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ARTICLE

Photochemical grown silver nanodecahedra with precise tuning of plasmonic resonance

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Shuai Ye^{†a}, Jun Song^{*†a}, Yuliang Tian^a, Linchun Chen^a, Dong Wang^a, Hanben Niu^a, Junle Qu^{*a}Received 00th January 2012,
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The ability to control the local surface plasmonic resonance (LSPR) absorption peaks of silver nanoparticles will greatly broaden the scope of their practical application. Conventional methods tune the LSPR peaks by modifying the shape or size of the silver nanoparticles. Here, we present a novel method to tune the LSPR band by controlling the particle corner sharpness. A modified photochemical method was used to prepare the silver nanoparticles. It was found that the nanoparticles irradiated by light-emitting diodes (LED) with a wavelength of 455 nm were decahedral, although the reaction temperature was different. However, the in-plane dipole LSPR peak of the as-prepared silver nanodecahedra exhibited an evident red shift from 460 nm to 500 nm during the synthesis process, and the wavelength of the LSPR peak increased linearly as the reaction time increased. A numerical simulation conducted to investigate the mechanism behind the shift revealed that the red shift of the LSPR peak was mainly induced by the evolution of the corner sharpness of the silver nanodecahedra. These results demonstrated the effectiveness of the method in precisely tuning the LSPR peak by controlling the reaction time. By turning off the irradiation light, the photochemical process could be immediately terminated, and the LSPR peak of the silver nanoparticles remained constant. Compared with conventional methods, the present tuning precision can reach 1 nm.

1. Introduction

Silver nanoparticles are receiving increasing attention due to their unique optical, chemical, and physical properties as well as their scalable use in optical, catalysis, surface enhanced Raman scattering (SERS), and numerous biological applications^[1-6]. As most of these applications are based on optical properties, the precise tuning of the LSPR band is essential to meet the special conditions required by such applications^[7-12].

The characteristics of the LSPR band are significantly associated with the nanoparticle size and shape, whose control has been the most efficient method to successfully tune the LSPR band^[13-15]. Engineering the plasmonic properties of silver nanoparticles by controlling their size or dimensions has been considered the simplest method to manipulate the LSPR response^[16-19]. The LSPR band of the silver nanoparticles exhibits a continuous red shift with increasing the dimensions or edge length^[20,21]. The number and position of the LSPR band are also influenced by the geometrical shape^[22]. Many silver nanoparticles with different geometrical shapes were successfully synthesized by chemical reduction methods or photochemical methods^[23-28], such as nanotetrahedra^[29],

nanoprisms^[30,31], nanoplates^[32], nanodecahedra^[33], nanocubes^[34], nanorods^[35], etc. Every different shape showed its peculiar LSPR band.

In addition, some researchers demonstrated that the corner sharpness largely affect the LSPR band of silver nanoparticles^[36]. Xia *et al.* reported a blue shift from 770 nm to 450 nm for triangular silver nanoplates, due to the transformation during the aging process^[37]. Huang *et al.* also reported a blue shift from 499 nm to 443 nm by etching the corner and edge of the as-prepared silver nanodecahedra in KBr solution^[38]. However, until now, a method capable of tuning the LSPR band by engineering the corners of the silver nanoparticles during the synthesis process has not been reported. In this work, a photochemical method was used to synthesize the silver nanodecahedra with different corner sharpness, and the effect of the corner sharpness on the LSPR band was investigated.

2. Experimental

Silver nitrate (AgNO₃) and sodium citrate were purchased from Aladdin Industrial Corporation (Shanghai, China). Irgacure 2059 (I-2959) was purchased from Fine Chemical Company (Shanghai, China). All chemical materials were used

without further purification. Ultrapure water ($>18\text{ M}\Omega$) was used in all of the experiments. The silver nanodecahedra were prepared by a photochemical method previously reported in details^[39, 40]. First, an aqueous solution of 0.2 mM AgNO_3 , 0.2 mM I-2959, and 1 mM trisodium citrate was prepared and purged with N_2 for 30 min. The solution was irradiated by ultraviolet (UV) light-emitting diodes (LEDs) with a wavelength of 355 nm for 50 min, and a pale yellow solution was obtained. The solution was then irradiated by a blue LED with a wavelength in the range of approximately 455–465 nm to obtain the colloidal silver nanodecahedra. To control the reaction temperature, the reacting solution was injected in a quartz cylinder reactor assembled by ourselves, as shown in Figure S1 of the supporting information. Hot water at a specific temperature was continuously pumped in the inner tube to keep the reaction temperature constant.

The morphologies of all the samples were analyzed by transmission electron microscopy (TEM; Joel JEM-2100); all the UV/visible (UV/vis) spectra were recorded at 25 °C on a Hitachi U-2800 spectrophotometer using a quartz cuvette.

3. Results and discussion

The UV/vis spectra and TEM images of silver nanodecahedra grown with and without temperature control are shown in Figure 1. Figure 1a shows the UV/vis spectral change versus irradiation time when the silver seed solution was irradiated by

LED with the wavelength of 455 nm without temperature control. The silver seed solution (at 0 min) showed a LSPR peak at $\sim 400\text{ nm}$, which implied that spherical silver seeds were obtained after that the silver solution was irradiated by UV LEDs at 355 nm. By increasing the irradiation time, the intensity of the peak at 400 nm decreased, whereas the intensity of the peak at 485 nm gradually increased, indicating that the silver seeds were progressively aggregating and being converted into nanodecahedra. When the reaction was conducted for 30 min, the peak at 485 nm reached the strongest intensity, indicating the complete conversion of the silver seeds to silver nanodecahedra. For reaction times above 30 min, the intensity of both peaks at 400 nm and 485 nm decreased until no signal could be detected in the colloidal solution (after 90 min), indicating that, owing to the excessive irradiation, the as-obtained silver nanodecahedra had been etched, and finally precipitated. These findings are very similar to the previous results reported in the studies of Huang et al. and Scaiano et al.[38,40]. The color of the as-prepared silver nanodecahedra colloidal solution was orange, as shown in the photograph in the inset of Figure 1a. The typical TEM morphologies of the corresponding silver nanodecahedra are shown in Figure 1c. Uniform and monodisperse silver nanodecahedra with the edge length of $\sim 35\text{ nm}$ were obtained.

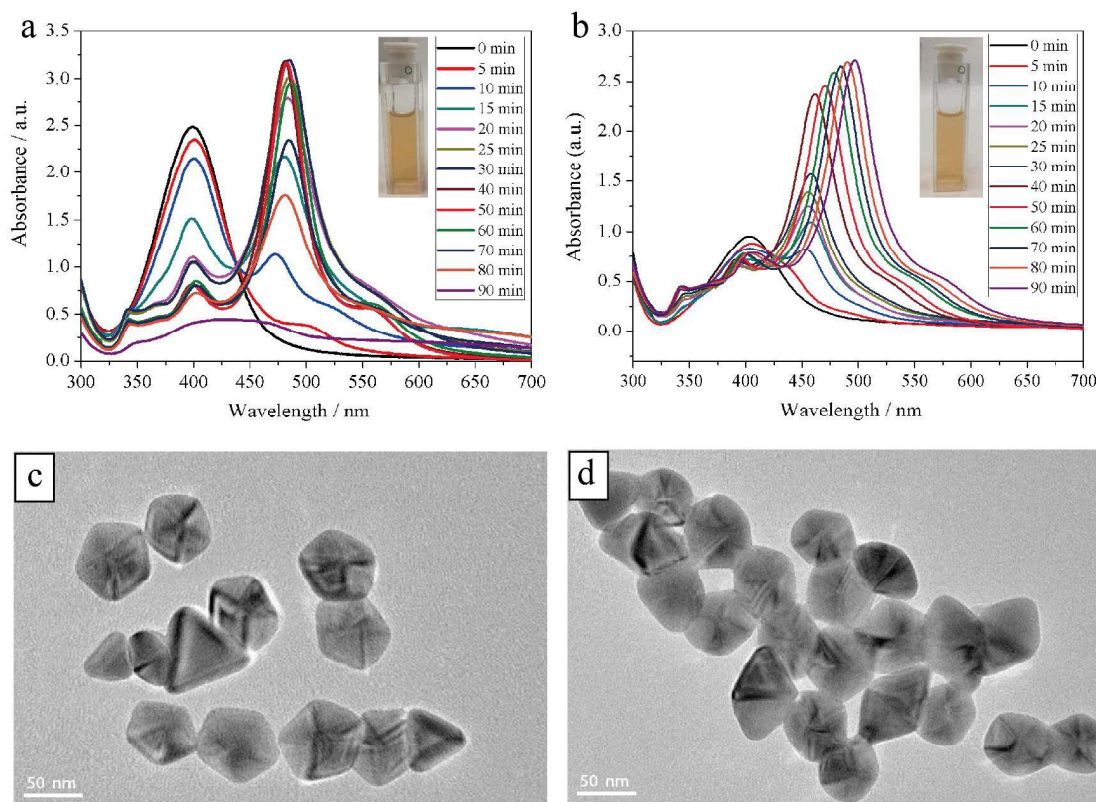


Fig. 1 UV/vis spectral change upon 455 nm irradiation against irradiation time grown a) without temperature control and b) at 50°C: the inset is the photographic images of colloidal solution of silver nanodecahedras, c) TEM image of silver nanodecahedras grown at 30 min without temperature control, d) TEM image of silver nanodecahedras grown at 90 min, 50°C

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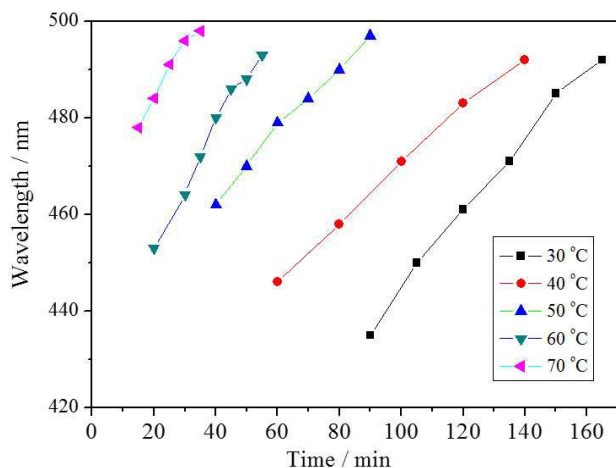


Fig.2 Effect of reaction time on the LSPR wavelength of silver nanodecahedras grown at different temperatures

Notably, an interesting result was observed when the photochemical process was performed at a certain constant

temperature. Figure 1b shows the UV/vis spectral change as a function of the irradiation time in the case of LED irradiation at 455 nm and temperature of 50 °C. In the early stages of the process (i.e., the first 40 min), the silver seeds appeared aggregated under LED irradiation, and the intensity of the LSPR peak at 460 nm increased gradually with the reaction time. In contrast to the case of the silver nanodecahedra grown without temperature control, the intensity of the LSPR peak increased slightly when the reaction time was above 40 min. Notably, this LSPR peak, attributed to the dipolar LSPR modes of the silver decahedra, showed an evident red shift from 461 nm to 498 nm. The color of the as-prepared silver nanodecahedra colloidal solution grown by the modified photochemical method was also orange (as shown in the photograph in the inset of Figure 1b). The as-obtained silver nanodecahedra appeared uniform, monodisperse, and with an edge length of ~36 nm, which is similar to that of the silver nanodecahedra grown without temperature control.

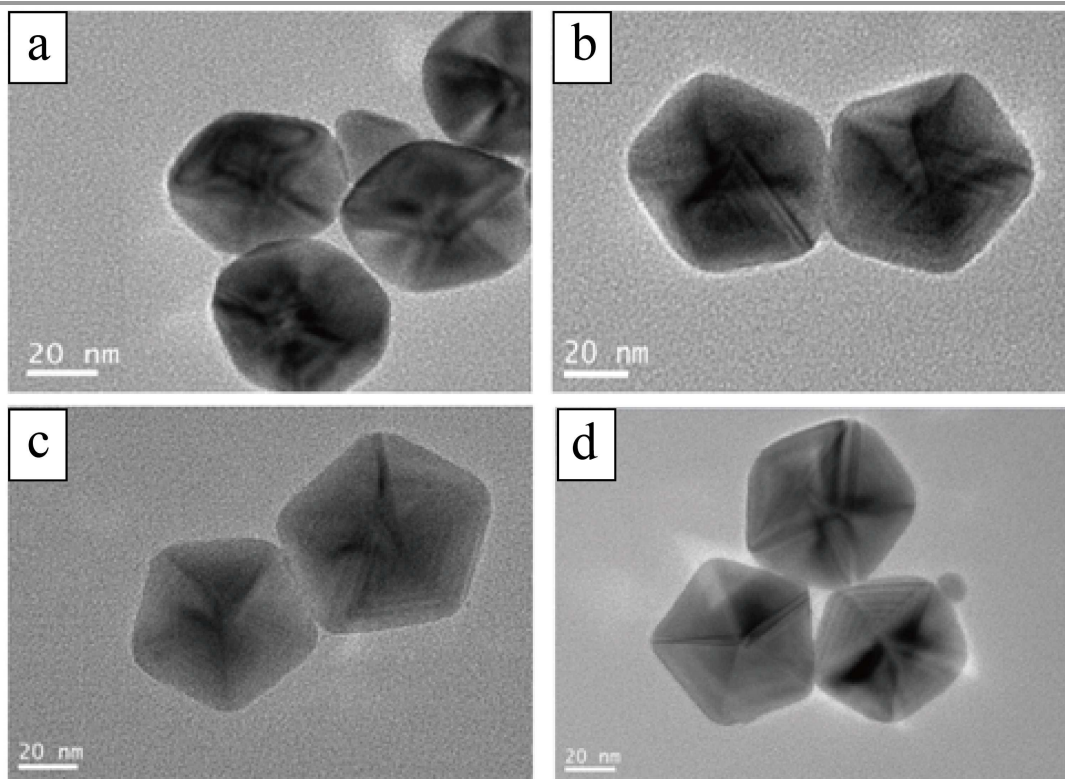


Fig. 3 Typical TEM morphologies of silver nanodecahedra grown at 50°C: a) 30 min, b) 50 min, c) 70 min, d) 90 min.

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These results demonstrate that the reaction temperature played a very important role in the photochemical growth of silver nanodecahedra. To investigate the effect of the reaction temperature on the properties of the particles, silver nanodecahedra colloidal solutions prepared at different temperatures were analyzed by UV/vis spectroscopy. All the spectra revealed a red-shift region, as shown in Figure S2 of the supporting information. Figure 2 shows the variation of the LSPR wavelength with the reaction time for the silver nanodecahedra colloidal solutions grown at 30, 40, 50, 60, and 70 °C in the red-shift region.

Here, T_s and W_s are defined as the corresponding time and LSPR wavelength of the start point of the red-shift region, respectively, and T_e and W_e are defined as the corresponding time and LSPR wavelength of the end point of the red-shift region, respectively. The W_e of the silver nanoparticles grown at different temperatures were all in the range of 490–500 nm, indicating that all the as-prepared silver nanoparticles were decahedral and their shapes did not vary when the reaction temperature changed. However, the reaction time in this photochemical process was influenced by the reaction temperature. As shown in Figure 2, the T_s and T_e both decreased as the reaction temperature increased, suggesting that the reaction temperature was an important parameter in the photochemical process, as in the thermal synthesis, and the higher temperature could accelerate the reaction, stimulating the aggregation of the silver seeds and the formation of

nanoparticles. The W_s increased and the range of the red-shift region (ΔW) was reduced as the reaction temperature increased.

Besides, it was also found that the LSPR peak was enhanced linearly as increasing the reaction time when the reaction temperature was kept constant. Therefore, this method could be proposed to tune the LSPR peak of silver nanoparticles precisely by controlling the reaction time directly in order to meet the requirements in practical application because this photochemical reaction could be terminated immediately by turning off the LEDs.

The mechanism on the red-shift of LSPR peak of silver nanodecahedras was investigated. The typical TEM morphologies of silver nanodecahedras grown at 50°C in different stage were shown in Figure 3. The average edge lengths of silver nanodecahedras grown at 30 min, 50 min, 70 min and 90 min were calculated to be 32.8 nm, 34.5 nm, 37.2 nm and 37.6 nm, respectively. It indicated that the size of silver nanodecahedras was enhanced as increasing the reaction time. A numerical simulation was carried out to access the effect of size variation on the LSPR peak of silver nanodecahedras with the commercial software package COMSOL Multiphysics (COMSOL Inc.), as shown in figure 4a). According to the simulation, a red-shift of 10 nm from 450 nm to 460 nm due to the size variation was obtained, which was not match with the results in the experiment. It was obvious that the size variation was not the main drive force of the LSPR peak shift of silver nanodecahedras.

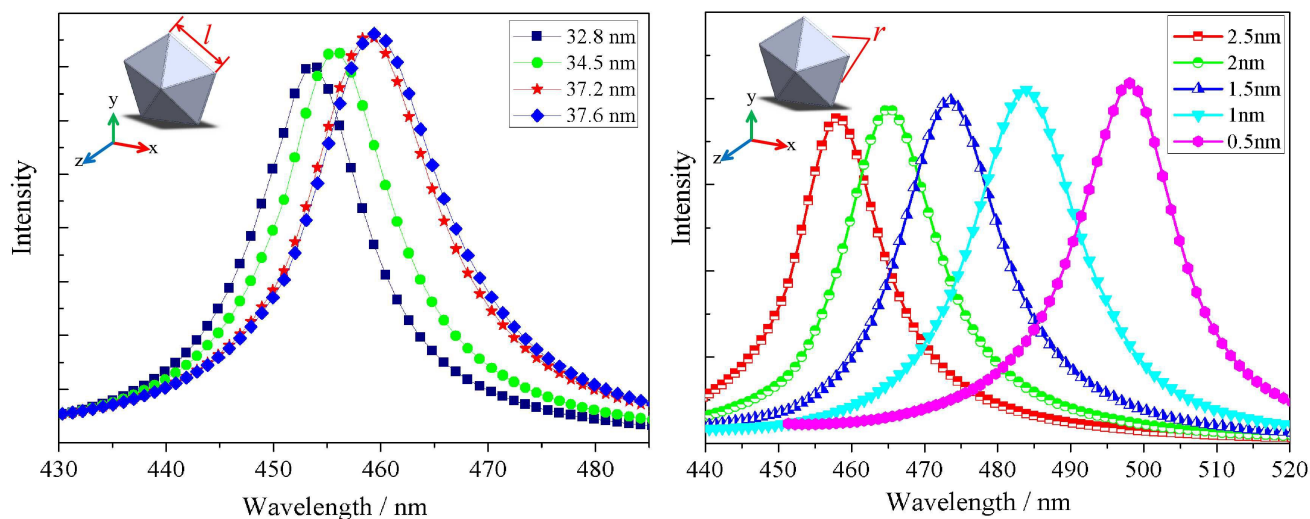


Fig. 4. Numerical simulation of the effect of (a) edge length and (b) radius of the corner on the LSPR peak of silver nanodecahedras.

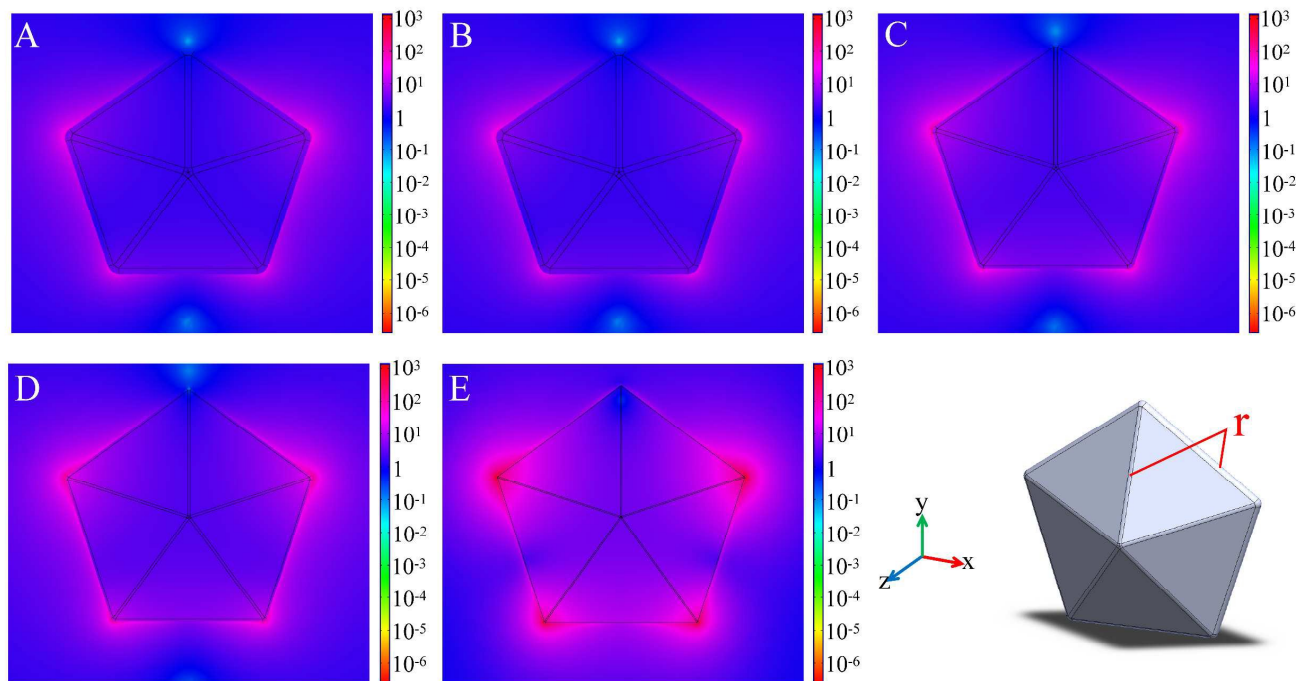


Fig. 5. Distribution of electric field of silver nanodecahedra with different corner radii: (a) 2.5 nm, (b) 2.0 nm, (c) 1.5 nm, (d) 1.0 nm, (e) 0.5 nm. Note that the electronic fields in five figures have been taken logarithm in order to contribute to a clear comparison of five field distributions with the same scale bar. The maximal values of the actual field intensity in five figures are 378 V/m (a), 506 V/m (b), 651 V/m (c), 985 V/m (d), and 2471 V/m (e), respectively.

As shown in figure 3, the corner variation of the silver nanodecahedras grown at different time was observed clearly. The silver nanodecahedras with round corner was observed at the early stage and the corner sharpness was enhanced as increasing the reaction time. Then, a further numerical simulation was carried out to access the effect of corner variation on the LSPR peak of silver nanodecahedras, as shown in figure 4b). In this simulation, radius of curvature was represented as corner sharpness. The smaller the radius of curvature was, the sharper the corner was. According to the simulation, a red-shift of 41 nm from 457 nm to 498 nm was obtained when the radius of curvature was reduced from 2.5 nm to 0.5 nm. The result in this simulation was almost as same as that in the experiment, indicating that the LSPR red-shift of the photochemical-derived silver nanodecahedras grown with temperature control was mainly generated by the corner variation.

The distribution of electric field of silver nanodecahedras with different corner sharpness was also simulated, as shown in figure 5. The localized energy of silver nanodecahedras was enhanced gradually as reducing the radius of corner. It

indicated that the intensity of LSPR peak of silver nanodecahedras was enhanced due to the sharpened corner. This result was also match with that in our experiment very well. As shown in figure 2b), the intensity of the LSPR in the red-shift region were improved gradually as increasing the reaction time when the reaction temperature was kept constant in the photochemical synthesis of silver nanodecahedras. This result gave another evidence that the red-shift of LSPR peaks of the photochemical-derived silver nanodecahedras grown with temperature control was generated by the corner variation.

4. Conclusion

We demonstrated a novel method to precisely tune the LSPR band of silver nanoparticles by controlling the reaction time of the photochemical synthesis. In the conventional photochemical process, the intensity of the in-plane dipole LSPR peak at 485 nm of silver nanodecahedra increased as the reaction time increased, but the wavelength did not change. However, when the reaction temperature was kept constant, a red shift of the in-plane dipole LSPR peak from 460 nm to 500 nm was observed, and the LSPR wavelength increased linearly with the reaction time in the red-shift region. Theoretical simulations

demonstrated that the red shift of the LSPR peak was mainly induced by variations in the corner sharpness. Therefore, based on the present improved method, we can accurately tune the LSPR peak to satisfy any practical application requirements with nanometer precision. Notably, in this study, we only investigated silver nanodecahedra as an experimental example. However, the modified photochemical method with appropriate temperature control can be similarly applied to silver nanoparticles with other geometrical shapes to obtain an accurate LSPR tuning.

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Notes and references

* Corresponding authors.

^a Institute of Optoelectronics, Key Lab of Optoelectronics Devices and Systems of Ministry of Education/Guangdong Province, Shenzhen University, 518060, Shenzhen, China; and Key Laboratory of Micro-Nano Measuring and Imaging in Biomedical Optics, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China.

[†] These authors contributed equally.

* E-mail: songjun@szu.edu.cn, jlqu@szu.edu.cn

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- (1) Malinsky M., Kelly K., Schatz G., Van Duyne R. Chain Length Dependence and Sensing Capabilities of the Localized Surface Plasmon Resonance of Silver Nanoparticles Chemically Modified with Alkanethiol Self-Assembled Monolayers, *J. Am. Chem. Soc.* 2001, 123, 1471-1482
- (2) Zito G., Rusciano G., Pesce G., Dochshanov A., Sasso A. Surface-enhanced Raman imaging of cell membrane by a highly homogeneous and isotropic silver nanostructure, *Nanoscale*, 2015,7, 8593-8606
- (3) Li J., Zhao T., Chen T., Liu Y., Choon N. O., Xie J. Engineering noble metal nanomaterials for environmental applications, *Nanoscale*, 2015,7, 7502-7519
- (4) Sanders A., Routenberg D., Wiley B., Xia Y., Dufresne E., Reed M. Observation of Plasmon Propagation, Redirection, and Fan-Out in Silver Nanowires, *Nano Lett.*, 2006, 6, 1822-1826
- (5) Ahn B., Duoss E., Motala M., Guo X., Park S., Xiong Y., Yoon J., Nuzzo R., Rogers J., Lewis J. Omnidirectional Printing of Flexible, Stretchable, and Spanning Silver Microelectrodes, *Science*, 2009, 323, 1590-1593
- (6) Xian J., Chen L., Niu H., Qu J., Song J. Significant field enhancements in an individual silver nanoparticle near a substrate covered with a thin gain film, *Nanoscale*, 2014, 6, 13994-14001
- (7) Noginov M., Zhu G., Belgrave A., Bakker R., Shalaev V., Narimanov E., Stout S., Herz E., Suteewong T., Wiesner U. Demonstration of a Spaser-Based Nanolaser, *Nature*, 460, 1110-1113
- (8) Kannan P., Rahim F., Teng X., Chen R., Sun H., Huang L., Kim D.-H. Enhanced Emission of NaYF₄:Yb,Er/Tm Nanoparticles by Selective Growth of Au and Ag Nanoshells, *RSC Advances*, 2013, 3, 7718-7721
- (9) Yuan P., Lee Y., Gnanasammandhan M., Guan Z., Zhang Y., Xu Q. Plasmon Enhanced Upconversion Luminescence of NaYF₄:Yb,Er@SiO₂@Ag core-shell Nanocomposites for Cell Imaging, *Nanoscale*, 2012, 4, 5132-5137
- (10) Gordon J. The Design and Simulated Performance of a Coated Nano-particle Laser, *Optical Express*, 2007, 15, 2622-2653
- (11) Chen X., Jia B., Saha J., Cai B., Stokes N., Qiao Q., Wang Y., Shi Z., Gu M. Broadband Enhancement in Thin-Film Amorphous Silicon Solar Cells Enabled by Nucleated Silver Nanoparticles, *Nano Lett.* 2012, 12, 2187-2192
- (12) Cassar R., Graham D., Larmour I., Wark A., Faulds K. Synthesis of Size Tunable Monodispersed Silver Nanoparticles and the Effect of Size on SERS Enhancement, *Vibrational Spectroscopy*, 2014, 71, 41-46
- (13) Personick M., Langille M., Zhang J., Mirkin C. Shape Control of Gold Nanoparticles by Silver Underpotential Deposition, *Nano Lett.* 2011, 11, 3394-3398
- (14) Wiley B., Im S., Li Z., McLellan J., Siekkinen A., Xia Y. Maneuvering the Surface Plasmon Resonance of Silver Nanostructures through Shape-Controlled Synthesis, *J. Phys. Chem. B* 2006, 110, 15666-15675
- (15) Sun Y., Xia Y. Shape-Controlled Synthesis of Gold and Silver Nanoparticles, *Science*, 2002, 298, 2176-2180
- (16) Rang M., Jones A., Zhou F., Li Z., Wiley B., Xia Y., Raschke M. Optical Near-Field Mapping of Plasmonic Nanoprisms, *Nano Lett.*, 2008,8, 3357-3363
- (17) Zheng X., Zhao X., Guo D., Tang B., Xu S., Zhao B., Xu W. Photochemical Formation of Silver Nanodecahedra Structural Selection by the Excitation Wavelength, *Langmuir*, 2009, 25, 3802-3807
- (18) Liu S.-Y., Huang L., Li J., Wang C., Li Q., Xu H., Guo H., Meng Z., Shi Z., Li Z. Simultaneous Excitation and Emission Enhancement of Fluorescence Assisted by Double Plasmon Modes of Gold Nanorods, *J. Phys. Chem. C* 2013, 117, 10636-10642
- (19) Cobley C., Rycenga M., Zhou F., Li Z., Xia Y. Controlled Etching as a Route to High Quality Silver Nanospheres for Optical Studies, *J. Phys. Chem. C* 2009, 113, 16975-16982
- (20) Zhang Q., Li W., Moran C., Zeng J., Chen J., Wen L., Xia Y. Seed-Mediated Synthesis of Ag Nanocubes with Controllable Edge Lengths in the Range of 30-200 nm and Comparison of Their Optical Properties, *J. Am. Chem. Soc.* 2010, 132, 11372-11378
- (21) Kelly K., Coronado E., Zhao L., Schatz G. The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment, *J. Phys. Chem. B* 2003, 107, 668-677

- (22). Rycenga M., Cobley M., Zeng J., Li W., Moran C., Zhang Q., Qin D., Xia Y. Controlling the Synthesis and Assembly of Silver Nanostructures for Plasmonic Applications, *Chem. Rev.* 2011, 111, 3669–3712
- (23). Jin R., Cao Y., Mirkin C., Kelly K., Schatz G., Zheng J. Photoinduced Conversion of Silver Nanospheres to Nanoprisms, *Science*, 2001, 294, 1901-1903
- (24). Yu H., Zhang Q., Liu H., Dahl M., Joo J., Li N., Wang L., Yin Y. Thermal Synthesis of Silver Nanoplates Revisited: A Modified Photochemical Process, *ACS Nano*, 2014, 8, 10252-10261
- (25). Wang H., Zheng X., Chen J., Wang D., Wang Q., Xue T., Liu C., Jin Z., Cui X., Zheng W. Transformation from Silver Nanoprisms to Nanodecahedra in a Temperature-Controlled Photomediated Synthesis, *J. Phys. Chem. C* 2012, 116, 24268–24273
- (26). Jin R., Cao Y., Hao E., Metraux G., Schatz G., Mirkin C. Controlling Anisotropic Nanoparticle Growth Through Plasmon Excitation, *Nature*, 2003, 425, 487-490
- (27). Callegari A., Tonti D., Chergui M. Photochemically Grown Silver Nanoparticles with Wavelength-Controlled Size and Shape, *Nano Lett.*, 2003, 3, 1565-1568
- (28). Millstone J., Hurst S., Metraux G., Cutler J., Mirkin C. Colloidal Gold and Silver Triangular Nanoprisms, *Small*, 2009, 5, 646–664
- (29). Zhou J., An J., Tang B., Xu S., Cao Y., Zhao B., Xu W., Chang J., Lombardi J. Growth of Tetrahedral Silver Nanocrystals in Aqueous Solution and Their SERS Enhancement, *Langmuir* 2008, 24, 10407-10413
- (30). Aherne D., Ledwith D., Gara M., Kelly J. Optical Properties and Growth Aspects of Silver Nanoprisms Produced by a Highly Reproducible and Rapid Synthesis at Room Temperature, *Adv. Funct. Mater.* 2008, 18, 2005–2016
- (31). Xue C., Metraux G., Millstone J., Mirkin C. Mechanistic Study of Photomediated Triangular Silver Nanoprism Growth, *J. Am. Chem. Soc.* 2008, 130, 8337–8344
- (32). An J., Tang B., Ning X., Zhou J., Xu S., Zhao B., Xu W., Corredor C., Lombardi J. Photoinduced Shape Evolution: From Triangular to Hexagonal Silver Nanoplates, *J. Phys. Chem. C* 2007, 111, 18055-18059
- (33). Pietrobon B., Kitaev V. Photochemical Synthesis of Monodisperse Size-Controlled Silver Decahedral Nanoparticles and Their Remarkable Optical Properties, *Chem. Mater.* 2008, 20, 5186–5190
- (34). Zhang Q., Cobley C., Au L., McKiernan M., Schwartz A., Wen L., Chen J., Xia Y. Production of Ag Nanocubes on a Scale of 0.1 g per Batch by Protecting the NaHS Mediated Polyol Synthesis with Argon, *ACS Appl. Mater. Inter.*, 2009, 1, 2044–2048
- (35). Zhang J., Langille M., Mirkin C. Synthesis of Silver Nanorods by Low Energy Excitation of Spherical Plasmonic Seeds, *Nano Lett.* 2011, 11, 2495–2498
- (36). Hao E., Schatz G. Electromagnetic Fields around Silver Nanoparticles and Dimers, *J. Chem. Phys.*, 2004, 120, 357-366
- (37). Zeng J., Roberts S., Xia Y. Nanocrystal-Based Time–Temperature Indicators, *Chem. Eur. J.* 2010, 16, 12559 – 12563
- (38). Yang L., Lai Y., Tsai C., Kong Y., Lee C., Huang C. One-Pot Synthesis of Monodispersed Silver Nanodecahedra with Optimal SERS Activities Using Seedless Photo-Assisted Citrate Reduction Method, *J. Phys. Chem. C* 2012, 116, 24292–24300
- (39). Maretti L., Billone P., Liu Y., Scaiano J. Facile Photochemical Synthesis and Characterization of Highly Fluorescent Silver Nanoparticles, *J. Am. Chem. Soc.* 2009, 131, 13972–13980
- (40). Stamplecoskie K., Scaiano J. Light Emitting Diode Irradiation Can Control The Morphology and Optical Properties of Silver Nanoparticles, *J. Am. Chem. Soc.* 2010, 132, 1825–1827