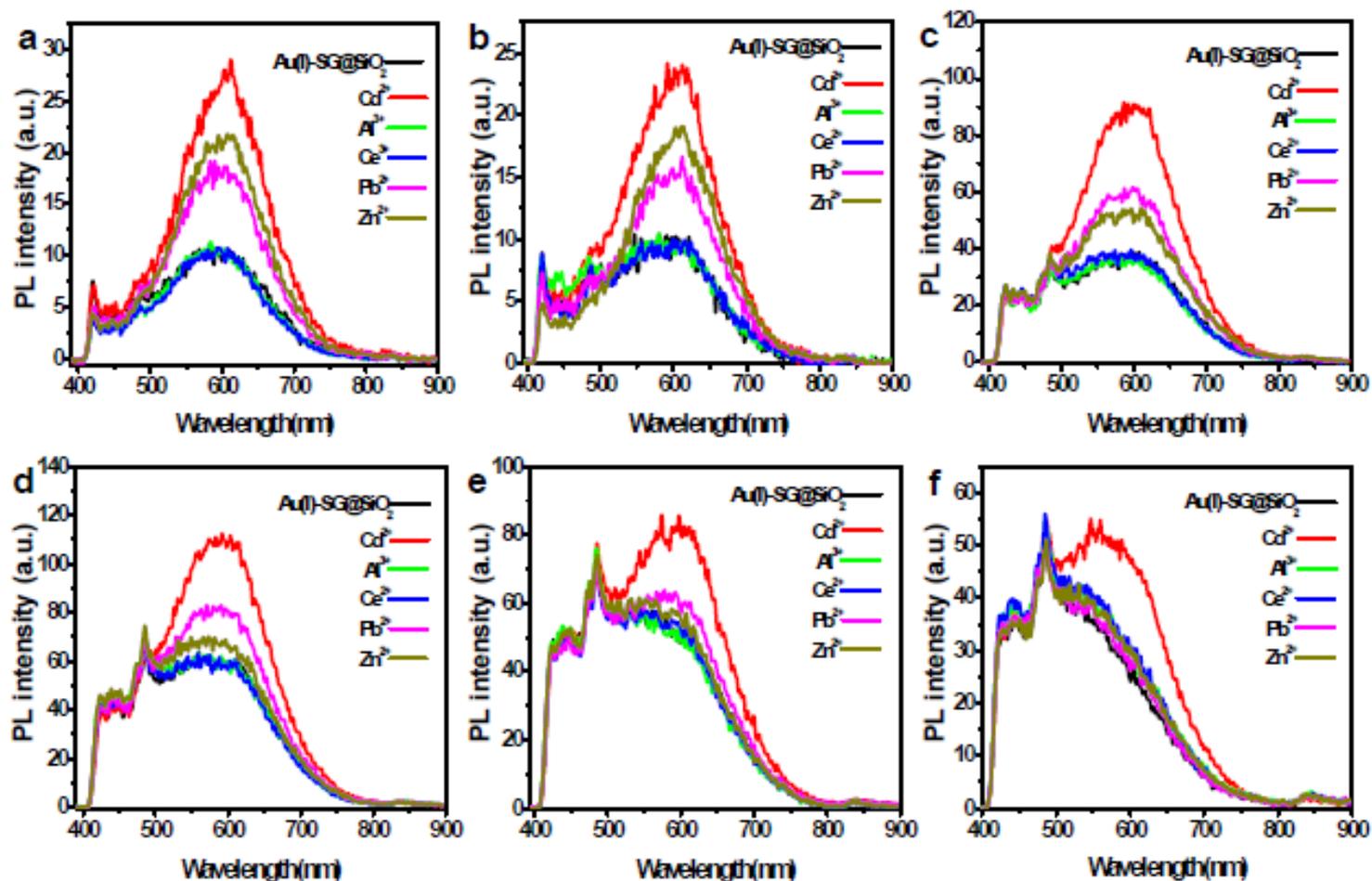
Digital photographs of a,e) Au(I)- SG complexes and c,f) Au(I)- SG@SiO₂ NPs under illumination in the presence of different metal ions with the concentration of $60 \cdot 10^{-6} \text{ M}$, respectively. Luminescence spectra of b) Au(I)-SG complexes and d) Au(I)- SG@SiO₂ NPs in aqueous solutions in the presence of $1 \cdot 10^{-3} \text{ M}$ and $60 \cdot 10^{-6} \text{ M}$ metal ions, respectively.



TEM images of Au(I)- SG@SiO₂ NPs with different silica shell thickness: a) 19.23 ± 1.19 nm, b) 23.5 ± 1.45 nm, c) 26.0 ± 0.75 nm, d) 29.5 ± 1.5 nm, and e) 40.3 ± 1.5 nm. f) Size distribution of silica shell , core, and the whole of Au(I)-SG@SiO₂ NPs with different silica shell thickness. (Inset) Size distribution of the thickness of silica shell.



g-m) Relative luminescence enhancement at $\lambda_{ex} = 365$ nm of Au(I)- SG complexes in the presence of 1×10^{-3} M different metal ions, and Au(I)-SG@SiO₂ NPs solution with different shell thickness in the presence of 60×10^{-6} M of various metal ions [(g) Au(I)- SG complexes; h) Au(I)-SG@SiO₂ (13.7 ± 1.59 nm); (i) 19.8 ± 1.53 nm, j) 23.5 ± 1.45 nm, k) 26.0 ± 0.75



Luminescence spectra ($\lambda_{\text{ex}} = 365 \text{ nm}$) of Au(I)-SG@SiO₂ NPs with different silica shell thickness (a. $13.7 \pm 1.53 \text{ nm}$; b. $19.8 \pm 1.59 \text{ nm}$; c. $23.5 \pm 1.45 \text{ nm}$; d. $26.0 \pm 0.75 \text{ nm}$; e. $29.5 \pm 1.5 \text{ nm}$; f. $40.3 \pm 1.5 \text{ nm}$) in the presence of various cations (Cd^{2+} , Al^{3+} , Ce^{2+} , Pb^{2+} , Zn^{2+}) at $60 \mu\text{M}$ concentration.

Summary

- They developed an efficient and facile light-up probe to determine the window size of silica shell in core-shell Au(I)-SG@SiO₂ NPs.
- The important aspect of this method is the semipermeable property of silica shell, which only allows the diffusion of small metal cations and repelling those larger ones.
- The as-diffused metal cations could interact with the Au(I)-SG complexes inside the NPs, inducing strong luminescence via the unique AIE pathway, which could be easily measured.
- The size probing method is rapid, precise, effective (due to the high sensitivity of AIE to metal ions), and easy to conduct.

Future

direction...

- In presence of Cd^{2+} and Pb^{2+} ions, luminescence enhancement was observed in AuBSA cluster. In such core-shell structure, kinetics of the diffusion of metal ions can be studied.
- Being biocompatibility, such core (protein cluster/ specific affinity towards As ions)- shell structure can be used as a sensor in water purification.

Thank you