SUPPORTING INFORMATION

Tuning the observability of surface plasmon in silica – gold raspberry shaped nanoparticles using cuprous oxide shell

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(A) Calculation of far field response of core-shell nanostructures

Following are the steps of calculating far field response of cuprous oxide coated silica@AuNP core shell nanostructures:

1. Use the following formula to calculate the dielectric function (ε(R, ω)) of AuNPs of various radii (R) at various frequencies 'ω'

$$\varepsilon(R,\omega) = \varepsilon_{bulk}\,(\omega) + \frac{\omega_p^2}{\omega(\omega + i\tau^{-1})} - \frac{\omega_p^2}{\omega(\omega + i\tau^{-1} + i\,v_F/R)}$$

where $\varepsilon_{bulk}(\omega)$ is dielectric function of bulk gold calculated by Johnson-Christy and,

$$\hbar\omega_p = 9\ eV \quad ; \quad \hbar\tau^{-1} = 0.05\ eV$$

2. Calculate the dielectric function (real and imaginary part) of core shell system shown below:

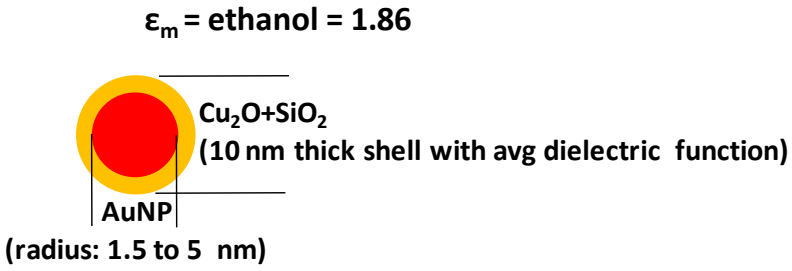


Fig. S1 Schematic of AuNP with an overcoat having dielectric function which is average of dielectric function of Cu_2O and silica.

We put average of dielectric function of silica and cuprous oxide as dielectric function of shell (ε_{shell}) in equation and evaluate dielectric function of core-shell ($\varepsilon_{Au\text{-}Cu}$) shown in Fig. 1S:

$$\varepsilon_{Au-Cu} = \left\{\frac{(\varepsilon_{shell} - \varepsilon_m)(\varepsilon_{core} - 2\varepsilon_{shell}) + (1-g)(\varepsilon_{core} - \varepsilon_{shell})(\varepsilon_m + 2\varepsilon_{shell})}{(\varepsilon_{shell} + 2\varepsilon_m)(\varepsilon_{core} + 2\varepsilon_{shell}) + (1-g)(2\varepsilon_{shell} - 2\varepsilon_m)(\varepsilon_{core} - \varepsilon_{shell})}\right\}$$

where, ε_m = dielectric constant of solvent, g = (inner radius/outer radius)^3, ε_{core}=dielectric constant of gold nanoparticle.

3. To calculate extinction of whole silica@AuNPs@cuprous oxide system (Fig. 2S), we use

$$Q_{abs} = 4r_2\left(\frac{2\pi}{\lambda}\right) Im\left\{\frac{(\varepsilon_{shell} - \varepsilon_m)(\varepsilon_{core} - 2\varepsilon_{shell}) + (1-g)(\varepsilon_{core} - \varepsilon_{shell})(\varepsilon_m + 2\varepsilon_{shell})}{(\varepsilon_{shell} + 2\varepsilon_m)(\varepsilon_{core} + 2\varepsilon_{shell}) + (1-g)(2\varepsilon_{shell} - 2\varepsilon_m)(\varepsilon_{core} - \varepsilon_{shell})}\right\}$$

(λ = wavelength, r_2 = outer radius) to calculate absorption coefficient of composite nanostructure by substituting $\varepsilon_{shell} = \varepsilon_{Au\text{-}Cu} = \varepsilon_{eff}$ and dielectric function of silica in place of ε_{core}.

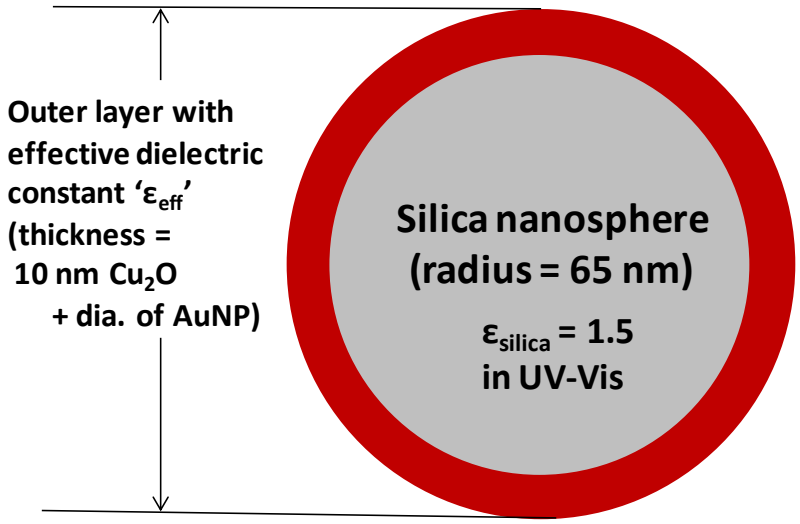


Fig. S2 Schematic of silica nanoparticle with a surrounding shell of dielectric constant $\varepsilon_{Au\text{-}Cu}$ or ε_{eff}.

Scattering cross-section is calculated as,

$$Q_{scat} = \frac{8}{3}\left(\frac{2\pi}{\lambda}r_2\right)^4 \left|\left\{\frac{(\varepsilon_{shell} - \varepsilon_m)(\varepsilon_{core} - 2\varepsilon_{shell}) + (1-g)(\varepsilon_{core} - \varepsilon_{shell})(\varepsilon_m + 2\varepsilon_{shell})}{(\varepsilon_{shell} + 2\varepsilon_m)(\varepsilon_{core} + 2\varepsilon_{shell}) + (1-g)(2\varepsilon_{shell} - 2\varepsilon_m)(\varepsilon_{core} - \varepsilon_{shell})}\right\}\right|^2$$

The extinction cross-section (Q_{ext}) of composite nanostructure silica@AuNP@Cu_2O is thus given by: $Q_{ext} = Q_{abs} + Q_{scat}$

We calculate absorption, scattering and extinction efficiencies for AuNP of 10 nm diameter (Fig. S3a) and silica@AuNP (SA10) particles (Fig. S3b) in air. Mie calculations for SA10 were done in a similar way as we did for SA10C but with air as surrounding medium. Though the calculation for SA10 is approximate only (since air does not form a spherical shell around AuNP like Cu_2O do for SA10C) but it gives us an indication that scattering from SA10 is significant in comparison to scattering from AuNPs of 10 nm diameter. Hence, when reflection spectrum of SA10 particles is measured, LSPR scattering manifests itself as dip in spectrum. Additionally, LSPR wavelength in calculated scattering (520 nm) spectra is greater than plasmon wavelength in calculated absorption (500 nm) and extinction (505 nm) spectra. The difference between LSPR in calculated Q_{sca} and Q_{ext} thus justifies the difference in LSPR characteristics of SA10 system in experimental transmission and reflection spectra.

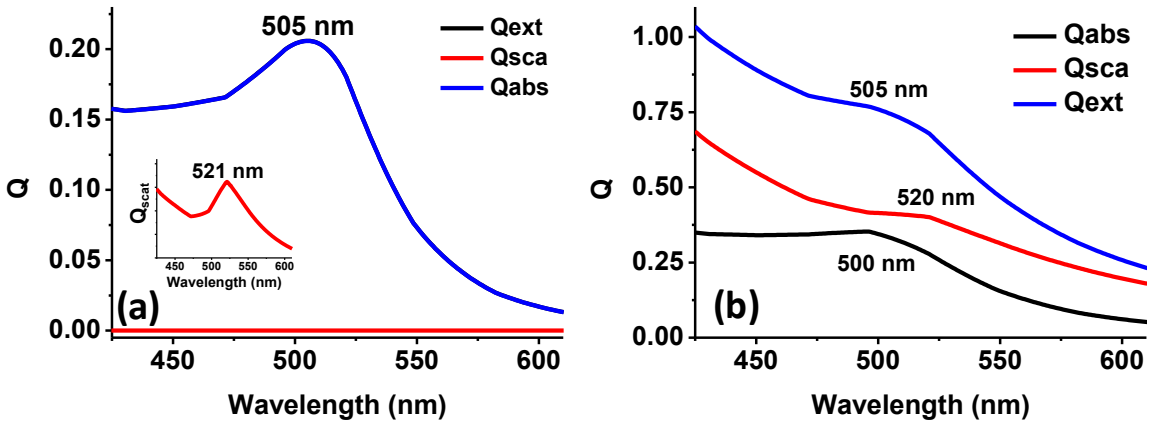
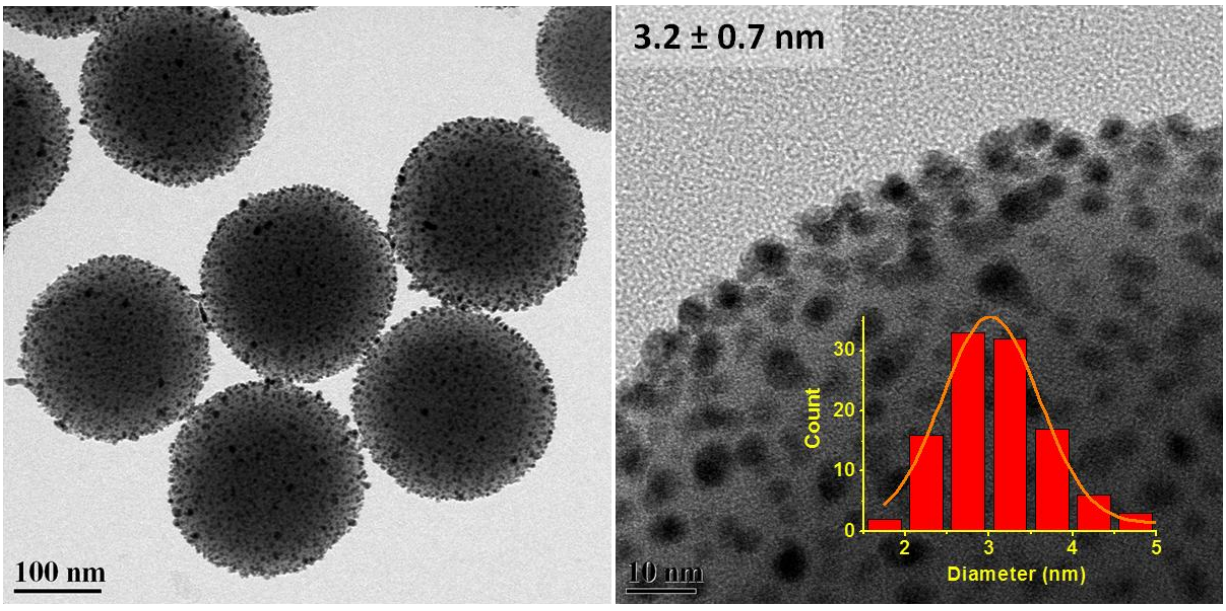


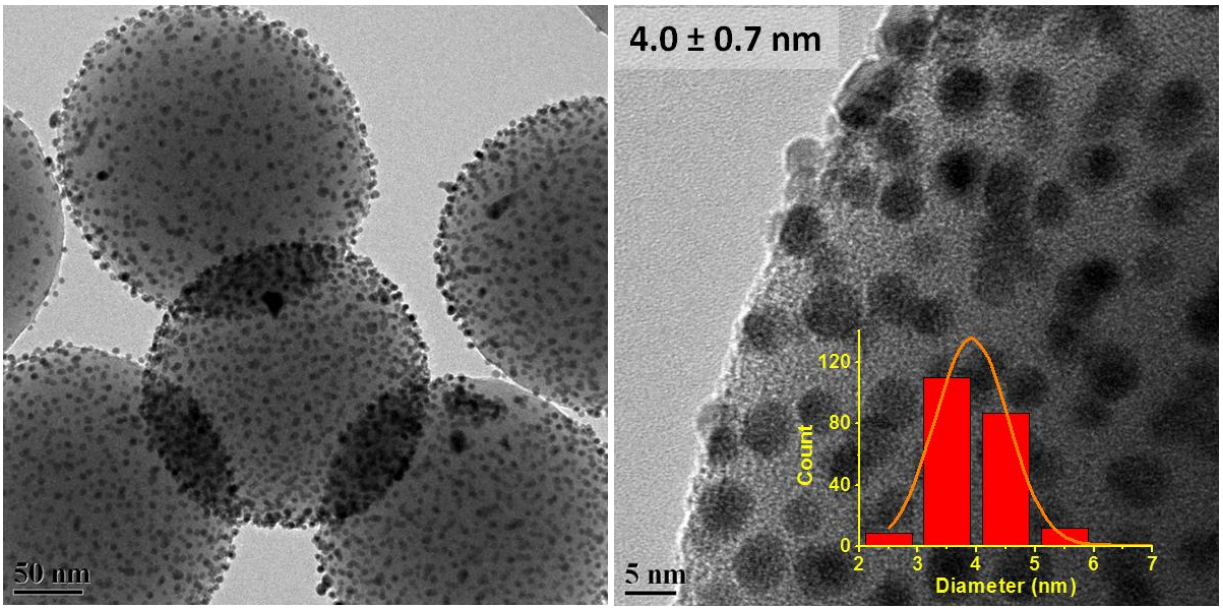
Fig. S3 Calculated extinction, scattering and absorption efficiencies for (a) AuNP with 10 nm diameter (inset shows plasmon peak in scattering after zooming into the Q_{sca} graph) and (b) silica@AuNP (SA10) particles.

(B) Large scale TEM images of silica@AuNP systems with different AuNP sizes

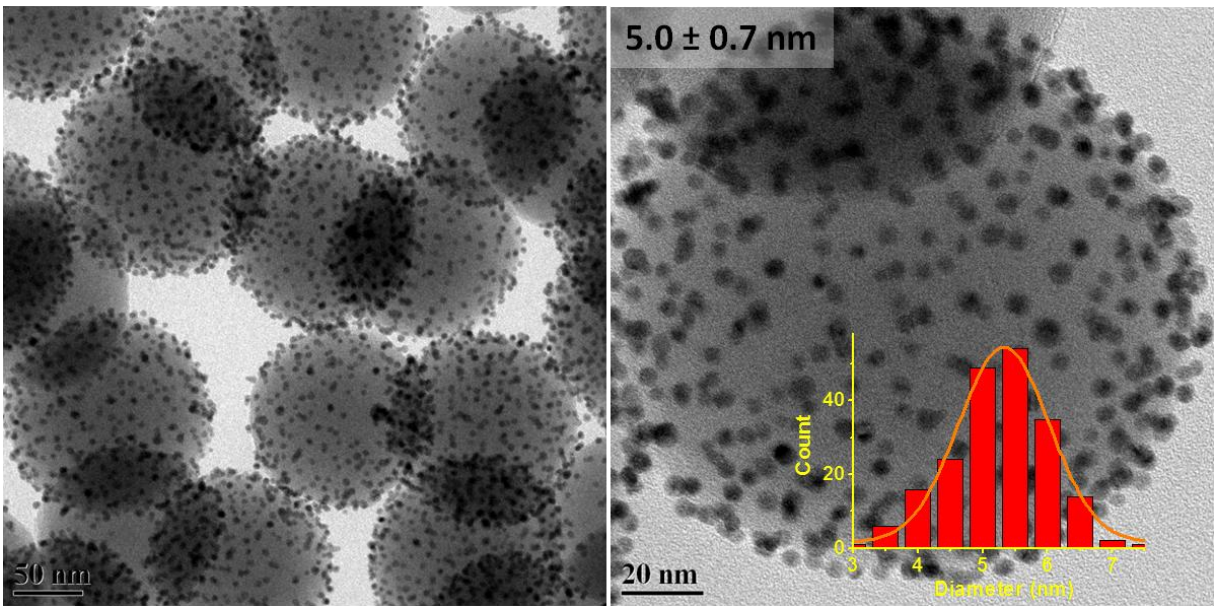
(1) 3 nm AuNPs attached over silica



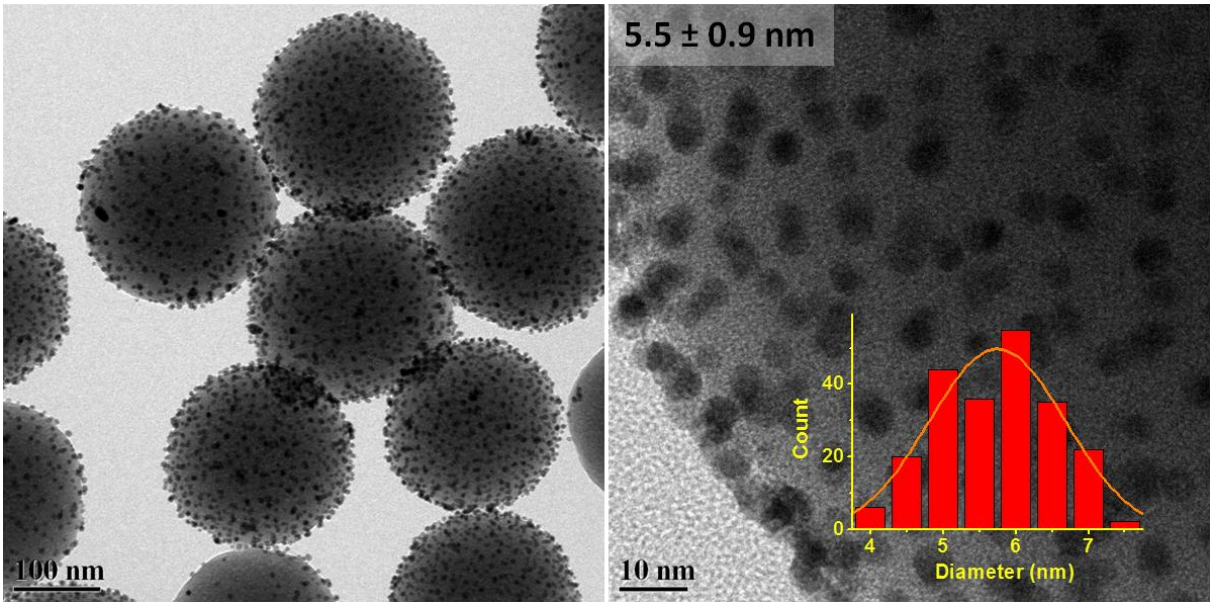
(2) 4 nm AuNPs attached over silica



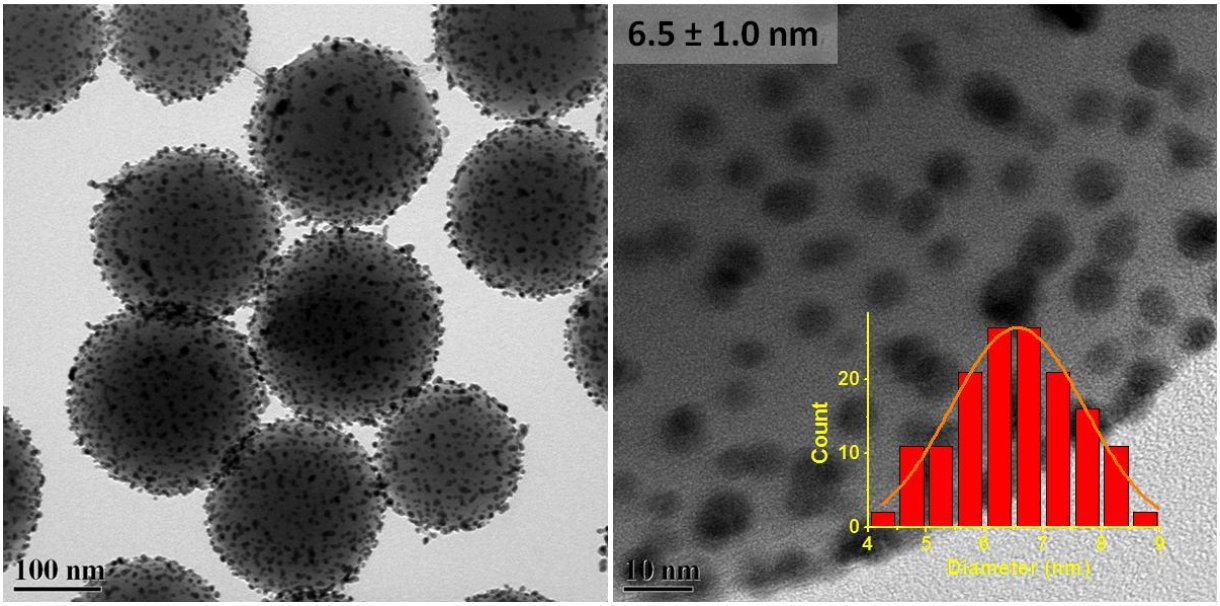
(3) 5 nm AuNPs attached over silica



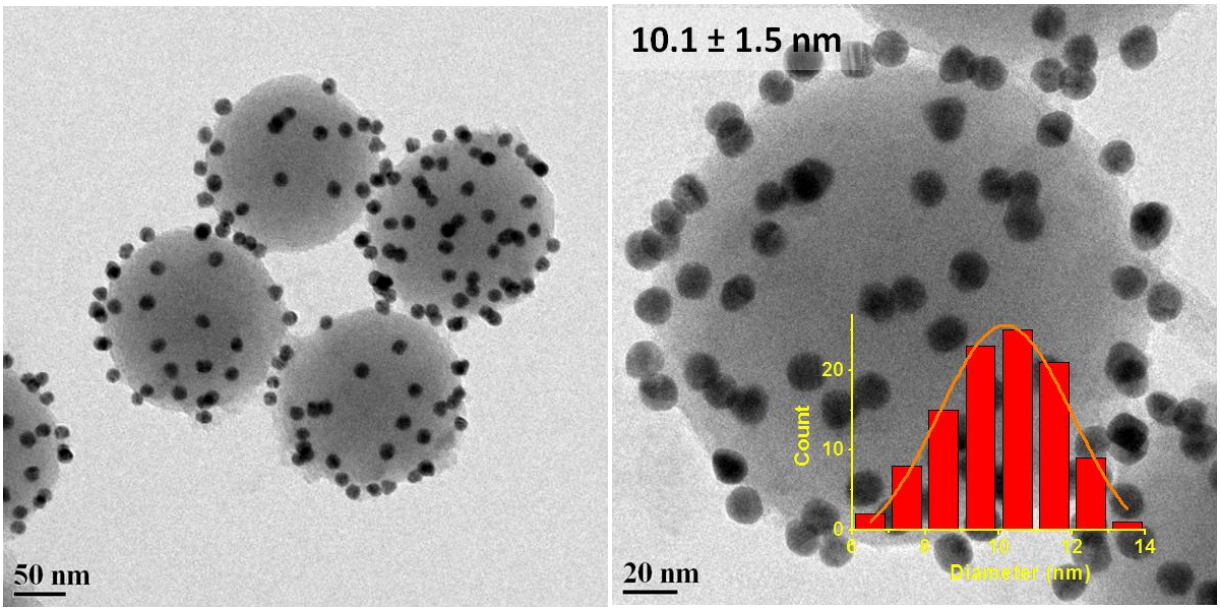
(4) 6 nm AuNPs attached over silica



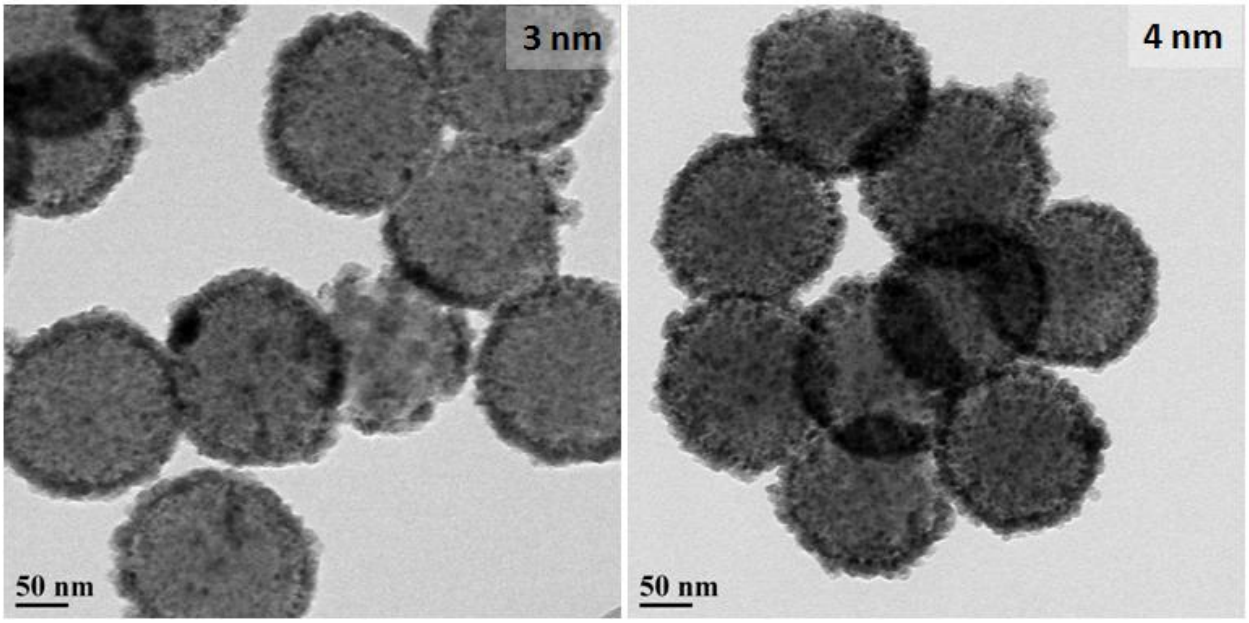
(5) 7 nm AuNPs attached over silica

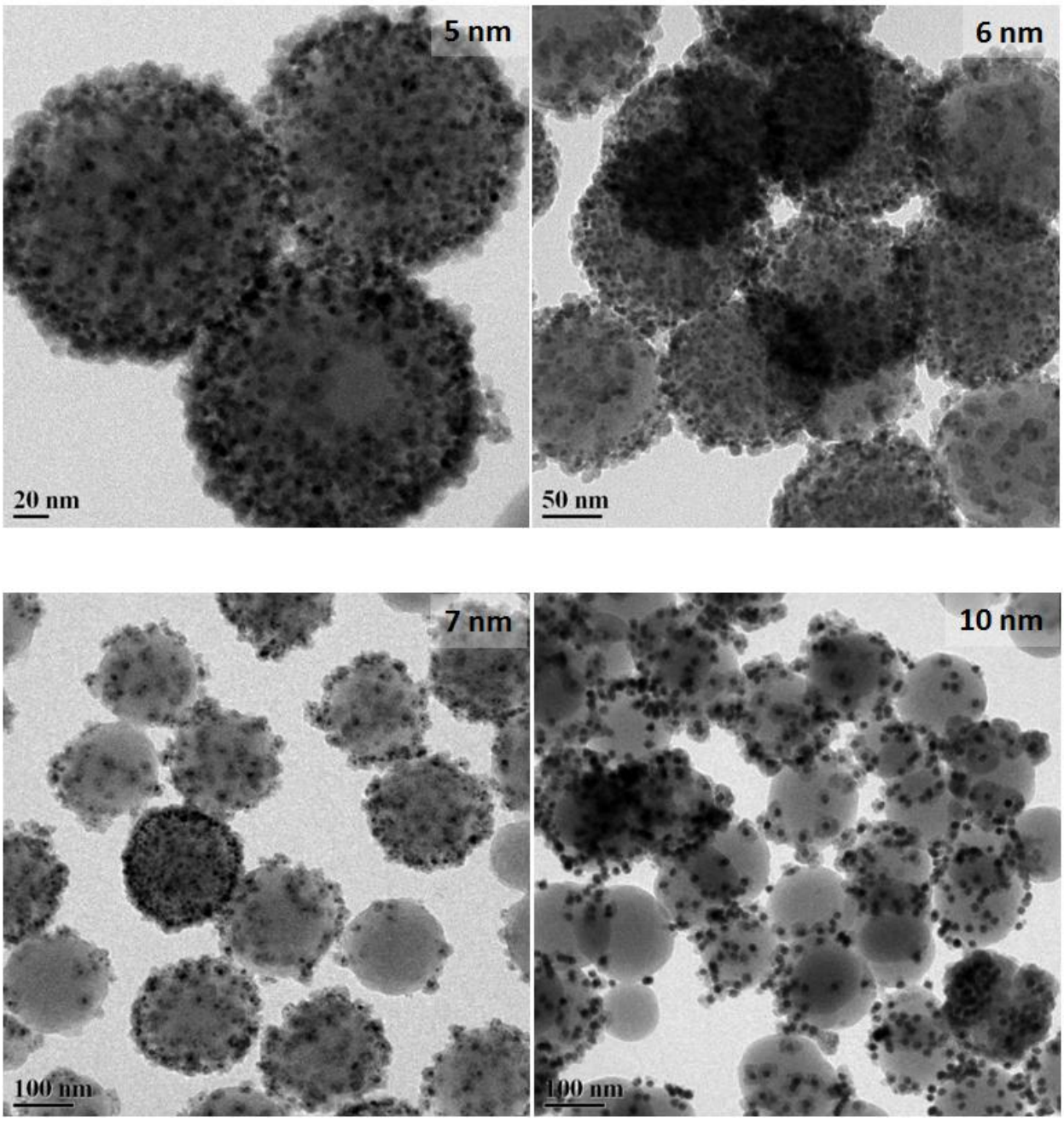


(6) 10 nm AuNPs attached over silica



(C) Large scale TEM images of silica@AuNP@Cu_2O composite with different AuNP sizes




5 nm
20 nm
6 nm
50 nm
7 nm
100 nm
10 nm
100 nm

(C) Role of PVP in synthesis of silica@AuNP@Cu_2O particles

It is found that if we do not use PVP during synthesis of silica@AuNP@Cu_2O particles, we get a non-uniform copper oxide shell around silica@AuNP particles. TEM imaging revealed that the thickness of the copper oxide shell varies from 10 nm to 35 nm and coagulation of particles is also observed in sample (Fig. S4a and S4b). Further, the absorbance spectra of silica@AuNP@Cu_2O particles (synthesized without using PVP) show a broad peak centered around 720 nm (Fig. S4d). Such a peak hints at formation of a thin layer of CuO around Cu_2O shell.[1] The HRTEM image of outer portion of copper oxide shell around silica@AuNP(3 nm) particle shows (200) crystalline planes of Cu_2O as well as (110) and (111) crystalline planes of CuO at periphery (Fig. S4c). CuO has a lower band-gap (1.2 eV – 1.5 eV) compared to Cu_2O (2.2 eV) and shows excitonic features at wavelengths < 1000 nm.[1] Since, we intend to study effect Cu_2O on silica@AuNP particles, presence of CuO is undesirable. Hence, PVP is necessary to get CuO-free and uniform Cu_2O shell around silica@AuNP particles.

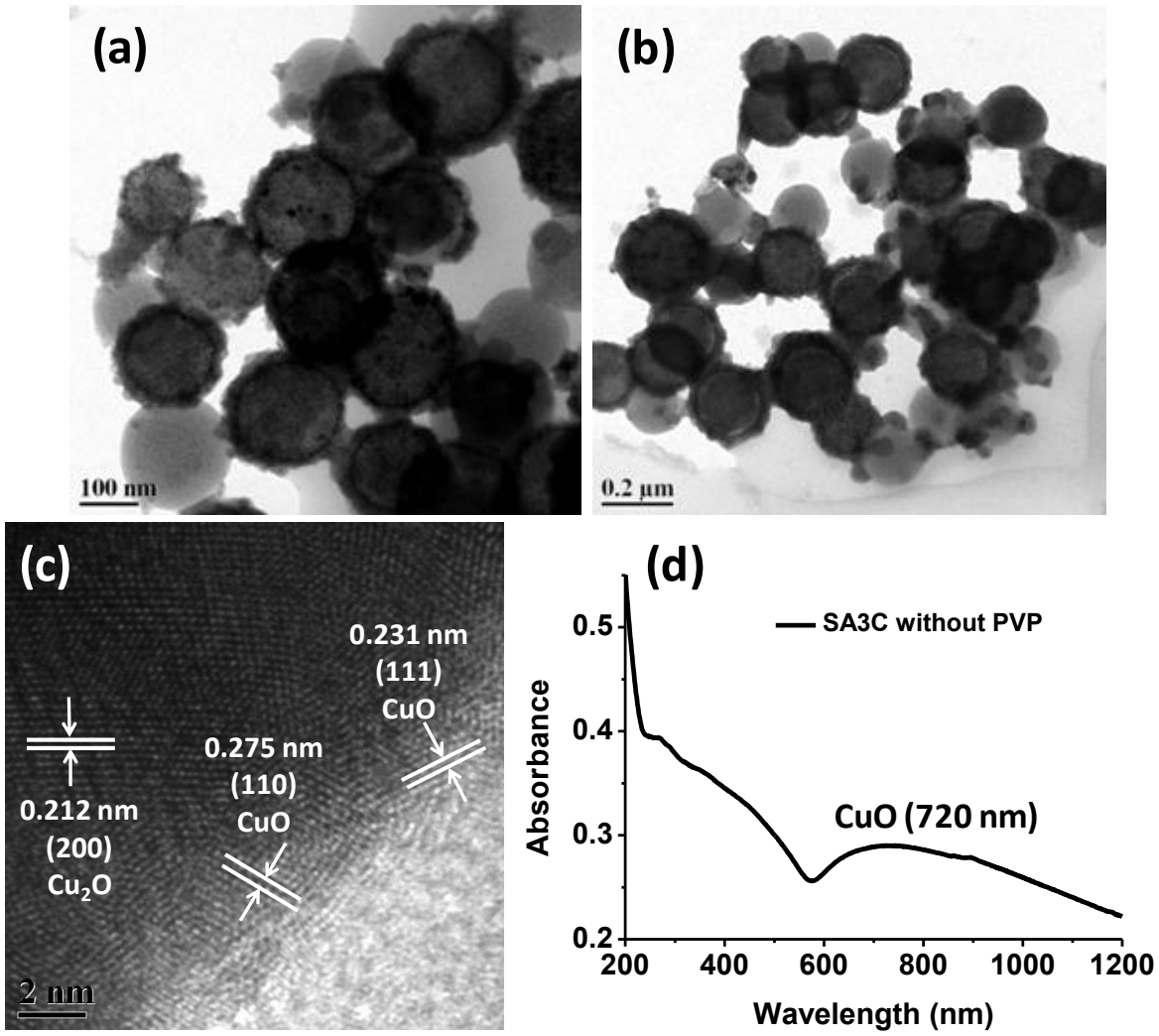


Fig. S4 TEM images showing (a) non-uniform coating copper oxide around silica@AuNP(3 nm) particles, (b) coagulation of particles at several places and (c) (111) crystalline planes corresponding to CuO in outer shell. (d) Absorbance spectra showing a excitonic band centered at 720 nm due to presence of CuO in shell.

References:

(1) Yin, M.; Wu, C. K.; Lou, Y.; Burda, C.; Koberstein, J. T.; Zhu, Y.; O'Brien, S. *J. Am. Chem. Soc.* **2005**, 127, 9506–9511.