

Nanoscale

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

Controlled Preparation of Au/Ag/SnO₂ Core-Shell Nanoparticles Using a Photochemical Method and Applications in LSPR based Sensing

Cite this: DOI: 10.1039/x0xx00000x

Na Zhou,^{a, b} Chen Ye,^a Lakshminarayana Polavarapu^a and Qing-Hua Xu^{*a, b}

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

A photochemical method for controlled preparation of core-shell Au/Ag/SnO₂ nanorods (NRs) and nanospheres (NSs) has been developed based on photo-induced electron transfer processes in the plasmonic metal-semiconductor system. Au/AgNR/SnO₂ and Au/AgNS/SnO₂ were prepared by UV irradiation on a mixture solution of mesoporous SnO₂ coated AuNRs or AuNSs and AgNO₃, in which AgNO₃ was reduced by electrons transferred from photo-excited mesoporous SnO₂ (semiconductor) to gold (metal). This method allows precise control over the composition and optical properties of the obtained nanoparticles. LSPR refractive index sensitivity of the obtained Au/AgNR/SnO₂ nanoparticles has been optimized to give a refractive index sensitivity of ~442 nm/RIU. The optimized nanoparticles were subsequently chosen for LSPR based sensing of glutathione (GSH) with limit of detection of ~7.5 × 10⁻⁷ M. This photochemical method allows controlled preparation of various Au/Ag/SnO₂ nanoparticles to adjust their LSPR to tailor various applications.

Introduction

Noble metal nanoparticles have attracted lots of attention due to their unique optical and electronic properties¹⁻⁴ and potential applications in various fields such as biosensors,^{5, 6} phototherapy,⁷⁻⁹ organic solar cells,¹⁰⁻¹² and catalysis.^{13, 14} In particular, they display unique localized surface plasmon resonance (LSPR) due to collective oscillation of conduction band electrons.^{4, 15} The optical properties of noble metal nanoparticles are strongly dependent on their morphology.^{16, 17} Different synthetic approaches have been developed to control nanoparticle morphology to tailor their properties.¹⁸⁻²⁰ Photochemical preparation of plasmonic nanoparticles has recently attracted a lot of attention as it allows precise control over nanoparticle growth through the modulation of light intensity or choice of excitation wavelength.^{21, 22} Light induced growth methods are attractive because they do not need chemical reducing agents.¹⁵ Since the discovery of light induced conversion of spherical silver (Ag) nanoparticles into Ag triangular nanoprisms by the Mirkin group,^{23, 24} Ag nanoparticles of various morphologies have been prepared by using various photochemical methods.²⁵⁻²⁷ Photochemical methods have also been extended to deposition of metal onto the surface of semiconductors.²⁸⁻³⁰ Light assisted nucleation of platinum on the surface of TiO₂ was first reported by Kraeutler et al.²⁸ Semiconductor materials can generate electron-hole pairs upon photo-excitation and the generated electrons could be utilized to reduce the nearby metal cations to prepare hybridized metal-semiconductor nanostructures.^{29, 30} Hybridized metal-semiconductor nanostructures have attracted lots of attention due to their wide variety of applications for

enhanced photo-catalytic activities,³¹ plasmon enhanced photovoltaics,³² and water splitting.³³

Motivated by the previous work on photo-induced deposition of metal on the surface of semiconductor,^{29, 30} here we developed a photochemical method for controlled preparation of core-shell Au/Ag/SnO₂ nanoparticles to precisely fine-tune their composition and LSPR bands. The core-shell Au/AgNR/SnO₂ and Au/AgNS/SnO₂ nanoparticles were prepared by UV light irradiation on a mesoporous SnO₂ coated AuNRs or AuNSs and AgNO₃ mixture solution. As the outer mesoporous SnO₂ shell is permeable to small molecules or ions, Ag ions that diffuse through the mesoporous SnO₂ shell can be reduced by electrons transferred from photo-excited SnO₂ to Au nanoparticles at the interface to form an interlaced Ag layer between the Au core and SnO₂ shell. A series of core-shell Au/AgNR/SnO₂ and Au/AgNS/SnO₂ with tunable LSPR bands have been successfully prepared by controlling the irradiation time. LSPR refractive index sensitivity of the Au/Ag/NR/SnO₂ nanoparticles has been optimized and the optimized one was subsequently chosen for applications in LSPR based sensing of GSH. This photochemical method allows controlled preparation of various Au/Ag/SnO₂ nanoparticles to adjust their LSPR to tailor various applications.

Experimental Section

Synthesis of Au/SnO₂ core/shell nanoparticles: Au nanorods (NRs) and Au nanospheres (NSs) were prepared according to a previously reported method.^{19, 34} SnO₂ coated AuNRs were prepared by hydrolysis Na₂SnO₃ in 75 °C.³⁵ Typically, 5.0 ml of CTAB capped Au NRs were diluted to 20 mL with DI water in a 50 mL round bottom flask. 0.1 M NaOH was added to adjust the pH of the

solution to 10.5. The round bottom flask was placed in a 75°C oil bath. The solution was vigorously stirred for 15 min followed by rapid addition of 2.5 mL freshly prepared Na_2SnO_3 (0.004 M) solution. The stirring was continued for another 2 hr and cooled down to the room temperature. The obtained AuNR/ SnO_2 core-shell nanoparticles were collected by centrifugation at a speed of 7000 rpm, then washed with DI water twice, and finally re-dispersed into 5 mL DI water. SnO_2 -coated Au NSs were prepared by using 5.0 mL of AuNSs and 1.0 mL of 0.004 M Na_2SnO_3 .

Preparation of Au/AgNR/ SnO_2 and Au/AgNS/ SnO_2 by light induced reduction of Ag^+ : 0.5 mL of as-prepared AuNR/ SnO_2 was diluted to 3 mL with DI water in a quartz cuvette followed by addition of 30 μL of 0.01 M AgNO_3 . The solution was purged with N_2 gas for 5 min to remove the dissolved air before sealing the cuvette. A 254 nm UV light source was utilized to irradiate the samples under stirring. The UV-vis spectrum was measured every 4 min. The Au/AgNS/ SnO_2 was prepared by UV light irradiation of the mixture of 2.0 mL of AuNS/ SnO_2 solution (4 times diluted from the as-prepared solution) and 40 μL of 0.01 M AgNO_3 .

Characterizations: The UV-vis extinction spectra were measured by using a Hitachi UH5300 spectrometer. Transmission electron micrograph (TEM) images were taken by using a Philips CM 300 FEGTEM electron microscope. High-angle annular dark field scanning-TEM (HAADF-STEM) measurements and detailed elemental composition analysis were carried out on a FEI Titan 80-300 electron microscope operating at 200 kV, which was equipped with an electron beam monochromator and energy dispersive X-ray spectroscopy (EDX).

Refractive index sensitivity measurements: The refractive index sensitivities of metal/ SnO_2 nanoparticles were determined by measuring the extinction spectra of the nanoparticles dispersed in water-DEG (Diethylene glycol) mixture solvents with varying volume percentages. The refractive indices of the mixture solvents were calculated according to the Lorentz-Lorentz equation.³⁶ The refractive index unit (RIU) was obtained by linear fitting of the plot of LSPR shifts versus solvent refractive indices.

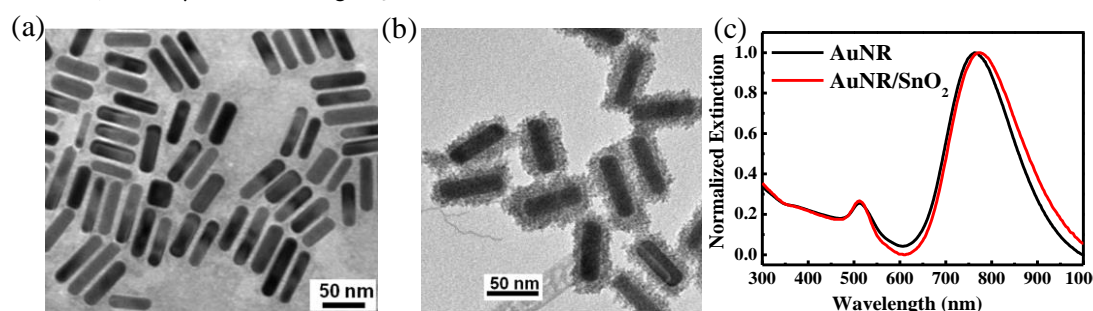


Figure 1 (a, b) TEM images and (c) UV-visible extinction spectra of AuNRs and AuNR/ SnO_2 core-shell nanoparticles.

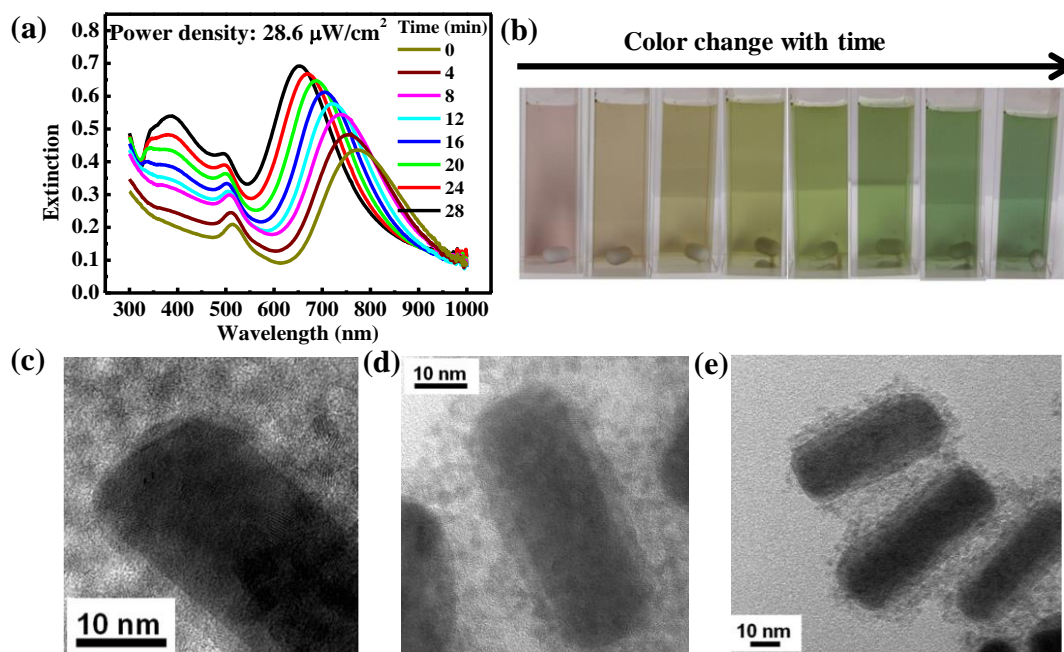


Figure 2 (a) UV-Vis extinction spectra and (b) photographs of the AuNR/ SnO_2 and AgNO_3 solution mixture under UV light irradiation every 4 min; (c, d, e) TEM images of Au/AgNR/ SnO_2 nanoparticles with LSPR band maximum at 720, 688 and 660 nm respectively.

Results and Discussion

Figure 1a shows the TEM image of the prepared AuNRs. The average length and diameter of the Au NRs are 59 ± 2 and 17 ± 1 nm, respectively. The extinction spectrum of AuNRs (**Figure 1c**) displays two LSPR bands at 510 and 763 nm,

corresponding to their transverse and longitudinal LSPR modes, respectively. Mesoporous SnO_2 shells were coated onto the AuNRs by a one-pot hydrothermal reaction using sodium stannate trihydrate ($\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$) as the precursor.^{35, 37} Uniform SnO_2 coating in AuNR/ SnO_2 was confirmed by the TEM image (**Figure 1b**). The averaged thickness of SnO_2 shell

on Au NRs is 10 ± 1 nm. The UV-Vis extinction spectrum of the obtained AuNR/SnO₂ in water (**Figure 1c**) displays a longitudinal LSPR band centered at 775 nm and a transverse LSPR band centered at 512 nm. Both the longitudinal and transverse LSPR bands were slightly red-shifted upon coating the Au NR with SnO₂ due to an overall increase in the refractive index of the dielectric environment surrounding the Au NRs.³⁸ X-ray diffraction (XRD) pattern and high-resolution TEM image of AuNR/SnO₂ (see **Figure S1** in the ESI) show that the lattice fringes obtained from HR-TEM match with the planes of SnO₂ obtained from XRD data. The mesoporous SnO₂ shell is permeable to solvents, small molecules and ions to

access the Au NR surface, which is critical for the following designed experiments.

It has been previously reported by Bard and co-workers^{30, 39} that Ag⁺ ions could be reduced on the surface of semiconductor under the UV light illumination. Upon absorption of UV light, electrons were promoted from the valance band to the conduction band of the semiconductor, which were subsequently captured by Ag⁺ ions. Motivated by this work, we extended this method to preparation of Au/AgNR/meso-SnO₂ core-shell nanostructures based on electron transfer processes in the plasmonic metal-semiconductor system.^{30, 40}

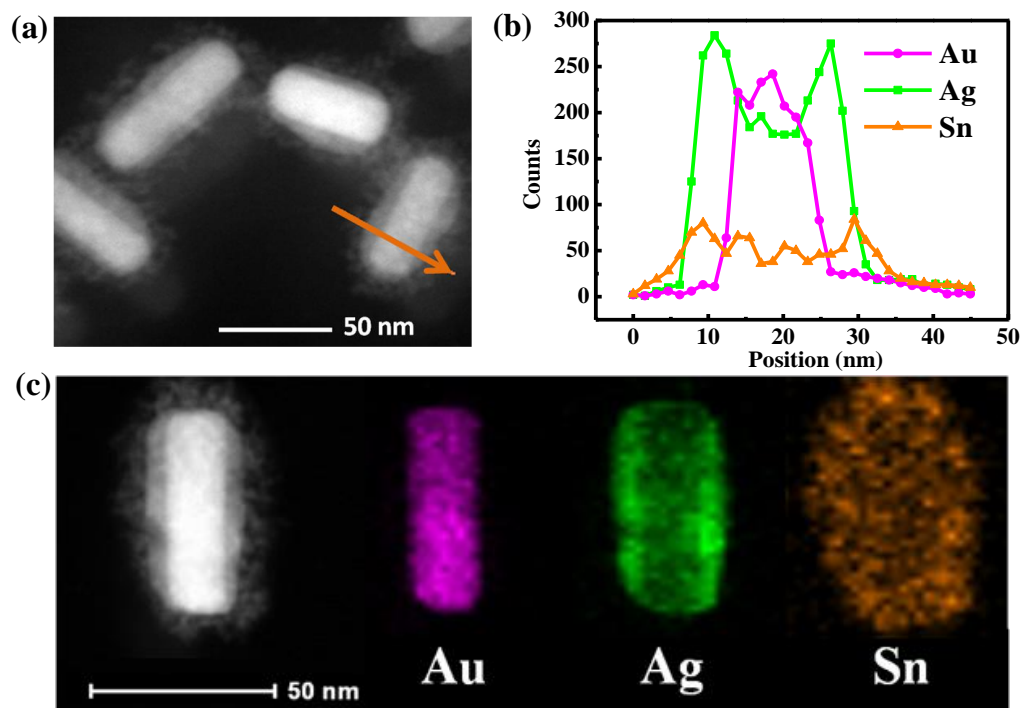


Figure 3 (a) High-angle annular dark-field scanning TEM (HAADF-STEM) image of the obtained Au/AgNR/SnO₂; (b) The EDX line scan and (c) element mapping of one Au/AgNR/SnO₂ for Au (purple), Ag (green), and Sn (orange), respectively. The scan step size is 1.55 nm.

Figure 2a shows the evolution of extinction spectra of AuNR/SnO₂ in the presence of AgNO₃ under the 254 nm UV light irradiation. The growth of Ag shells on AuNRs is manifested by the dramatic change in their extinction spectra.⁴¹⁻⁴³ The longitudinal LSPR band of AuNR/SnO₂ was centered at 775 nm before the UV light irradiation. Upon UV light irradiation, the longitudinal LSPR band gradually shifted to blue with simultaneous increase in its intensity. At the same time, a broad band appeared in the 350-450 nm range with steady increase in its intensity under prolonged light irradiation. During the course of UV-light irradiation, the solution color changed dramatically from red to green (**Figure 2b**). These observations are similar to those when formation of Ag shell on Au NRs was induced by chemical reduction of Ag⁺ using ascorbic acid.^{42, 43} The formation of Ag shell was confirmed by the TEM images of three samples with LSPR band centered at 720, 688 and 660 nm, respectively. The boundary between Au, Ag and SnO₂ can be clearly distinguished by the brightness contrast (**Figure 2c-2e**). The thicknesses of Ag shell were estimated to be 2.0, 3.3, and 5.1 nm, respectively, for these three samples.

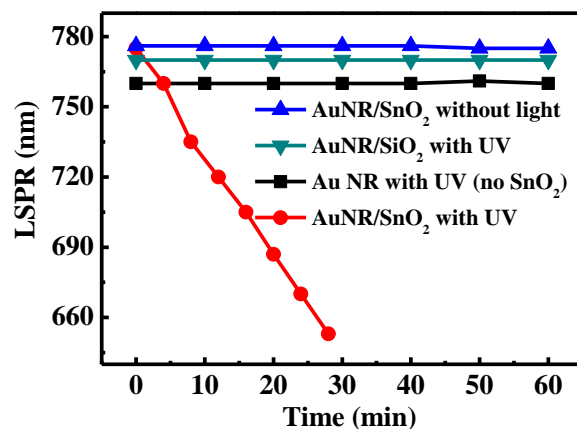
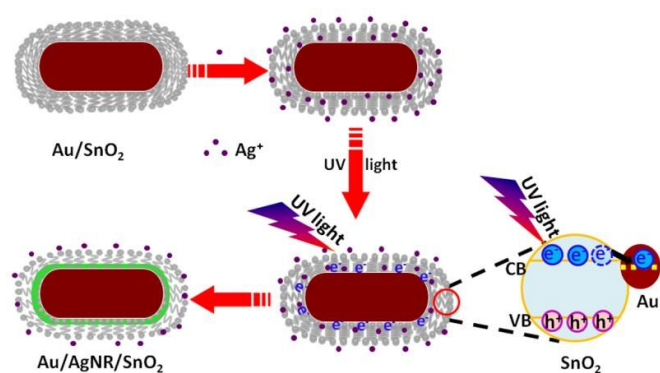


Figure 4 Time dependent change of LSPR band in extinction spectra of AuNR/SnO₂ and AgNO₃ mixture solution with or without UV irradiation, AuNR/SiO₂ and AgNO₃ mixture solution with UV irradiation and the mixture solution of AuNR and AgNO₃ with UV light irradiation.



Scheme 1. Proposed mechanism for light-induced growth of Au/AgNR/SnO₂.

The formation of Ag shell has been further confirmed by the high-angle annular dark-field scanning TEM (HAADF-STEM) images. The HAADF-STEM image (**Figure 3a**) yielded a clear contrast between AuNR, Ag shell and SnO₂ shell. The corresponding EDX line scan results (**Figure 3b**) show the presence of Au, Ag and Sn elements in the nanoparticle. The relative positions of these elements indicate that Ag (green line) grew on the Au (purple line) surface to form a core-shell nanostructure. The Sn (orange line) element was across the whole nanoparticle, indicating that the SnO₂ shell was located at the outside layer. The composition of the nanostructure was further confirmed by elemental mapping of Au, Ag and Sn on one single nanoparticle (**Figure 3c**). Different colors indicate the presence of different elements. It can be clearly seen that the distribution of Au element matches well with the core of

composite while the Ag element distributes around the Au core and the Sn element was across the whole nanoparticles. The element mapping clearly indicates that the Ag shell was formed inside the SnO₂ shell.

The formation of Ag shell under UV light irradiation can be explained by the mechanism as shown in **Scheme 1**. 254 nm UV light irradiation excites SnO₂ shell to promote the electrons from the valence band to the conduction band. The electrons in the conduction band were subsequently transferred to the Au NRs at the interface.^{30, 44} As mesoporous SnO₂ shell is permeable to Ag⁺ ions, the electrons at the interface can be captured by Ag⁺ ions that diffuse through the mesoporous SnO₂ shell. AgNO₃ became reduced at the interface of Au/SnO₂, resulting in formation of a thin layer of Ag inside the mesoporous SnO₂. Consequently an interlaced thin layer of Ag/SnO₂ was formed between the AuNR core and the outside SnO₂ shell.

To confirm the proposed mechanism, we have also done control experiments on the uncoated or SiO₂ coated AuNRs and AgNO₃ mixture solution. Under 254 nm UV light irradiation, neither solution displayed the above blue-shift in the longitudinal LSPR band (**Figure 4** and **Figures S2-S3** in the ESI). These results indicated that SnO₂ plays a key role for the formation of Ag shell. When there is no UV light irradiation, no change in the longitudinal LSPR band was observed in the mixture of AuNR/SnO₂ and AgNO₃ (**Figure 4** and **Figure S4** in ESI), which confirmed the essential role of the UV light. We have also done control experiments by adjusting the UV light intensity. As the intensity of the UV light increased, the LSPR peak shifted to blue with a faster rate (**Figures S5**). All these results support our proposed mechanism.

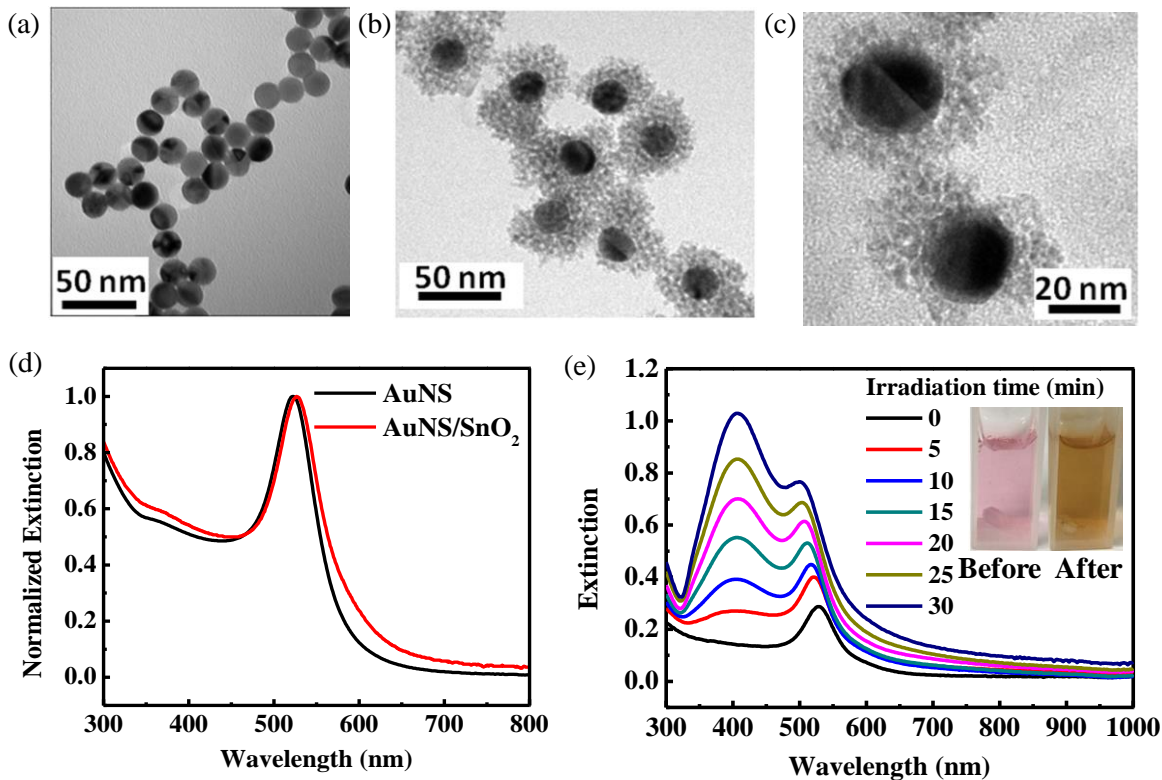


Figure 5 TEM images of (a) AuNS, (b) AuNS/SnO₂ and (c) Au/AgNS/SnO₂; (d) UV-visible extinction spectra of AuNS and AuNS/SnO₂; (e) UV-vis extinction spectra of the AuNS/SnO₂ and AgNO₃ solution mixture under UV light irradiation. Inset e shows the photographs of the sample before and after UV light irradiation.

This photochemical method could be further extended to deposition of Ag shells into metal-semiconductor nanostructures of other shapes. To confirm the generality of this method, the same method has been utilized to the prepare Au/AgNS/SnO₂ core-shell nanostructure. AuNS/SnO₂ nanoparticles were first prepared by coating AuNSs of 20±1 nm in diameter (Figure 5a) with a mesoporous SnO₂ shell with thickness of 16±2 nm (Figure 5b). The LSPR band of AuNS/SnO₂ was centered at 527 nm (Figure 5d). When the mixture of AuNS/SnO₂ and AgNO₃ was irradiated with 254 nm UV light, the original LSPR band became blue-shifted with an increase in its intensity, which can be explained by the increase in particle volume and the dielectric properties of silver.⁴⁵ A new peak between 350 to 450 nm appeared arising from the deposited of Ag shell (Figure 5e). After irradiation for 30 min, the solution color changed from pink to yellow (Figure 5e inset). The TEM image of the obtained sample further confirmed the formation of an Ag shell between the AuNS and outer SnO₂ shell. The thickness of Ag shell was estimated to be around 3.5±0.3 nm (Figure 5c).

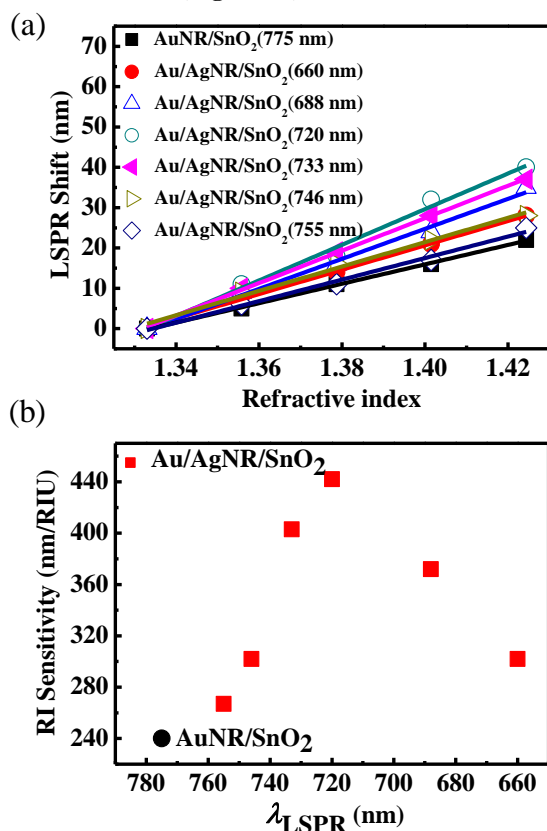


Figure 6. (a) LSPR band shift of AuNR/SnO₂ and different Au/AgNR/SnO₂(λ_{LSPR}) versus refractive index of the medium and (b) their refractive index sensitivity.

LSPR band of noble metal NPs has been known to be highly sensitive to refractive index of their surrounding environments, which allows their applications in LSPR based molecular sensing.^{5, 6} The mesoporous SnO₂ shells can stabilize metal nanoparticles in water and various organic solvents.³⁷ It was also reported that the metal/SnO₂ NPs were quite stable in aqueous solution of different pH.⁴⁶ Our experiments showed that these Au/Ag/SnO₂ nanoparticles displayed excellent long term stability (Figure S6). Most importantly, the mesoporous

SnO₂ shells are permeable to solvent or small molecules to allow their access to the metal core. Mesoporous SnO₂ shell coated metal nanoparticles are good candidates for LSPR based molecular sensing. To investigate the LSPR sensitivities of AuNR/SnO₂ and Au/AgNR/SnO₂ with different LSPR bands to the solvent refractive index, extinction spectra of these SnO₂ coated metal nanoparticles in the water-DEG mixture solvents with various ratios were measured. The longitudinal LSPR bands of all these nanoparticles were found to redshift with the increasing refractive index of the solvent (Figure S7). The refractive index sensitivities of these nanoparticles were obtained by linear regression analysis of redshift in LSPR band (Figure 6a). The refractive index units (RIUs) of different nanoparticles are summarized in Figure 6b. The refractive index sensitivity of AuNR/SnO₂(775 nm) (240 nm/RIU) was similar to that of AuNR with a similar aspect ratio of 3.4 (224 nm/RIU),³⁶ which indicates that the mesoporous SnO₂ coating does not compromise its sensitivity to the surrounding environments. After photochemical growth of Ag shell onto the AuNR, the refractive index sensitivity of the nanoparticles increased first from 240 nm/RIU for AuNR/SnO₂(775nm) to 442 nm/RIU for Au/AgNR/SnO₂(720 nm), then decreased to 302 nm/RIU for Au/AgNR/SnO₂(660 nm). The initial increase in refractive index is consistent with the previous results that Ag nanoparticles display larger refractive index sensitivity than Au nanoparticles of the same shape.⁴⁷ The decrease in RIU of Au/AgNR/SnO₂ for thick Ag shells can be ascribed to decreased aspect ratios when the Ag shell became thicker. It has been known that metal nanorods with larger aspect ratios are more sensitive the surrounding environments.³⁶

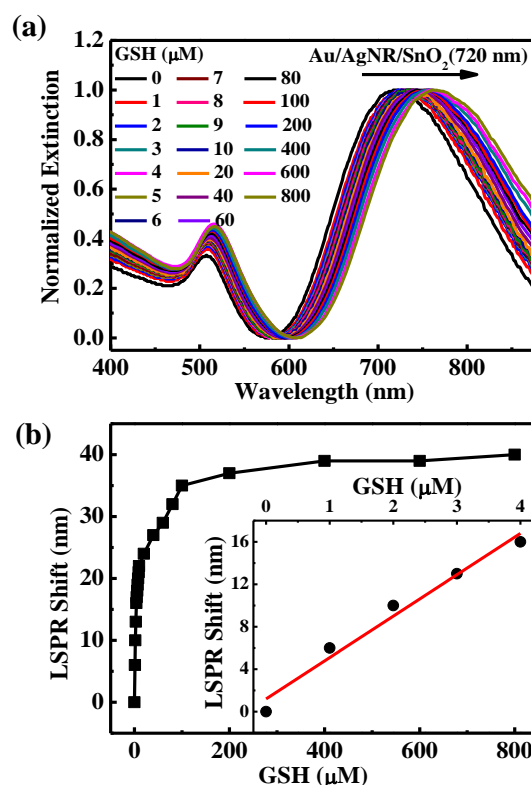


Figure 7. (a) Normalized extinction spectra and (b) LSPR shift of Au/Ag/SnO₂(720nm) in the presence of different concentrations of GSH. The inset shows that the LSPR shift is linearly proportional to the [GSH] in the low concentration range.

The photochemical methods allowed us to fine-tune LSPR band of Au/AgNR/SnO₂ to achieve the nanostructure with the optimum refractive index sensitivity. Au/AgNR/SnO₂(720nm) displayed the best sensitivity (442 nm/RIU) of the series and was chosen for applications in LSPR based detection of glutathione (GSH) (Figure 7). GSH has thiol groups and displays high affinity to metal surface.⁴⁸ It can be seen that LSPR band of Au/Ag/SnO₂(720nm) gradually shifted to red with a total redshift of up to 40 nm as the concentration of GSH increased. In contrast, maximum LSPR shifts of AuNR and AuNR/SiO₂ after GSH binding were previously reported to be 1.5 nm or 6 nm, respectively.⁴⁸ This result suggests that Au/Ag/SnO₂(720 nm) can provide a more sensitive response than AuNR or AuNR/SiO₂ in GSH sensing. The limit of detection (LOD) was determined to be $\sim 7.5 \times 10^{-7}$ M.

Conclusions

A photochemical method for controlled preparation of core-shell Au/Ag/SnO₂ nanoparticles has been developed. This method is based on photo-induced electron transfer processes in plasmonic metal-semiconductor system. As the outer mesoporous SnO₂ shell is permeable to small molecules or ions, Ag ions that diffuse through the mesoporous SnO₂ shell can be reduced by electrons transferred from photo-excited SnO₂ to Au at the interface to form an interlaced Ag layer between the Au core and SnO₂ shell. A series of core-shell Au/AgNR/SnO₂ with tunable LSPR have been successfully prepared by UV illumination of AuNR/SnO₂ and AgNO₃ mixture solution. LSPR refractive index sensitivity of these AuNR/SnO₂ nanoparticles has been optimized. AuNR/SnO₂ (720nm) was found to give the largest refractive index sensitivity (442 nm/RIU) and was subsequently chosen for LSPR based sensing of GSH. The limit of detection (LOD) was determined to be $\sim 7.5 \times 10^{-7}$ M. This method has been further extended to preparation of Au/AgNS/SnO₂. This photochemical deposition Ag shell method is expected to be useful in preparation of many metal/semiconductor core-shell nanostructures. This photochemical method allows controlled preparation of various Au/Ag/SnO₂ nanoparticles to adjust their LSPR to tailor various applications. Compared to the conventional chemical deposition method, this photochemical method shows some advantages such as easy control of their LSPR band position and room temperature preparation.

Acknowledgements

This work is supported by the NUS AcRF Tier 1 grant (R-143-000-533-112 and R-143-000-607-112) and the National Research Foundation, Prime Minister's Office, Singapore under its Competitive Research Program (CRP Award No. NRF-CRP10-2012-04).

Notes and references

^a Department of Chemistry, National University of Singapore, Singapore 117543. E-mail: chmxqh@nus.edu.sg.

^b National University of Singapore (Suzhou) Research Institute (NUSRI), Suzhou, Jiangsu, China 215123

Electronic Supplementary Information (ESI) available: Detailed preparation procedures of AuNR and AuNS; High-resolution TEM images of metal/SnO₂ NPs, UV-Vis extinction spectra of AuNR or Au/SiO₂ in the presence of AgNO₃ under UV light irradiation, UV-Vis extinction spectra of Au/SnO₂ and AgNO₃ without any light irradiation,

or with UV light at intensity of 21μW/cm² and 37μW/cm²; Long term stability test of one Au/AgNR/SnO₂ sample; Extinction spectra of AuNR/SnO₂ and Au/AgNR/SnO₂ in water-DEG mixture solvents. See DOI: 10.1039/b000000x/.

- G. V. Hartland, *Chem. Rev.*, 2011, **111**, 3858-3887.
- J. F. Hicks, D. T. Miles and R. W. Murray, *J. Am. Chem. Soc.*, 2002, **124**, 13322-13328.
- C. Novo, A. M. Funston, A. K. Gooding and P. Mulvaney, *J. Am. Chem. Soc.*, 2009, **131**, 14664-14666.
- K. L. Kelly, E. Coronado, L. L. Zhao and G. C. Schatz, *J. Phys. Chem. B*, 2002, **107**, 668-677.
- K. M. Mayer and J. H. Hafner, *Chem. Rev.*, 2011, **111**, 3828-3857.
- J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao and R. P. Van Duyne, *Nature Mater.*, 2008, **7**, 442-453.
- T. Zhao, X. Shen, L. Li, Z. Guan, N. Gao, P. Yuan, S. Q. Yao, Q. H. Xu and G. Q. Xu, *Nanoscale*, 2012, **4**, 7712-7719.
- R. Vankayala, A. Sagadevan, P. Vijayaraghavan, C. L. Kuo and K. C. Hwang, *Angew. Chem., Int. Ed.*, 2011, **50**, 10640-10644.
- X. Huang, I. H. El-Sayed, W. Qian and M. A. El-Sayed, *J. Am. Chem. Soc.*, 2006, **128**, 2115-2120.
- M. D. Brown, T. Suteewong, R. S. Kumar, V. D'Innocenzo, A. Petrozza, M. M. Lee, U. Wiesner and H. J. Snaith, *Nano Lett.*, 2011, **11**, 438-445.
- S. Chang, Q. Li, X. Xiao, K. Y. Wong and T. Chen, *Energ. Environ. Sci.*, 2012, **5**, 9444-9448.
- J. Qi, X. Dang, P. T. Hammond and A. M. Belcher, *ACS Nano*, 2011, **5**, 7108-7116.
- J. Zeng, Q. Zhang, J. Chen and Y. Xia, *Nano Lett.*, 2010, **10**, 30-35.
- C. Xiao, S. Chen, L. Zhang, S. Zhou and W. Wu, *Chem. Commun.*, 2012, **48**, 11751-11753.
- M. Grzelczak and L. M. Liz-Marzan, *Chem. Soc. Rev.*, 2014, **43**, 2089-2097.
- H. Chen, Z. Sun, W. Ni, K. C. Woo, H.-Q. Lin, L. Sun, C. Yan and J. Wang, *Small*, 2009, **5**, 2111-2119.
- C. Noguez, *J. Phys. Chem. C*, 2007, **111**, 3806-3819.
- T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein and M. A. El-Sayed, *Science*, 1996, **272**, 1924-1926.
- B. Nikoobakht and M. A. El-Sayed, *Chem. Mater.*, 2003, **15**, 1957-1962.
- M. Rycenga, C. M. Copley, J. Zeng, W. Li, C. H. Moran, Q. Zhang, D. Qin and Y. Xia, *Chem. Rev.*, 2011, **111**, 3669-3712.
- M. R. Langille, M. L. Personick and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2013, **52**, 13910-13940.
- C. Xue and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2007, **46**, 2036-2038.
- R. Jin, Y. C. Cao, E. Hao, G. S. Metraux, G. C. Schatz and C. A. Mirkin, *Nature*, 2003, **425**, 487-490.
- R. Jin, Y. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz and J. G. Zheng, *Science*, 2001, **294**, 1901-1903.
- B. Pietrobon and V. Kitaev, *Chem. Mater.*, 2008, **20**, 5186-5190.
- M. R. Langille, J. Zhang and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2011, **50**, 3543-3547.
- J. Zhou, J. An, B. Tang, S. Xu, Y. Cao, B. Zhao, W. Xu, J. Chang and J. R. Lombardi, *Langmuir*, 2008, **24**, 10407-10413.

- 28 B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, 1978, **100**, 4317-4318.
- 29 C. T. Dinh, T. D. Nguyen, F. Kleitz and T. O. Do, *ACS Appl. Mater. Interfaces*, 2011, **3**, 2228-2234.
- 30 A. Takai and P. V. Kamat, *ACS Nano*, 2011, **5**, 7369-7376.
- 31 N. Zhou, L. Polavarapu, N. Gao, Y. Pan, P. Yuan, Q. Wang and Q. H. Xu, *Nanoscale*, 2013, **5**, 4236-4241.
- 32 Z. Liu, W. Hou, P. Pavaskar, M. Aykol and S. B. Cronin, *Nano Lett.*, 2011, **11**, 1111-1116.
- 33 A. Tanaka, S. Sakaguchi, K. Hashimoto and H. Kominami, *ACS Catal.*, 2012, **3**, 79-85.
- 34 X. Kou, Z. Sun, Z. Yang, H. Chen and J. Wang, *Langmuir*, 2009, **25**, 1692-1698.
- 35 G. Oldfield, T. Ung and P. Mulvaney, *Adv. Mater.*, 2000, **12**, 1519-1522.
- 36 H. Chen, X. Kou, Z. Yang, W. Ni and J. Wang, *Langmuir*, 2008, **24**, 5233-5237.
- 37 N. Zhou, L. Polavarapu, Q. Wang and Q.-H. Xu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 4844-4850.
- 38 Y. T. Yu and P. Dutta, *J Solid State Chem*, 2011, **184**, 312-316.
- 39 W. W. Dunn, Y. Aikawa and A. J. Bard, *J. Am. Chem. Soc.*, 1981, **103**, 6893-6897.
- 40 T. Hirakawa and P. V. Kamat, *J. Am. Chem. Soc.*, 2005, **127**, 3928-3934.
- 41 A. Sanchez-Iglesias, E. Carbo-Argibay, A. Glaria, B. Rodriguez-Gonzalez, J. Perez-Juste, I. Pastoriza-Santos and L. M. Liz-Marzan, *Chem.-Eur. J.*, 2010, **16**, 5558-5563.
- 42 R. B. Jiang, H. J. Chen, L. Shao, Q. Li and J. F. Wang, *Adv. Mater.*, 2012, **24**, Op200-Op207.
- 43 Y. Okuno, K. Nishioka, A. Kiya, N. Nakashima, A. Ishibashi and Y. Niidome, *Nanoscale*, 2010, **2**, 1489-1493.
- 44 N. Zhou, V. Lopez-Puente, Q. Wang, L. Polavarapu, I. Pastoriza-Santos and Q.-H. Xu, *RSC Adv.*, 2015, **5**, 29076-29097.
- 45 A. K. Samal, L. Polavarapu, S. Rodal-Cedeira, L. M. Liz-Marzán, J. Pérez-Juste and I. Pastoriza-Santos, *Langmuir*, 2013, **29**, 15076-15082.
- 46 S. H. Lee, I. Rusakova, D. M. Hoffman, A. J. Jacobson and T. R. Lee, *ACS Appl. Mater. Interfaces*, 2013, **5**, 2479-2484.
- 47 A. D. McFarland and R. P. Van Duyne, *Nano Lett.*, 2003, **3**, 1057-1062.
- 48 C. Wu and Q. H. Xu, *Langmuir*, 2009, **25**, 9441-9446.

Table of Content

A photochemical method based on photo-induced electron transfer processes was developed to prepare core-shell Au/Ag/SnO₂ nanoparticles with tailored optical properties.

