

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231648728>

# Distinctive Enhanced and Tunable Plasmon Resonant Absorption from Controllable Au@Cu<sub>2</sub>O Nanoparticles: Experimental and Theoretical Modeling

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY C · FEBRUARY 2012

Impact Factor: 4.77 · DOI: 10.1021/jp211565c

CITATIONS

31

READS

56

8 AUTHORS, INCLUDING:



**Song-Yuan Ding**

Xiamen University

15 PUBLICATIONS 206 CITATIONS

SEE PROFILE



**Feng Fan**

Jiangsu University

91 PUBLICATIONS 2,493 CITATIONS

SEE PROFILE



**Bin Ren**

Xiamen University

272 PUBLICATIONS 8,629 CITATIONS

SEE PROFILE



**Zhong-Qun Tian**

Xiamen University

355 PUBLICATIONS 10,133 CITATIONS

SEE PROFILE

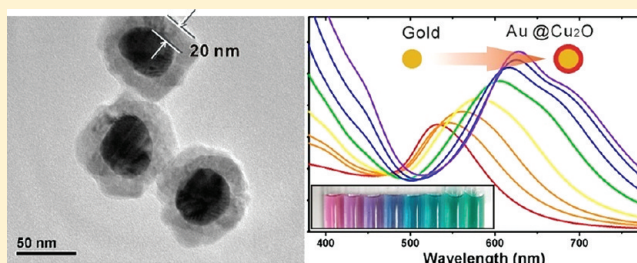
# Distinctive Enhanced and Tunable Plasmon Resonant Absorption from Controllable Au@Cu<sub>2</sub>O Nanoparticles: Experimental and Theoretical Modeling

De-Yu Liu,<sup>†</sup> Song-Yuan Ding,<sup>†</sup> Hai-Xin Lin, Bi-Ju Liu, Ze-Zhong Ye, Feng-Ru Fan, Bin Ren, and Zhong-Qun Tian\*

State Key Laboratory of Physical Chemistry of Solid Surfaces and College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China

**S** Supporting Information

**ABSTRACT:** Aiming to explore cooperative interactions between plasmonic metal and semiconductor nanostructures as well as their special plasmon resonant properties, we synthesized Au@Cu<sub>2</sub>O core-shell nanoparticles to demonstrate the dramatic influence of dielectric shell both experimentally and theoretically. The extinction spectra of Au@Cu<sub>2</sub>O nanoparticles with controllable shell thickness from a few layers to over 20 nm show not only a tunable red shift of resonant peak but also distinctive enhanced absorption intensity and peak splitting. We then built an analytical model based on an approximate Mie's theory to interpret their optical features. From this model, we found that the overall optical cross section and absorption portion of Au@Cu<sub>2</sub>O are dramatically enlarged. It has been shown that the proper dielectric shell-coated plasmonic nanoparticles could be very promising, especially for the applications that need effective enhancement of the plasmon resonant absorption.



## 1. INTRODUCTION

Metal nanoparticles (NPs) with localized surface plasmon resonance (LSPR) have attracted great attention for the interesting interactions with light and are widely applied as the optical responsive component in informatics, biomedicine, and other cutting-edge technologies. The LSPR properties of these NPs are most commonly tuned by engineering their sizes, morphologies, and geometry (aspect ratio and hollow cavity structures, etc.)<sup>1–7</sup> or, more fundamentally, by tailoring the components or carrier density.<sup>8</sup>

In addition to those parameters, the LSPR of metal NPs is also highly relevant to the surroundings. Basically, LSPR is generated by the dielectric difference between metal (negative) and surrounding (positive), which makes it highly sensitive to the environment. For example, adsorbed analytes can be detected via monitoring the change of LSPR frequency quantitatively.<sup>9–13</sup> This shift is also commonly witnessed at gold or silver NPs in colloid after various dielectric coating<sup>14–21</sup> or reversed configuration, i.e., the dielectric core with the SPR metallic shell; the dielectric difference also exerts a significant influence.<sup>22</sup> Recently, the metal chalcogenide shell is coated on a gold nanorod on purpose.<sup>23–25</sup> Not only the new optical properties from the coupling between CdS and gold NP, the surface plasmonic band also changes over a very considerable range that reaches several hundred nanometers. Furthermore, a moderate enhancement of LSPR was spotted after coating in

some cases,<sup>16,25</sup> which strongly correlates with the dielectric shell but has rarely been discussed.

Metal oxides as a group of semiconductive materials are widely used in many photochemical studies because of their facile sol-gel chemistry and relatively wide band gaps. Regarding the combination of oxide semiconductors and metallic NPs with SPR, more attention is usually paid to the chemical processes on oxides and the electron interactions between them.<sup>14,20,21,26,27</sup> The SPR changes of those coated metallic NPs are always considered to be a minor side effect. As one typical combination of LSPR NPs and oxide semiconductors, Au@Cu<sub>2</sub>O has attracted many attentions for its novel structure and potential applications in solar energy conversion.<sup>28–31</sup> Besides the interesting p-type semiconducting nature, Cu<sub>2</sub>O has an appropriate high refractive index (2.705 in visible region),<sup>32</sup> which leads to a very strong influence of Cu<sub>2</sub>O toward the LSPR of embedded NPs. The structure of Au NP with a Cu<sub>2</sub>O shell shows interesting shell-dependent SPR light extinction. Such yolk-shell structure and relative large size leads to several multipolar LSPR modes with fine structures on the spectrum.<sup>28</sup> However, the influence of a dielectric shell toward the SPR dipole mode was not well performed yet. For instance, with too many subtle bands, as well as the influence

**Received:** December 1, 2011

**Revised:** January 5, 2012

**Published:** January 10, 2012

from geometric parameters of core or shell part, the aforementioned SPR enhancement is hard to be discussed.

In our earlier works, we have successfully fabricated pinhole free nanoparticles with gold cores and different metallic shells in aqueous solution. The controllable shell thickness enables us to study various shell-dependent influences.<sup>33,34</sup> Just as our previously synthesized Au@Pd NPs with epitaxial grown shell, a great similarity between gold and Cu<sub>2</sub>O crystals (both are fcc crystals and the lattice mismatch between them are less than 5%) suggests that the Cu<sub>2</sub>O overgrowth layer is also likely to be deposited on the surface of gold without strong lattice stresses.<sup>32</sup> On the basis of this fact, we successfully prepared Au@Cu<sub>2</sub>O NPs with controllable thickness. Besides the uniform and compact coating, their suspension status in colloid is well maintained, which serves to be a basic for the comparison of LSPR intensities between samples and for the realistic simulation model. Interestingly, both our experimental spectra and simulations indicate that the final profile of LSPR peak is much more sensitive to the geometry of core NP rather than shell. More significantly, the LSPR, especially the absorption intensity, is distinctly enhanced with the increasing shell thickness in all cases. The comparison between Au@Cu<sub>2</sub>O and homogeneous gold NP suggests that the light extinction is dominated by absorption rather than scattering. All these new features mentioned above motivate this core-shell structure to be very promising for the conversion of light energy.

## 2. EXPERIMENTAL SECTION

**Materials.** Polyvinylpyrrolidone (PVP) with  $M_w$  of 55 000 was purchased from Aldrich. HAuCl<sub>4</sub> (Analytical Reagents, AR), AgNO<sub>3</sub> (Guaranteed Reagent, GR), CuSO<sub>4</sub> (AR), ascorbic acid (AR), sodium citrate (AR), and absolute ethanol (AR) were purchased from Shanghai Reagent Co. of Chinese Medical. Water purified with a Milli-Q system was used throughout the study; the resistivity is no less than 18.2 MΩ·cm.

**Synthesis of Gold Nanoparticles.** Gold NPs were synthesized according to Frens' method. Briefly, 100 mL of aqueous solution containing 0.01% HAuCl<sub>4</sub> is refluxed for several minutes, and then 0.7 mL of 1% trisodium citrate aqueous solution was injected to the flask rapidly. The flask is kept refluxing for another 30 min. The solution turns to black in several minutes and finally becomes purple-red. The average size of gold NPs is about 60 ± 10 nm counted under a scanning electron microscope.

**Synthesis of Au@Cu<sub>2</sub>O Core-Shell Nanoparticles.** All reagents applied in this synthesis are aqueous solution. The whole procedure of Cu<sub>2</sub>O coating is performed in an ice-water bath. Typically, 10 mL of as-prepared gold hydrosol was mixed with 1 mL of 10 mM PVP and 0.2 mL of 0.1 M sodium citrate and followed by 0.5 mL of 20 mM CuSO<sub>4</sub>. After being diluted to 25 mL and cooled to 0 °C, the hydrosol is blended with 0.28 mL of 1 M NaOH and 2 mL of 0.1 M ascorbic acid consequently. For Au@Cu<sub>2</sub>O with thicker shell (Cu<sub>2</sub>O shell more than ~30 nm), the Cu<sup>2+</sup> concentration will be too high to maintain a stable colloid. Correspondingly, the procedure was modified to tune shell thickness by reducing the amount of Au NP. The color of reacting colloid turns to green in about half an hour. Then the solution was kept in ice-water bath for 4 h to complete the reaction. The precipitates were separated from matrix solution by centrifugation at 5000 rpm for 10 min. After being washed with distilled water and ethanol several times, the

NPs were loaded on silicon chips or copper grid for further electron microscopic characterization.

**Instruments.** The UV-vis extinction spectra of NP hydrosol were taken by a Varian Cary-300 UV-vis spectrometer at their origin disperse state, with 1 cm optical path of quartz cuvette. All samples are normalized to the same concentration (by particle number). Dark-field images and single particle scattering spectra of NPs were collected by a Renishaw inVia Raman system with a Leica DMI 3000 M inverted microscope. The NPs were loaded on a quartz glass slide by drop-casting directly. Specimens were illuminated with a 100× dark-field condenser lens of 0.75 NA, and the signal was collected by a 50× objective lens of 0.55 NA. Raman spectra of hydrosol were recorded on a LabRam I confocal microprobe Raman system. SEM images were taken by a LEO1530 SEM and Hitachi S-4800 scanning electron microscope. Both TEM and SAED images of the NPs were acquired with an FEI Tecnai F30 microscope operating at 300 kV. X-ray diffraction data were collected with a PANalytical X'pert PRO diffractometer.

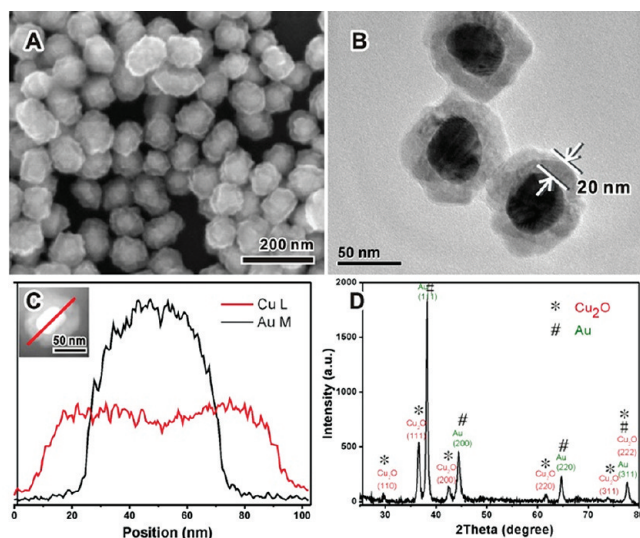
## 3. RESULTS AND DISCUSSION

Briefly, spherical gold NPs with size about 60 nm synthesized by Frens' method<sup>35</sup> are used as the LSPR core. Because of the good affinity of Cu<sub>2</sub>O to the surface of gold NP, which is reported in the literature as their similar crystal symmetry and only about 4.5% lattice mismatch, Cu<sub>2</sub>O highly prefers to form a compact and crystallized shell rather than amorphous islands.<sup>29,36,37</sup> Besides, the reaction pH and temperature were also finely controlled to obtain the proper reducing rate, in the case of the homogeneous seeding of Cu<sub>2</sub>O. Furthermore, to prevent gold colloid from flocculation, we applied PVP and additional citrate to stabilize the hydrosol (Figure S1). As shown in Figure S1, the SPR feature is well maintained with these protections. To the contrary, if Cu<sup>2+</sup> was added solely, the SPR features are totally erased.

Figure 1 shows the structural characterizations of Au@Cu<sub>2</sub>O core-shell NPs. The SEM image of Figure 1A indicates the NPs have a good monodispersity with narrow size distribution. The average size of gold core is 60 ± 10 nm, while after being coated with Cu<sub>2</sub>O the total size increased to 105 ± 8 nm. Because of the different electron penetration depths and secondary electron intensities of two components, every particle shows a brighter core in the center. The TEM image shows each gold NP (Figure 1B) is encapsulated by a compact crystallized layer. So far in our experiment, we did not find any particles with multiple cores in the product. Besides, the STEM-EDS line profile analysis (Figure 1C) of a single Au@Cu<sub>2</sub>O NP reveals that gold element mainly locates at the central area, while copper locates on the fringe, which well matches the core-shell structure. X-ray diffraction pattern also confirmed that the phase compositions are gold and Cu<sub>2</sub>O (Figure 1D, JCPDS 5-667 and JCPDS 4-784, respectively), which corresponds to the proper reduction of Cu(II) to Cu(I).

Au@Cu<sub>2</sub>O NPs with other thickness are investigated by electron microscopy as well (Figure S2). Particle sizes of a series of samples have been measured under SEM to obtain the size distributions (Figure S3). The histogram of Au@Cu<sub>2</sub>O NP with different shell thickness agrees quite well with the predicted thickness and justifies the effective deposition of Cu<sub>2</sub>O. As the shell thickness increases, this histogram well maintained the single peak profile. Statistically, the correlation between average size and relative standard deviation of size distribution (Figure S4) proves the coating is effective and





**Figure 1.** (A) SEM image and (B) TEM image of Au@Cu<sub>2</sub>O core-shell NPs with the shell thickness about 20 nm. (C) The line scanning STEM-EDX analysis of one core-shell NP with copper and gold distribution (inset is the corresponding STEM image of the particle and EDX scanning track). (D) XRD pattern (powder) of Au@Cu<sub>2</sub>O NP; two sets of peaks correspond to the lattice of gold and cuprous oxide.

uniform. In terms of the large dielectric particle, some higher multipolar Mie's scattering could overlap with LSPR peak. Since the influence of a thick shell and void inside has been well demonstrated,<sup>28</sup> we only focused on those smaller particles with typical dipole SPR band.

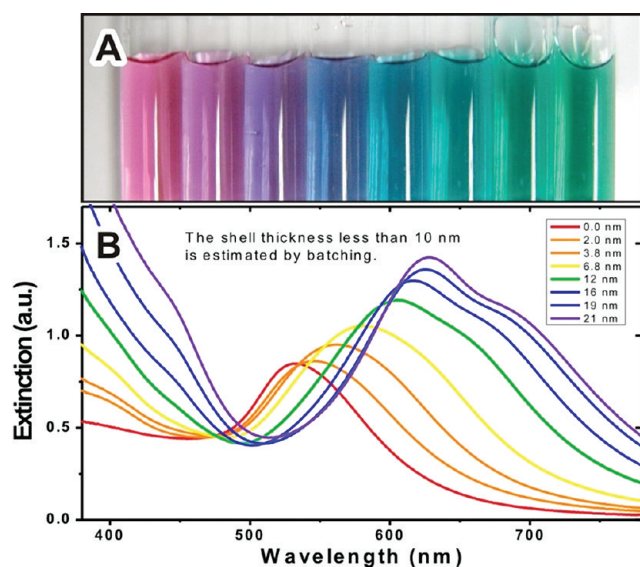
Considering the importance of silver as a surface plasmonic material and its similar crystal structure of gold, we think it is interesting and necessary to demonstrate the same coating on silver nanoparticles. By a similar procedure, we also achieved Ag@Cu<sub>2</sub>O NPs with a uniform coating on silver surface (Figure S5). However, because of the component differences between Ag and Au colloid, we modified the amounts of reagents, and it might cause slight differences between these NPs, which might result in the different acidity of colloid based on our observation. Generally, the coating is still reliable and uniform on the surface of Ag NP. However, the Ag NP we used here is not as high quality as Au NP. Considering the minor statistical significance, we did not further count the particle size distribution.

Apparently, the morphology of shell not only has effects on the SPR feature of whole core-shell NP but also serves as a critical factor needed to be considered in theoretical modeling. Because of various possible growth mechanism of oxide from solution chemistry, the morphologies during reaction are not necessarily fit in the same model. A concentric layered structure is very different from the scenario of small islands decorating on the gold nanoparticle. Compared with the NPs with smooth and compact Cu<sub>2</sub>O coating of 20 nm thick that mentioned above, those NP with very thin Cu<sub>2</sub>O shells are even more important because less Cu<sub>2</sub>O makes it more possible to form a discrete layer composed by many islands. Thus, experiments on clarifying the growth mode of Cu<sub>2</sub>O on gold nanoparticle in our conditions is very helpful for building a proper model. Considering epitaxial growth is one of the most common layer-by-layer modes among crystals, we verified the experimental conditions are suitable for an epitaxial Cu<sub>2</sub>O layer on crystal

structure well-defined gold nanocrystals (gold nanocube, Figure S6). However, it is well-known that the gold nanospheres synthesized by Frens' method are crystallized but not necessarily single crystals, especially for those particles as large as in this work. The epitaxial growth on one particle but different crystal region leads to a random orientated shell; therefore, the epitaxial growth on gold nanospheres is hard to be confirmed directly.

Concentric layered structure of our prepared nanoparticles with shell thickness down to about 10 nm is confirmed by TEM (Figure S2). Several unsuccessful trial toward thinner shells (approximately less than 5 nm) has failed, which suggests the shell seems to be too thin to suffer the long time fine HR-TEM characterizations. To get around this problem, we then applied a very powerful surface-sensitive method, surface enhanced Raman scattering (SERS), to determine the growth quality of thin shell and as a circumstantial evidence of concentric structure. The pinhole on a coating over Au or Ag nanostructure can be detected by checking the signal from specifically adsorbed molecule on metal surface. As what SERS spectra indicate (Figure S7), gold NP colloid effectively enhances the signal from adsorbed MGITC molecules; three feature bands are noted on the spectra. To the contrast, even though the NP is coated with a very thin Cu<sub>2</sub>O shell, the intensities of bands decrease sharply, which is apparently due to the Cu<sub>2</sub>O layer that creates the separation of probe molecule and gold surface. In order to double-check whether this decreasing is caused by other physical effects induced by the shell, we synthesized another batch of core-shell NP as the control experiment in which MGITC probe was functionalized to gold surface before coating (Figure S8). This group NPs has similar morphology and extinction to the default group samples (which are functionalized with MGITC after the coating). On the basis of our observation, even the shell is as thick as over 20 nm, the peaks in this control group are still not strongly weakened. Thus, without isolating probe molecule from gold, the sole existence of Cu<sub>2</sub>O is not likely to attenuate the signal. If there were some pinholes on the coating layer of the default group, the intensity would not decrease so much as well, especially with the NP with thinnest shell. Therefore, our experiments convincingly demonstrated that the Cu<sub>2</sub>O coating layer is indeed pinhole-free. Thus, the validated pinhole-free and thickness-controllable Au@Cu<sub>2</sub>O NPs will pave the road to build a realistic model for the following concentric core-shell computation studies.

Along with the increase of Cu<sub>2</sub>O shell thickness, the LSPR extinction of the Au@Cu<sub>2</sub>O NP changes dramatically. As the photograph shows (Figure 2A), the color of hydrosol is very different before and after the coating of Cu<sub>2</sub>O. The hydrosols present different colors changing gradually from magenta red to cyan blue and green according to different shell thickness. This dramatic change is apparently related to the core-shell interaction and suggests the light extinction has shifted to red as the complementary color. The UV-vis spectra clearly show a LSPR red shift correlated with increasing shell thickness (Figure 2B). Meanwhile, the interband transitions of Cu<sub>2</sub>O get stronger and stronger at about 2.5 eV (450–480 nm). To experimentally estimate the gold nanoparticle LSPR red shift caused by Cu<sub>2</sub>O shell, we have drawn a fitting curve of SPR peak position to the shell thickness with a good exponential correlation ( $R^2 = 0.99$ ) (Figure S9). Roughly, this relationship could resemble to the refractive index response of propagating surface plasmons on a planar noble metal surface:



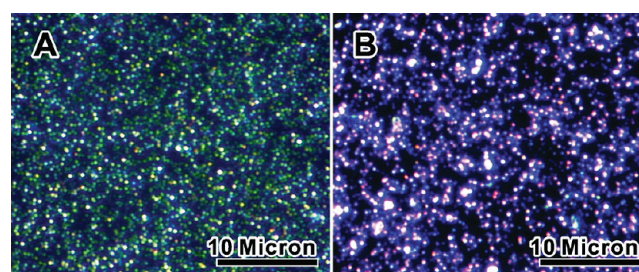
**Figure 2.** (A) Photograph and (B) UV-vis spectra of Au@Cu<sub>2</sub>O NPs with Cu<sub>2</sub>O shell of increasing thickness, from left to right clearly showing the red shift of LSPR extinction.

$$\Delta\lambda_{\max} = m\Delta n[1 - \exp(-2d/l_d)] \quad (1)$$

where the  $\Delta\lambda_{\max}$  is the wavelength shift,  $m$  is the refractive index sensitivity,  $\Delta n$  is the refractive index difference between shell and surroundings,  $d$  is the thickness of adsorbed dielectric layer, and  $l_d$  is the characteristic electromagnetic field decay length.<sup>38</sup> This equation correlates the SPR shift with dielectric shell thickness and the exponential decay of electromagnetic field from inner core. We also attained the UV-vis spectra of Ag@Cu<sub>2</sub>O (Figure S10). The spectra show that silver LSPR peak is also tunable over whole visible region that similar to Au@Cu<sub>2</sub>O.

Besides the shift, we noticed an abnormal peak broadening along with shell thickening, which then further turns to peak splitting at longer wavelength. Moreover, the split peak looks like an overlapping of two bands with the same width of initial LSPR. The nature of this broadening could be either the broadening of every single band or small differences between some very close bands have been enlarged.

To clarify this question, it is helpful to study the LSPR spectra of individual particles rather than their collective properties. We used the dark field (DF) mode of the optical microscope, which only collects the emission light from sample, to study the LSPR scattering of Au@Cu<sub>2</sub>O particles. Several snapshots were taken under this mode to give a direct view of the dielectric effect caused by Cu<sub>2</sub>O coating. As the micrograph shows, those bared gold NPs are green (Figure 3A); to the sharp contrast (Figure 3B), most of Au@Cu<sub>2</sub>O NPs appear red in color. This phenomenal color change is according to the scattering portion of affected LSPR extinction, which is the light received under DF mode. Furthermore, we also tried to acquire emission spectra from single nanoparticles. However, since the signal from bared gold NP is too weak for our setup, we only obtained spectra from the Au@Cu<sub>2</sub>O NPs (Figure S11). Few spectra of single NPs are similar to the collective extinction UV-vis spectrum. Besides, the profiles of those single particle spectra are with shoulders and even dual peaks. Thus, the shoulder peak on Au@Cu<sub>2</sub>O colloid UV-vis spectrum is possible to be a result of averaging many different



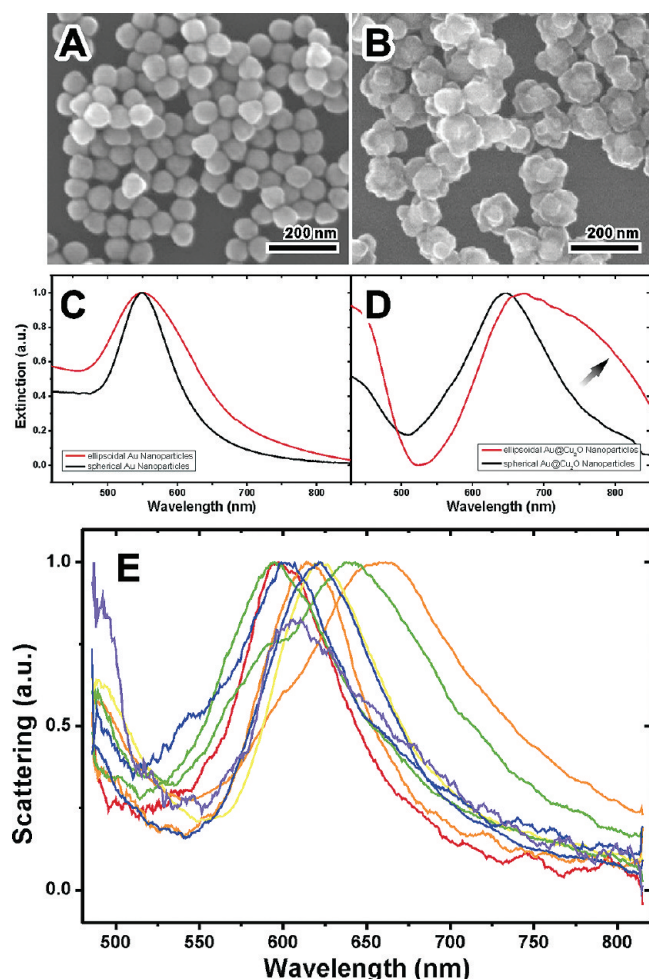
**Figure 3.** Dark field micrograph of (A) bared gold NP and (B) Au@20 nm Cu<sub>2</sub>O NP.

spectra containing several bands. Interestingly, each of the half bandwidth is very close to the typical value of gold LSPR, which is about 100 nm. Even when the gold NPs have not been coated, those subtle band structures might already exist, which could just possess some very similar peak positions that do not strongly broadened the UV-vis spectrum of gold colloid. After gold NPs are coated with Cu<sub>2</sub>O, these close bands are separated and shifted to different positions. This variety of spectra suggests that the band from each LSPR mode might not be broadened, but their differences got enlarged by Cu<sub>2</sub>O coating.

Consequently, we designed a control experiment to reveal the morphology effect of gold NP core. Gold NP with smaller aspect ratio was synthesized according to the report of Eychmüller (denoted as spherical, previous gold NP is called as ellipsoidal)<sup>39</sup> and then coated with Cu<sub>2</sub>O by the same protocol mentioned in the Experimental Section. Corresponding SEM images shows the morphologies of perfect spherical Au NPs before and after coating (Figure 4, A and B, respectively). The average aspect ratio is nearly 1.0 (while the aspect ratio of ellipsoidal gold NPs is ~1.2). By contrasting to the same coating procedure for two kinds of gold NP cores (the same 22 nm coating), their LSPR shift shows quite a significant difference. Figures 4C and 4D show the UV-vis extinction spectra without and with Cu<sub>2</sub>O coating, respectively. Both the spherical and ellipsoidal gold NP have a very typical surface plasmonic band located around 550 nm with symmetric peak shape. Because the spherical Au NPs have a better size distribution and more uniform morphology, its SPR band is slightly narrower. In contrast to their similar SPR before coating and peak shift after coating, Au@Cu<sub>2</sub>O NP with spherical core maintained their symmetric peak profile pretty well, but its ellipsoidal analogue shows clearly a shoulder peak. Moreover, as dark field spectra shown in Figure 4E, the individual difference between perfect spherical Au@Cu<sub>2</sub>O is much smaller than their ellipsoidal counterpart (Figure S11). Thus, this experiment directly confirms that the broadening and peak splitting are from anisotropic gold NP.

Interestingly, besides the frequency shifting, both UV-vis spectra and DF study suggest that the LSPR from Au@Cu<sub>2</sub>O is much stronger than bare gold NP. The LSPR peak area is enlarged by 20 nm Cu<sub>2</sub>O shell for about 1 order. Compared with silica or other well study shell, this enhancement is very significant. In the literature, this enhancement could be found occasionally with well-defined core-shell structure but almost has never been further discussed as an important issue.<sup>14–17,23,25–27,40</sup> To our knowledge, the SPR intensity of a core-shell NP is strongly related to the dielectric difference between shell and surroundings. For example, in terms of Au NPs coated by silica, even though the shell thickness is several hundreds of nanometers, its LSPR intensity barely changes.<sup>41</sup>



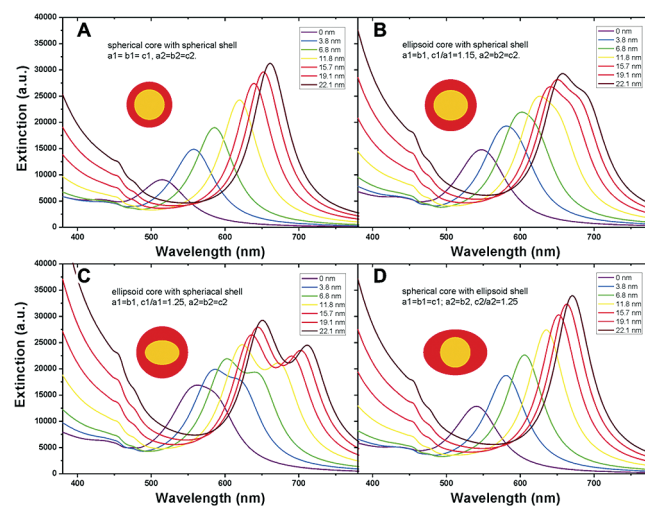


**Figure 4.** SEM image of multistep synthesized spherical Au NPs before (A) and after (B) coated with  $\text{Cu}_2\text{O}$ ; UV-vis spectra of Au NPs before (C) and after coated (D) with  $\text{Cu}_2\text{O}$ , red and black lines corresponding with ellipsoidal and spherical Au NPs, respectively. (E) is a set typical dark field spectra from single  $\text{Au}@\text{Cu}_2\text{O}$  core-shell NPs with spherical cores; note that there is no shoulder shape peak compared with the ellipsoidal core.

(A simulation corresponding to this  $\text{Au}@\text{SiO}_2$  NP has been shown as Figure S12 as well.) By comparison,  $\text{Cu}_2\text{O}$  has larger refractive difference with the surrounding than silica. For an Au NP coated with  $\text{Cu}_2\text{O}$ , a thinner shell can still create a significant LSPR intensity enhancement.

In an attempt to better understand the dramatic shell-thickness dependence of the LSPR extinction changes, we built a core-shell model to simulate the light scattering properties of  $\text{Au}@\text{Cu}_2\text{O}$  NPs which are nearly spherical or ellipsoidal. As the sizes of NPs are much smaller than the incident wavelength, electrostatic approximation can be taken to simplify the general scattering problem of ellipsoid particles by simply considering the induced dipole moment. This method can be easily extended to the coated ellipsoid problem.<sup>42</sup>

Interestingly, we found that the extinction peak answers quite differently to the core and shell geometries. Their influences are demonstrated by alternating the aspect ratio of either core or shell (eccentricity), respectively. Figure 5 shows that, generally, the  $\text{Cu}_2\text{O}$  shell contributes to a red shift and larger optical cross section to the whole particle. (For more computational details, please refer to the modeling part in the Supporting Information, p 18.) If both the core and shell are spherical,

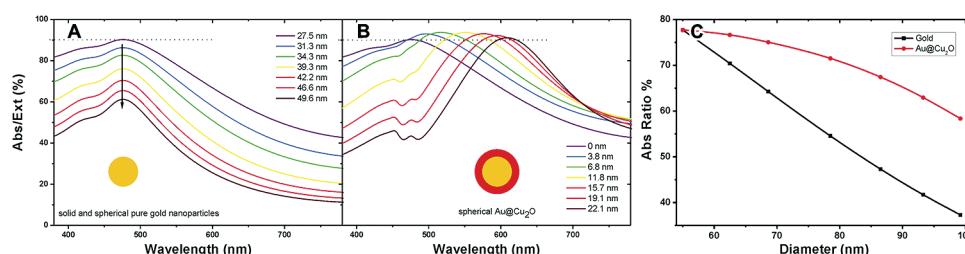


**Figure 5.** Simulated extinction spectra with different core-shell geometric parameters: (A) spherical gold core with spherical  $\text{Cu}_2\text{O}$  shell; (B, C) ellipsoid core of small and larger aspect ratio with spherical shell respectively; (D) for spherical core with ellipsoid shell ( $a_1, b_1$ , and  $c_1$  are semi-axes of the core ellipsoid;  $a_2, b_2$ , and  $c_2$  are those of the outer ellipsoid). See the detailed parameter setting on p 20 in the Supporting Information.

no splitting appears on the spectra; while the Au core is elongated to ellipsoid as Figure 5B, the peaks split a shoulder to lower energy in contrast to the spherical core and spherical shell counterpart (Figure 5A). Furthermore, these two peaks separate more individually due to a larger designated core aspect ratio (Figure 5C). On the contrary, even change the shell solely to a very large aspect ratio, the peak does not split at all (Figure 5D). Similarly, the roughness on shell surface should only have a secondary role to the SPR as well. Compared with the real gold core aspect ratio of 1.2 on average (200 counts by SEM), the simulation matches very well with the corresponding UV-vis spectra. In addition, the modeling points out increasing shell thickness lead to larger peak split. This also agrees quite well with our observation. In short, the morphological difference on shell surface barely contributes to the peak profile, but the  $\text{Cu}_2\text{O}$  shell can greatly enhance the difference in LSPR peak position between transverse and longitudinal modes from the metal core.

Furthermore, in accordance with the experimental spectra, the modeling clearly shows the LSPR intensity is enhanced by the  $\text{Cu}_2\text{O}$  shell for several times. For most applications of LSPR nanostructures, the intensity is always considered as a critical factor and the stronger the better. From the experimental spectra, this tendency is acquired from observation of our whole series of shell thickness.

The coating not only changes the intensity and peak position of LSPR but also results in a quite different energy pathway. For bare gold NPs, with an increase of radius, the portion of absorption decreases dramatically, indicating more energy emitted by scattering (Figure 6A), which is considered to be important for surface enhanced spectroscopy. In the case of gold NPs coated with  $\text{Cu}_2\text{O}$  (Figure 6B), the maximum absorption ratio still maintains over 90% around the SPR peak vertex, even the overall particle size is already over 100 nm. Their overall absorption ratio of whole integrated LSPR band from 380 to 800 nm is also shown in Figure 6C. With the total size increasing from 55 to 100 nm, the overall absorption ratio of homogeneous Au NP decreases dramatically from 80% to



**Figure 6.** (A) Simulated absorption/extinction percentage of solid and spherical pure gold NPs of different diameters and (B) that of spherical core-shell Au@Cu<sub>2</sub>O with the same total size series. (C) Integrated overall SPR absorption ratio of Au NP and Au@Cu<sub>2</sub>O change against total particle diameter from 55 to 100 nm.

less than 40%, whereas this decay of Au@Cu<sub>2</sub>O is only about 20%. (For full simulation data please refer to Figures S13 and S14.) This enhancement of LSPR absorption finally converts more light to other forms of energy, for instance, a stronger photothermal effect if there is no other photochemistry process. Accounting for both the issues of energy and material efficiency (for gold is a precious metal with high price), this coating with Cu<sub>2</sub>O is very promising to LSPR nanoparticles for the photoenergy conversion.

#### 4. CONCLUSIONS

In summary, we successfully prepared Au@Cu<sub>2</sub>O core-shell NPs with tunable thickness by controlling epitaxial growth of Cu<sub>2</sub>O on as-prepared gold NP in aqueous solution. As what the structural characterizations indicated, the growth of compact layer is pinhole-free and uniform. With the very controllable shell thickness from few layers to over 20 nm, the NPs exhibit a considerable red shift of SPR (dipole band) for over 100 nm and, also more importantly, with enlarged optical cross sections significantly. The LSPR especially the absorption intensity is strongly enhanced by the dielectric coating. We then built an approximate Mie's scattering model for our NPs to understand the physical nature of its shell-tuned SPR change and peak splitting. Interestingly, the difference between anisotropic SPR modes is amplified in the presence of an appropriate dielectric surrounding, while the morphology of shell is less influential on the total profile of the extinction spectra. After coating, a much larger portion of energy from the strongly enhanced LSPR is absorbed rather than scattered in the longer wavelength interval without interband transitions. This unique behavior might be quite potential for photothermal therapy.

The SPR band can be even shifted to NIR region by using a larger gold core and a thicker Cu<sub>2</sub>O shell. In that scenario, the Cu<sub>2</sub>O shell and other multipole SPR modes will be effective to the extinction peak than in our experiment.<sup>28</sup> In addition to the role that only serves as a dielectric material around the LSPR NPs, Cu<sub>2</sub>O also has some interesting exciton features which can be observed from both our computational and experimental results (around 450 nm). Concerning silver NP, which usually has a typical LSPR wavelength around 400 nm, the exciton bands are expected to couple with LSPR from core NP. Thus, such a cooperative effect would be of significance for revealing the interaction between LSPR nanostructures and semiconductors. Furthermore, we consider these SPR-core-dielectric-shell NPs to be especially promising in the cutting-edge researches in energy and life sciences, such as photocatalysis, photothermal therapy, light harvest systems, and so on.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Experimental details and additional data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### ■ AUTHOR INFORMATION

##### Corresponding Author

\*E-mail: [zqtian@xmu.edu.cn](mailto:zqtian@xmu.edu.cn).

##### Author Contributions

<sup>†</sup>Both authors contributed equally to this work.

#### ■ ACKNOWLEDGMENTS

We are thankful for the financial support of NSF of China (21033007), Ministry of Scientific and Technological Projects (2010IM040100), and 973 Program (2009CB930703); the authors are grateful to Profs. N. J. Halas and P. Norlander for helpful comments on the dielectric functions of gold, to Profs. M. Moskovits and Zhao-Xiong Xie for useful and stimulating discussions, and to Xiao-Shan Zheng and Wei Shen for their help in the Raman characterization. D.Y.L. and H.X.L. are especially thankful for the support of NFFTBS, No. J0630429.

#### ■ REFERENCES

- (1) Freeman, R. G.; Hommer, M. B.; Grabar, K. C.; Jackson, M. A.; Natan, M. J. *J. Phys. Chem. C* **1996**, *100*, 718–724.
- (2) Sun, Y.; Mayers, B. T.; Xia, Y. *Nano Lett.* **2002**, *2*, 481–485.
- (3) Nikoobakht, B.; El-Sayed, M. A. *Chem. Mater.* **2003**, *15*, 1957–1962.
- (4) Jin, R.; Cao, Y.; Mirkin, C. A.; Kelly, K. L.; Schatz, G. C.; Zheng, J. G. *Science* **2001**, *294*, 1901–1903.
- (5) Sun, Y.; Xia, Y. *Science* **2002**, *298*, 2176–2179.
- (6) Sau, T. K.; Murphy, C. J. *J. Am. Chem. Soc.* **2004**, *126*, 8648–8649.
- (7) Sun, Y.; Xia, Y. *J. Am. Chem. Soc.* **2004**, *126*, 3892–3901.
- (8) Luther, J. M.; Jain, P. K.; Ewers, T.; Alivisatos, A. P. *Nature Mater.* **2011**, *10*, 361–366.
- (9) Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. *J. Phys. Chem. B* **2003**, *107*, 668–677.
- (10) Malinsky, M. D.; Kelly, K. L.; Schatz, G. C.; Van Duyne, R. P. *J. Am. Chem. Soc.* **2001**, *123*, 1471–1482.
- (11) Malinsky, M. D.; Kelly, K. L.; Schatz, G. C.; Van Duyne, R. P. *J. Phys. Chem. B* **2001**, *105*, 2343–2350.
- (12) Sherry, L. J.; Jin, R.; Mirkin, C. A.; Schatz, G. C.; Van Duyne, R. P. *Nano Lett.* **2006**, *6*, 2060–2065.
- (13) Haes, A. J.; Van Duyne, R. P. *J. Am. Chem. Soc.* **2002**, *124*, 10596–10604.
- (14) Wu, X.-F.; Song, H.-Y.; Yoon, J.-M.; Yu, Y.-T.; Chen, Y.-F. *Langmuir* **2009**, *25*, 6438–6447.
- (15) Liu, M.; Guyot-Sionnest, P. *J. Mater. Chem.* **2006**, *16*, 3942–3945.
- (16) Lee, J.-S.; Shevchenko, E. V.; Talapin, D. V. *J. Am. Chem. Soc.* **2008**, *130*, 9673–9675.

- (17) Shi, W.; Zeng, H.; Sahoo, Y.; Ohulchanskyy, T. Y.; Ding, Y.; Wang, Z. L.; Swihart, M.; Prasad, P. N. *Nano Lett.* **2006**, *6*, 875–881.
- (18) Wang, W.; Li, Z. P.; Gu, B. H.; Zhang, Z. Y.; Xu, H. X. *ACS Nano* **2009**, *3*, 3493–3496.
- (19) Banholzer, M. J.; Harris, N.; Millstone, J. E.; Schatz, G. C.; Mirkin, C. A. *J. Phys. Chem. C* **2010**, *114*, 7521–7526.
- (20) Yu, H.; Chen, M.; Rice, P. M.; Wang, S. X.; White, R. L.; Sun, S. *Nano Lett.* **2005**, *5*, 379–382.
- (21) Shevchenko, E. V.; Bodnarchuk, M. I.; Kovalenko, M. V.; Talapin, D. V.; Smith, R. K.; Aloni, S.; Heiss, W.; Alivisatos, A. P. *Adv. Mater.* **2008**, *20*, 4323–4329.
- (22) Bardhan, R.; Grady, N. K.; Ali, T.; Halas, N. J. *ACS Nano* **2010**, *4*, 6169–6179.
- (23) Sun, Z.; Yang, Z.; Zhou, J.; Yeung, M. H.; Ni, W.; Wu, H.; Wang, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2881–2885.
- (24) Li, M.; Yu, X. F.; Liang, S.; Peng, X. N.; Yang, Z. J.; Wang, Y. L.; Wang, Q. Q. *Adv. Funct. Mater.* **2011**, *21*, 1788–1794.
- (25) Chen, W.-T.; Yang, T.-T.; Hsu, Y.-J. *Chem. Mater.* **2008**, *20*, 7204–7206.
- (26) Tom, R. T.; Nair, A. S.; Singh, N.; Aslam, M.; Nagendra, C. L.; Philip, R.; Vijayamohanan, K.; Pradeep, T. *Langmuir* **2003**, *19*, 3439–3445.
- (27) Oldfield, G.; Ung, T.; Mulvaney, P. *Adv. Mater.* **2000**, *12*, 1519–1522.
- (28) Zhang, L.; Blom, D. A.; Wang, H. *Chem. Mater.* **2011**, *23*, 4587–4598.
- (29) Kuo, C.-H.; Yang, Y.-C.; Gwo, S.; Huang, M. H. *J. Am. Chem. Soc.* **2011**, *133*, 1052–1057.
- (30) Wang, W.-C.; Lyu, L.-M.; Huang, M. H. *Chem. Mater.* **2011**, *23*, 2677–2684.
- (31) Kong, L.; Chen, W.; Ma, D.; Yang, Y.; Liu, S.; Huang, S. J. *Mater. Chem.* **2012**, *22*, 719–724.
- (32) Speight, J. G. *Lange's Handbook of Chemistry*, 16th ed.; McGraw-Hill: New York, 2004.
- (33) Hu, J. W.; Li, J. F.; Ren, B.; Wu, D. Y.; Sun, S. G.; Tian, Z. Q. *J. Phys. Chem. C* **2007**, *111*, 1105–1112.
- (34) Bao, F.; Li, J. F.; Ren, B.; Yao, J. L.; Gu, R. A.; Tian, Z. Q. *J. Phys. Chem. C* **2008**, *112*, 345–350.
- (35) Frens, G. *Nat. Phys. Sci.* **1973**, *241*, 20–22.
- (36) Kuo, C.-H.; Hua, T.-E.; Huang, M. H. *J. Am. Chem. Soc.* **2009**, *131*, 17871–17878.
- (37) Connell, J. G.; Al Balushi, Z. Y.; Sohn, K.; Huang, J.; Lauhon, L. J. *J. Phys. Chem. Lett.* **2010**, *1*, 3360–3365.
- (38) Jung, L. S.; Campbell, C. T.; Chinowsky, T. M.; Mar, M. N.; Yee, S. S. *Langmuir* **1998**, *14*, 5636–5648.
- (39) Ziegler, C.; Eychmuller, A. *J. Phys. Chem. C* **2011**, *115*, 4502–4506.
- (40) Liz-Marzán, L. M.; Giersig, M.; Mulvaney, P. *Langmuir* **1996**, *12*, 4329–4335.
- (41) Lu, Y.; Yin, Y. D.; Li, Z. Y.; Xia, Y. N. *Nano Lett.* **2002**, *2*, 785–788.
- (42) Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; John Wiley & Sons Ltd.: New York, 1998.