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Synthesis of Copper-Silica Core-Shell Nanostructures with Sharp and Stable Localized Surface Plasmon Resonance

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Abstract

Copper nanoparticles exhibit intense and sharp localized surface plasmon resonance (LSPR) in the visible region; however, the LSPR peaks become weak and broad when exposed to air due to the oxidation of Cu. In this work, the Cu nanoparticles are successfully encapsulated in SiO₂ by employing trioctyl-n-phosphine (TOP) capped Cu nanoparticles for the sol-gel reaction, yielding an aqueous Cu-SiO₂ core-shell suspension with stable and well-preserved LSPR properties of the Cu cores. With the TOP capping, the oxidation of the Cu cores in the microemulsion was significantly reduced, thus allowing the Cu cores to sustain the sol-gel process used for coating the SiO₂ protection layer. It was found that the self-assembled TOP-capped Cu nanoparticles were spontaneously disassembled during the sol-gel reaction, thus recovering the LSPR of individual particles. During the disassembling progress, the extinction spectrum of the nanocube agglomerates evolved from a broad extinction profile to a narrow and sharp peak. For a mixture of nanocubes and nanorods, the spectra evolved to two distinct peaks during the dissembling process. The observed spectra match well with the numerical simulations. These Cu-SiO₂ core-shell nanoparticles with sharp and stable LSPR may greatly expand the utilization of Cu nanoparticles in aqueous environments.

Introduction

Plasmonic metal nanostructures have attracted considerable interests because of their superior ability to manipulate light at the nanoscale, which make them particularly useful for sensing, optical waveguiding, telecommunication, biomedicine, and plasmon-enhanced photocatalysis.¹⁻⁸ Several metals, such as Ag, Au, and Cu, exhibit plasmonic resonances in the visible region.⁹ Compared to Ag and Au, Cu is more earth abundant, thus particularly appealing as a low-cost plasmonic metal for practical applications. While much effort has been devoted to the nanostructures made of noble metals Ag and Au,¹ only limited success has been met with Cu. For example, Cu nanoparticles made by lithography on a substrate could display an intense localized surface plasmon resonance (LSPR) peak with a narrow band-width comparable to that of Ag and Au.¹⁰ By varying the geometry, the plasmonic resonance of Cu nanoshells can be tuned away from the interband transitions of Cu to the near infrared (NIR) region similar to that of the Au nanoshells.¹¹ Similar to the Ag one-dimensional (1-D) array, a 1-D Cu array has been demonstrated to propagate surface plasmons at the Cu-silicon interface at infrared (IR) wavelengths which could offer a promising plasmonic interconnection in silicon-based integrated circuits.¹² Moreover, Cu nanoparticles supported on graphene could excite energetic electrons under visible irradiation to enable a photocatalytic route for the production of azo compounds.¹³ Despite these exciting applications of Cu, the superior plasmonic properties of Cu nanoparticles are often compromised by surface oxidation. Being a much more reactive metal than Au or Ag, when exposed to air, the oxidation significantly broadens the LSPR peak and decreases the peak intensity of Cu nanoparticles. The surface oxidation to form oxides (i.e., Cu₂O, CuO, and CuO_{0.67}) is difficult to prevent by the use of surface ligands, especially for long periods of

time.^{10, 14} The oxidation issue is a major challenge that has yet to be overcome for practical applications involving Cu nanostructures.

Several strategies have been used to address the oxidation issue of Cu nanoparticles. One approach was to remove oxides post facto from the Cu nanostructures by oxide removal agents (e.g. acetic acid).^{10, 15} Alternatively, reducing agents (e.g. N_2H_4 or ascorbic acid) could be used to slow the formation of oxides during synthesis;¹⁵⁻¹⁶ however, the agents used with either approach could change the surface morphology of the nanostructures, especially for smaller particles, which may result in the change of their optical properties. Another commonly-used method relied on the choice of stabilizers during chemical synthesis. For example, polyvinylpyrrolidone (PVP) was used as a capping agent for Cu nanoparticles to limit oxidation.¹⁷⁻¹⁹ XRD results showed that these PVP-capped Cu nanoparticles were stable in a vial for fairly long time (e.g. 20 days) under ambient conditions;¹⁷ however, large amount of PVP were required to reduce the oxidation rate.¹⁹ In oil-based synthesis, trioctylphosphine (TOP) was demonstrated as a good capping ligand that can prevent the oxidation of Cu nanostructures.²⁰ A similar method that employed TOP during particle growth has been shown to yield stable and uniform cubic Cu nanoparticles; however, the particles had to be suspended in organic solvents.²¹ It remains very challenging to synthesize stable Cu nanoparticles with controllable optical properties in aqueous solutions. Herein, we develop a SiO_2 coating method to transfer TOP-capped Cu nanoparticles to aqueous solution and demonstrate that the LSPR properties of these Cu- SiO_2 nanoparticles can be preserved for a long period of time.

SiO_2 has been widely used as an excellent protective material against corrosion.²² Many efforts have been made to coat metal nanoparticles with silica shells with controllable thickness; however, these studies were limited to noble metals (i.e., Au and Ag) using the modified Stöber

method. For example, Stöber growth of the silica shell mediated by a silane primer was developed to coat silica on citrate-coated Au nanoparticles or Ag colloids.²³⁻²⁴ A layer-by-layer technique was employed to form an intermediate layer prior to the Stöber method for coating silica on CTAB-stabilized Au nanorods.²⁵ Methods were also developed to coat Au or Ag nanoparticles in one step without involving the primers.²⁶⁻²⁷ Combination of reduction and encapsulation of Cu in a one-pot synthesis has been demonstrated to produce ultrafine Cu nanoparticles inside thick SiO₂ shells.²⁸ Despite this progress, applying a Stöber approach to active metals was proven to be nontrivial due to their high reactivity with oxygen and ammonia.^{24, 27} To the best of our knowledge, no reports were found to successfully coat silica on the active metal Cu nanoparticles while still maintaining their optical properties, although thermal annealing of Cu nanoparticles in glass²⁹ or in SiO₂ matrices³⁰⁻³¹ was demonstrated to embed small Cu nanoparticles in bulk SiO₂ for optical measurements. The challenge in coating Cu nanoparticles with SiO₂ shells arises from the high instability of Cu nanoparticles in the sol-gel reactions. This work for the first time successfully overcomes the instability challenge of Cu nanoparticles in the sol-gel reactions and demonstrates the successful synthesis of stable Cu-SiO₂ core-shell nanoparticles with sharp and intense LSPR. It is accomplished by introducing the TOP-passivated Cu nanoparticles with controllable size and shape for the synthesis of Cu-SiO₂ core-shell structures using a sol-gel process in a water/oil (W/O) microemulsion. The use of TOP dramatically improves the stability of Cu nanoparticles in the sol-gel process, thereby preserving the optical properties of Cu nanoparticles after the synthesis. The thickness of the SiO₂ shell increases with increased reaction time, but the shell remains accessible to solvent molecules such as water. Furthermore, the self-assembled TOP-capped nanoparticles suspended in toluene could be effectively disassembled during the sol-gel reaction to recover their optical properties of

individual nanoparticles in aqueous solution. This process was monitored by the optical spectra during the reaction and the results are compared with numerical simulations. This method may enable further use of plasmonic Cu nanoparticles in aqueous solution for biological and catalytic applications.

Methods

Chemicals. Copper (II) 2,4-pentanedionate ($\text{Cu}(\text{acac})_2$, 98%), 1-octadecene (ODE, 90%), tetraethoxysilane (TEOS, 98%), tri-n-octylphosphine (TOP, 90%), and sodium hydroxide (NaOH, 98%) were purchased from Alfa Aesar. Oleylamine (OLAM, 70%) and poly-(oxyethylene) nonylphenyl ether (Igepal CO-520) were purchased from Sigma-Aldrich. Hexanes (ACS grade) and formic acid (99%) were purchased from EMD. Sulfuric acid (ACS grade, 98%) was purchased from BDH. All experiments were performed using 18 M Ω H₂O unless specified otherwise. All chemicals were used as received.

Synthesis of Copper Nanoparticles. Cu nanoparticles were synthesized by reducing Cu precursor in a mixture of ODE and OLAM in the presence of CO and formic acid vapor. Typically, $\text{Cu}(\text{acac})_2$ (52.4 mg, 0.2 mmol) was added in the mixture of 4 mL ODE and 1 mL OLAM in a 25-mL 3-neck round bottom flask equipped with magnetic stirring and connected to a water-cooled condenser. Ar was used to displace air and protect the mixture in the reaction flask prior to the addition of 1 mL TOP. While maintaining the Ar protection, the reaction mixture was heated to 220 °C. To produce cubes, a small amount of CO (~15 mL) generated from the dehydration of formic acid by sulfuric acid was flown over the hot reaction solution at 200 °C. To produce mixtures of cubes and rods, CO was introduced by flowing the vapor over the reaction at 140 °C. After the reaction proceeded at 220 °C for another 20 min, the reaction

was quenched by removal of the heating mantle and was allowed to cool to room temperature. Ethanol/toluene at a 4:1 ratio (25 mL) was added to the reaction mixture prior to centrifugation at 7800 rcf for 5 min to remove excess Cu precursor and surfactants. After discarding the supernatant, the pellet was dispersed in toluene for future use.

Synthesis of Cu-SiO₂ Core-Shell Nanostructures. The Cu-SiO₂ core-shell nanostructures were synthesized by modifying our established W/O microemulsion method.³² Typically, 1.2 mL Igepal CO-520 was added to 20 mL hexane in a 50-mL round bottom flask, followed by addition of Cu nanoparticles (~8 pmol or ~1 mg) and 30 μ L TEOS. The sol-gel reaction was catalyzed by adding 140 μ L of 20 mM NaOH. The reaction was then allowed to precede either ~24 h to produce thin silica shells or > 48 h for thicker silica shells. After the reaction completed, equal volume of ethanol was added the reaction mixture, followed by centrifuging at 12,000 rcf for 30 min to collect the product. The product was further purified with 30 mL ethanol twice, and collected by centrifuging at 12,000 rcf for 30 min or until a solid pellet was formed. The pellet was dispersed in water for further use.

Characterization. Transmission electron microscopy (TEM) images were captured using a transmission electron microscope (JEOL JEM-1011) with an accelerating voltage of 100 kV. X-ray powder diffraction (XRD) was performed using a bench-top x-ray diffractometer (Rigaku Miniflex II). The hydrodynamic diameters of the products were measured using a dynamic light scattering (DLS) instrument (Brookhaven ZetaPALS). The concentration of Cu was determined using a flame atomic absorption (AA) spectrometer (GBC 932). UV-vis spectra were taken on a UV-vis spectrophotometer (Agilent Cary 50).

Simulation. The optical properties were calculated according to the discrete dipole approximation (DDA) using the DDSCAT 7.3 program.³³⁻³⁴ In this formalism, the structure is

represented by an array of dipole moments residing within its volume. Each volume element is represented as a dielectric continuum with the complex dielectric response function of bulk Cu.³⁵ The optical cross sections were averaged over the two orthogonal polarization directions of the incident light. The optical efficiency, Q , is reported as the ratio of the respective optical cross section to $\pi \cdot a_{eff}^2$, where the effective radius, a_{eff} , is defined as the radius of a sphere whose volume is equal to that of the structure. Optical spectra including extinction, absorption, and scattering were simulated for each structure in water.

Results and Discussion

The Cu cores were synthesized by reducing the Cu precursor, Cu(acac)₂, in ODE at 220 °C in presence of TOP and OLAM. To improve the uniformity of the cores, a vapor of CO was generated *in situ* from the dehydration of formic acid by sulfuric acid and added to the reaction at 200 °C. The vapor also contained formic acid due to its high vapor pressure. **Figure 1A** shows a representative TEM image of the cubic Cu cores. The size distribution of the nanocubes was plotted in the histogram (**Fig. 1B**), indicating an average edge length of 28±3 nm. The inset and **Figure S1** shows the HRTEM of an individual nanoparticle with the lattice spacing corresponding to the d spacing of the {200} planes of the face-centered cubic (*fcc*) structure of Cu. To clarify the role of CO and formic acid in the synthesis, we performed the reaction under four different conditions: 1) no CO and formic acid, 2) CO alone, 3) formic acid vapor alone, and 4) both CO and formic acid vapor present. TEM characterization of the products from these reactions clearly shows that the presence of both CO and formic acid is important to improve the yield of cubic shape nanoparticles (**Fig. S2**). The reaction kinetics was followed by UV-vis spectroscopy based on the extinction peak at ~580 nm, which is due to the formation of Cu

nanoparticles turning the solution slightly red. (**Fig. S3**). The rate and extent of this color change from yellowish to red can be used to follow Cu nanoparticle formation at different reaction conditions. At 220 °C, even without the addition of CO and formic acid, it takes approximately 10 minutes for the reaction to turn red, the introduction of either CO or formic acid or both do not appreciably change the kinetics. At 200 °C, compared to the flow of formic acid vapor, the flow of CO dramatically slows down the formation of Cu nanoparticles (**Fig. S4**). Although we could not completely rule out the possibility of the role of CO being a reducing agent, this result suggests that the reducing power of formic acid is far stronger than CO for Cu reduction. This is consistent with a previously published electrochemical study,³⁶ which showed that the reduction of Cu^{2+} to Cu^+ was very slow with CO under acidic conditions, indicating CO being a weak reducing agent for Cu synthesis, thus it may only serve as a capping agent³⁷.

The SiO_2 shells were then coated on the surface of the Cu cores by modifying our previously established W/O microemulsion method.³² To prevent the dissolution of Cu nanoparticles during the sol-gel reaction, the catalyst NH_4OH used in our previous work was replaced by NaOH . The TOP capping is critical for passivating the surface of the Cu cores and protecting them from oxidation during the sol-gel process. The resulting core-shell nanostructures were imaged by TEM as shown in **Figure 1C**. The silica coating was uniform and the shell thickness was measured to be 4.6 ± 0.8 nm. The optical spectra were measured before and after silica coating. Without the coating, the as-synthesized nanocubes were insoluble in water and therefore suspended in toluene, showing an LSPR peak at 581 nm with a shoulder at ~680 nm (**Fig. 1D, black line**). The shoulder could be attributed to the aggregation of the nanoparticles in toluene. In contrast, the optical spectrum of the core-shell nanoparticles suspended in aqueous solution

displays a sharp LSPR peak at 587 nm with no shoulder (**Fig. 1D, red line**), indicating the core-shell nanoparticles are well dispersed in aqueous solution.

Figure 1. (A) TEM image of Cu nanocubes with edge length of 28 ± 3 nm. The inset is the HRTEM of an individual nanocube taken from the [100] zone axis. (B) Histogram of size distribution of the sample in (A). The average edge length is 28 ± 3 nm. (C) TEM image of SiO₂ coated Cu nanoparticles with coating thickness of 4.6 ± 0.8 nm. The inset is the HRTEM image of an individual particle with the scale bar of 10 nm. (D) UV-vis spectra of sample (A) Cu nanocubes in toluene (black line) and sample (C) Cu-SiO₂ core-shell nanoparticles in aqueous solution (red line).

The LSPR of the Cu-SiO₂ core-shell structures were further quantified by fitting to the Beer-Lambert Law. The optical spectra of the core-shell structure aqueous suspensions were taken at a series of dilutions as shown in **Figure 2A**. The absorbance at the LSPR maximum (587 nm) was plotted as a function of particle concentration (the inset of **Fig. 2A**). Based on the Beer-Lambert Law, the extinction coefficient of the suspension was determined to be $4.77 \times 10^9 \text{ M}^{-1}\text{cm}^{-1}$ from

the linear fit of the plot. From the extinction coefficient and the average size of the nanocubes (i.e. edge length of 28 nm), the extinction cross section of an individual nanocube was estimated to be $7.92 \times 10^{-16} \text{ m}^2$. To further analyze the optical properties, we calculated the optical spectra for individual nanoparticles suspended in water using the DDA method. Initially, the DDA simulation was performed using two geometries with the same volume: a cube with edge length of 30 nm and a sphere with diameter of 37 nm (**Fig. 2, B and C**). The cube exhibits an extinction peak at 600 nm while the sphere shows an extinction maximum at 560 nm. In both cases, the extinction spectra were dominated by the absorption component. Optical efficiency of the cube is approximately twice as high as the sphere with the simulated extinction cross section being $3.06 \times 10^{-15} \text{ m}^2$ and $1.38 \times 10^{-15} \text{ m}^2$, for the cube and sphere, respectively. Although there is a small difference between the experimental and simulated peak position and cross section, the differences can be explained by the slightly different sizes, shape, and the approximate nature of the experimental concentration measurement.

We anticipate that the shape deviations of the synthesized nanocube from a perfect cube with sharp corners have a large influence on both peak position and intensity. According to TEM characterization (**Fig. 1C**), the synthesized nanocubes lost part of their mass from the corner regions, and thus do not have sharp corners as in a perfect cube. We performed DDA simulations also on rounded cubic targets by removing up to 2 % of the total mass from a perfect cube at the corner regions. The spectra of the rounded cubes are shown in **Figure 2D**. It can be seen the peak position shifted by 14 nm by removing the sharp corners. The rounded cube has an extinction maximum close to 586 nm and is thus in perfect agreement with experiments (**Fig. 2A**). The simulation result indicates that the plasmon peak red shifts for nanocubes of the same volume when compared to corresponding nanospheres. The same shape effects on the plasmon maxima

were observed for Au and Ag in the simulated spectra as shown in **Figure S5**. These simulation results are in agreement of the previous experimental study showing that shapes of similar sizes but with sharp corners and edges tend to have red shifted plasmon resonance³⁸. For Cu, the shape induced red shift associated with the nanocubes thus shifting the plasmon resonance away from the interband transition of Cu material, leading to sharper plasmon bands.

Figure 2. (A) UV-vis spectra of the Cu-SiO₂ core-shell nanoparticles at different concentrations. The inset is the plot of the extinction at LSPR maxima as a function of concentration. The red line is the linear fit of the data ($y = 4.77 \times 10^9 x$, $R^2 = 0.9998$). (B) DDA simulated spectra of an isolated Cu nanocube with an edge length of 30 nm. The inset is the schematic drawing of the cross section of the nanocube. (C) DDA simulated spectra of an isolated Cu nanosphere with the same volume as the nanocube in (B). The inset is the schematic drawing of the cross section of the nanosphere. (D) DDA simulated spectra of a rounded Cu nanocube with ~2% of the total mass of the nanocube in (B) removed from the corners. The inset shows the schematic drawing of the rounded nanocube viewed from the front. All simulated spectra were calculated using water as the medium.

We further examined the stability of the core-shell nanostructures in aqueous solution. The stability was assessed by both structural analysis using XRD and optical spectra using UV-vis. We obtained the XRD patterns of the core-shell nanoparticles before and after being stored for one month in aqueous solution as samples (a) and (b), respectively (**Fig. 3A**). The peaks at 43.3, 50.4, and 74.0 degree were indexed to {111}, {200}, and {220} planes of the face-centered cubic (*fcc*) Cu, confirming that the core-shell nanostructures contain pure Cu. There is no change in the XRD patterns in sample (b) when compared to sample (a), suggesting that no obvious oxidation occurred in the core-shell nanostructures during the one month storage. The UV-vis spectra showed a sharp LSPR peak of Cu at 585 nm and remained unchanged before and after storage (**Fig. 3B**). These results indicate that the Cu cores are well protected by the SiO₂ shell from oxidation and agglomeration.

Figure 3. (A, B) Characterization of the Cu-SiO₂ core-shell nanostructures suspended in aqueous solution: (A) XRD patterns; and (B) UV-vis spectra. (C, D) Characterization of TOP-capped Cu nanocubes suspended in toluene: (C) XRD patterns; and (D) UV-vis spectra. In all panels, (a) and (b) represent the samples before and after 1-month storage, respectively.

The use of TOP-capped Cu nanoparticles is critically important for the successful synthesis of well-dispersed Cu-SiO₂ core-shell nanoparticles with sharp and stable LSPR. TOP serves as a capping agent to protect Cu nanoparticles from oxidation during the sol-gel reactions. We examined the stability of TOP-capped nanoparticles of Cu by the XRD and UV-vis analysis before and after storage for a month in toluene. The XRD patterns before and after the storage were essentially the same, indexed to *fcc* Cu, showing no peaks from oxides (**Fig. 3C**). We also performed the XRD analysis on the solid sample after storage for six months. Compared to the XRD result prior to the storage, the XRD pattern essentially has no changes, indicating that no

obvious oxidation after the solid sample has been stored for six months (**Fig. S6**). However, significant changes were found in the optical spectra of TOP-capped nanoparticles in toluene between before and after storage as shown in **Figure 3D**. The initial sharp extinction peak at 585 nm red-shifted to ~600 nm with reduced intensity and a broad shoulder centered at 775 nm arose in the optical spectrum after the TOP-capped nanoparticles were stored for a month. Since the XRD results showed no sign of oxidation, the spectral change is likely due to the particle agglomeration in solution.

It is known that the agglomeration of TOP-capped nanoparticles is much more severe without sonication. We monitored the spectral changes of TOP-capped nanoparticles in toluene over 15 min at a 100-fold dilution (~100 pM) compared to the typical concentration for storage (**Fig. 4A**). Two peaks, 595 and 700 nm, were observed in the initial spectrum, which was taken 1 h after the reaction was completed. The 590-nm peak can be attributed to individual nanoparticles while the 700-nm peak belongs to the nanoparticle agglomerates. Over the course of 15 min after dilution, the 700-nm peak became broader and shifted to the red to ~800 nm, suggesting the increased numbers of agglomerates. These results were verified by the DLS measurements on the corresponding time course samples (**Fig. 4, B-D**). Two populations with different hydrodynamic diameters (HD) were observed: the one with HD <100 nm assigned to individual nanoparticles and the other with HD between 300-500 nm assigned to nanoparticle agglomerates. By comparing **Figure 4, B-D**, the relative percentage of nanoparticle agglomerates increased over time. The nanoparticle agglomeration was further confirmed by TEM as shown in the inset of **Figure 4D**. Each particle cluster seen in the TEM images contains about 10-20 TOP-capped nanoparticles. The agglomeration of TOP-capped nanoparticles stems from the

hydrophobic interaction among long carbon chains of the TOP molecules attached to the particle surface in toluene.²⁰

Figure 4. (A) Optical spectra of diluted Cu nanoparticles in toluene over time; and (B-D) DLS data of the corresponding sample in (A) measured at the time of initial, 5 min, and 15 min.

Although TOP can protect the capped Cu nanoparticles from oxidation, the TOP-capped nanoparticles tend to agglomerate in toluene. Once the agglomerates form in toluene, it is difficult to separate them into individual nanoparticles using mechanical methods, such as sonication. This tendency led us to investigate the effect of agglomeration on the formation of the core-shell nanostructures. The SiO₂ coating process of the TOP-capped nanoparticle agglomerates was monitored over time using UV-vis spectroscopy. **Figure 5** shows the extinction spectra of the aliquots taken from the reaction mixture during the sol-gel reaction.

During the SiO₂ coating, the broad peak at ~800 nm indicative of particle agglomeration gradually decreased and eventually disappeared as the reaction progresses to completion. The peak at 580 nm increased in intensity and became prominent as the reaction proceeded. This spectral evolution suggests that the agglomerates could be completely disassembled into individual particles and coated with SiO₂ during the sol-gel process in microemulsion. As a control experiment, we have performed the microemulsion in the absence of sol-gel precursor TEOS and found individual particles along with aggregates in the microemulsion as shown in the TEM images (**Fig. S7**) and DLS measurements (**Fig. S8**). With the silica precursors, the individual particles are coated and prevented from joining the aggregates, thus shifting the equilibrium.

Figure 5. Spectral evolution of the time-course study on the SiO₂ coating process of the Cu nanoparticles.

Our study shows that the TOP-mediated sol-gel process in a W/O microemulsion can be used to break apart particle assemblies and allow good dispersity of individual nanoparticles in aqueous solution, using the SiO₂ coating as a physical barrier. The TOP-capped nanostructure

samples often display a broad LPSR band between 600-900 nm which could be attributed to nanoparticle agglomeration or the size distribution (i.e. possibly containing rods). This silica coating method could be used to recover the spectral signatures of different nanostructures thus qualitatively determining composition of shapes (i.e. nanoparticle versus nanorod) in the sample without costly TEM imaging. It can provide us a rapid screening method of the product for shape-controlled synthesis. To demonstrate the feasibility, we applied the microemulsion method to coat SiO₂ on a mixture sample containing nanorods. A mixture of Cu nanocubes and nanorods was synthesized when in situ generated CO from the dehydration of formic acid by sulfuric acid was added to the reaction at a lower temperature. Based on the previous report by Murphy and co-workers³⁹, rod growth is promoted in a relatively-weaker reducing environment. In our case, the slower reduction kinetics at lower temperature compared to that used for the cube synthesis increases the yield of nanorods. **Figure 6A** shows the TEM image of the mixture sample with the histogram plots in **Figure S9**, indicating a composition of ~80% nanocubes with an average edge length of ~40 nm and ~20% nanorods with an average of 2.5 aspect ratio (~36 × 90 nm). The UV-vis spectrum shows a broad peak at 615 nm with a shoulder at 700 nm (**Fig. 6B**) which is similar to the spectrum of nanoparticle agglomerates (**Fig. 4A**). This particle suspension was then added into hexane, followed by the addition of Igepal CO-520, TEOS, and NaOH solution to create a microemulsion environment for the sol-gel process. After the sol-gel process, the nanostructures were coated by SiO₂ as seen in the TEM image (**Fig. 6C and S10**) with a mostly uniform shell and the sample is well-dispersed in aqueous solution. As predicted, the UV-vis spectrum of the sample in water exhibits two distinct peaks at 578 nm and 700 nm (**Fig. 6D**), corresponding to the rounded nanocubes and nanorods, respectively. When the reaction is monitored by UV-vis spectroscopy (**Fig. 6E**), the extinction peaks of the nanocubes and

nanorods clearly arise as the coating process proceeds. During the coating process, the peak at 700 nm was gradually recovered while the peak at 615 nm shifted to the blue, indicating that the nanostructure agglomerates were separated to yield individual nanostructures. After coating with SiO₂, the nanorods could potentially be separated from the nanoparticles based on their difference in mass using centrifugation.⁴⁰⁻⁴¹

Figure 6. (A, B) Characterization of the as-synthesized mixture of Cu nanocubes and nanorods: (A) TEM image; and (B) UV-vis spectrum of the particle suspension in toluene. (C, D) Characterization of the mixture sample after silica coating process: (C) TEM image with a magnified view in the inset; and (D) UV-vis spectrum of the particle suspension in water. (E) Spectral evolution of the mixture over time during the silica coating process.

The spectral shifts due to the nanorods with different aspect ratios were further analyzed by DDA simulations. The simulations were performed on nanorods with a diameter of 37 nm. As shown in **Figure 7, A and B**, the nanorods with aspect ratios of 2:1 and 3:1 possess extinction peaks at 640 nm and 770 nm, respectively. The relative ratio of absorption to scattering was compared based on the optical efficiency which is the ratio of the optical cross-section to the physical cross-section of a nanoparticle. The efficiency of absorption is twice that of scattering for the nanorod with aspect ratio of 2:1, but becomes comparable to the scattering efficiency for the nanorod with aspect ratio of 3:1. **Figure 7C** shows the extinction peaks of nanospheres (1:1) and nanorods with aspect ratios from 2:1 to 3:1 and 4:1 increase from 560 nm to 641, 773, and 931 nm. The extinction peaks of nanorods further increase to 1097 and 1263 nm for aspect ratios of 5:1 and 6:1, respectively. Similar to that of the Au and Cu₃Au nanorods,⁴²⁻⁴³ the peak positions for the extinction spectra were proportional to aspect ratios of the nanorods, as plotted in **Figure 7D**. A linear least square fitting of the peak position and the aspect ratio gives a Pearson R^2 of 0.997 showing good linearity ($y = 313.8 + 156.8x$). Such a good fit allows the aspect ratio of the synthesized nanorods to be determined by examining the position of the LSPR maximum. Our UV-vis shows the sharp peak at 700 nm, which is consistent with an aspect ratio of 2.5:1. This result agreed well with the aspect ratio of 2.5 estimated from analyzing the TEM image.

Figure 7. Simulated optical spectra of Cu nanorods with two different aspect ratios suspended in water: (A) 37×74 nm and (B) 37×112 nm. (C) Extinction spectra of Cu nanorods with a fixed width of 37 nm but different aspects: 1:1 (black), 2:1 (red), 3:1 (blue), and 4:1 (purple). (D) The position of the extinction peak as a function of the aspect ratio for the Cu nanorods shows excellent linearity. The red line ($y = 313.8 + 156.8x$, $R^2 = 0.997$) is a linear least square fit of the simulated peak positions.

The SiO_2 shell thickness could be varied by adjusting the reaction time of the sol-gel process. In our study, the sol-gel process is typically allowed to proceed for 24 h, yielding a shell thickness of ~ 5 nm. It is possible to coat the Cu cores with a shell thickness less than 5 nm; however, it would be difficult to image a thinner shell on the Cu core. Alternatively, the core-shell nanoparticles could be treated by 0.3 mM FeCl_3 for 10 min to etch the Cu cores, resulting in hollow SiO_2 shell for imaging (**Fig. S11**). Thicker shells could be generated by increasing the sol-gel reaction time, as shown in **Figure 8**. The shell thickness was ~ 5 nm at 24 h and increased to ~ 10 nm at 72 h. Increased shell thickness does not show appreciable changes on the LSPR peak. The HRTEM images show that both the thinner shell (**inset of Fig. 8A**) and the thicker

shell (**Fig. 8C**) are mostly uniform and discrete. We note with the increased thickness the amount of excess silica also increases. The UV-vis spectra of the samples in aqueous solution depicts extinction maximum at ~ 580 nm (**Fig. 8D**). Thus the insensitivity of the optical spectra with thickness indicates that the excess silica does not influence the optical properties and the different thickness also have negligible effect on the peak locations due to the porous nature of the silica coating. The amount of red shift is within the margin of error. As shown previously by Liz-Marzán and co-worker with silica coating on Au and Ag,^{23, 26} it is indeed possible that a systematic red shift can be observed with even thicker coating which can be optimized for Cu in future studies. In this work, we demonstrate for the first time that Cu nanoparticles having superior optical properties can indeed be produced in aqueous solution.

Figure 8. (A-C) TEM characterization of the SiO₂ coated Cu nanoparticles synthesized by different reaction time: (A) 24 h (HRTEM in the inset); (B) 72 h; and (C) HRTEM of an individual particle in the 72-h sample (B). (D) UV-vis spectra of the particles suspended in water corresponding to the sample (A) in black line and the sample (B) in red line.

Conclusions

A TOP-mediated, sol-gel process in a microemulsion was successfully developed to produce Cu-SiO₂ core-shell nanoparticles that were well dispersed in water. The SiO₂ coating acts as a protective layer to prevent oxidation of Cu, thus preserving the superior LSPR properties of Cu nanoparticles in aqueous solution. The cubic nanoparticles synthesized in this work exhibit a narrow and intense LSPR peak at ~590 nm while the nanorods possess an LSPR peak at 700 nm and aspect ratio of 2.5:1. Unlike spherical nanoparticles, the LSPR of the nanocubes and the longitudinal mode of nanorods are narrow and intense due to the shape effect red shifting of the LSPR from the interband transitions of Cu. These experimental results match well with the DDA numerical simulations. These aqueous Cu-SiO₂ core-shell nanostructures may find use in sensing, catalysis, and antimicrobial applications. The ligand-mediated microemulsion sol-gel method may provide a versatile approach to spontaneously disperse ligand-induced nanoparticle agglomerates and recover the individual particle dispersion for various applications in aqueous environments.

SUPPORTING INFORMATION

HRTEM image and analysis of the nanocubes; TEM images of the Cu nanoparticles synthesized at different conditions; UV-vis spectra and photographs of time course study for the Cu nanoparticle synthesis; DDA simulation of the extinction spectra of a cube, a rounded cube, and a sphere for Cu, Au, and Ag; XRD pattern of the solid TOP-capped nanoparticles; TEM images, DLS and UV-vis measurements of the time course study for the microemulsion without TEOS; Histograms of the size distribution of the mixture sample of nanocubes and nanorods; the close-up view of the core-shell nanostructures; and TEM image of the hollow SiO₂ shells.

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