Supporting Information

Silver Nanocubes Coated in Ceria: Core/Shell Size Effects on Light-induced Charge Transfer

Devin B. O’Neill\textsuperscript{a}, Daniel Prezgot\textsuperscript{b}, Anatoli Ianoul\textsuperscript{b}, Cees Otto\textsuperscript{c}, Guido Mul\textsuperscript{a}, Annemarie Huijser\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a} PhotoCatalytic Synthesis Group, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

\textsuperscript{b} Department of Chemistry, Carleton University, Ottawa, Canada

\textsuperscript{c} Medical Cell BioPhysics group, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

\*j.m.huijser@utwente.nl
Figure S1: X-ray diffraction pattern of A) 47±7 nm and B) 71±9 nm silver nanocubes, coated with ceria shells with thicknesses indicated in the legend. While ceria is generally not resolved, a shielding of the silver core with thicker ceria shells is observed. The peaks are shifted due to height, as the samples were deposited on quartz slides, which elevated the sample by 1 mm. The silver peaks are ascribed to (111) at 38° (▲), (220) at 47° (●), and (220) at 64° (□). Silver nanocubes are known to be single crystal,¹ as twinning would lead to different morphologies, this is supported by the sharpness of the silver peaks and the presence of monochromator artifacts. The lack of peaks from ceria is consistent with literature data for uncalcined ceria²,³ and likely due to the very small particle size, causing extreme peak broadening. An argument could be made that weak ceria peaks are visible for the thickest ceria shells: (111) at 28°, (220) at 47°, (311) at 56° and (331) at 77° (yellow stars).
Table S1: Overview of the Ag@CeO$_2$ shell thickness/coverage for each different core and shell sizes, obtained from TEM measurements (N>20). The coverage was determined by relating the LSPR shift to the distance dependent refractive index sensitivity (see main text).

| 47±7 nm  | 71±9 nm  |
|----------|----------|
| 2.6±0.3 nm / 20% | 2.3±0.2 nm / 82% |
| 4.6±1.3 nm / 63% | 3.7±1.1 nm / 95% |
| 14.1±3.9 nm / 69% | 17.6±3.5 nm / 33% |
Figure S2: Raman measurements taken for 47±7 nm cubes with a 14.1±3.9 nm shell at 488 nm excitation at different incident intensities, showing invariance with incident intensity after normalization to the amplitude of the 1070 cm\(^{-1}\) mode.
Figure S3: I) TEM images of A) 47 nm Ag cubes with 14.1 nm ceria shell and B) 71 nm Ag cubes with 17.6 nm ceria shell. While there is some geometric distribution in the samples, even with the thickest shells there are no large, or loose ceria particles. II) SEM images of 47 nm Ag cubes with A) 2.6 nm crystallites, B) 4.6 nm shell, and C) 14.1 nm shell. III) SEM images of 71 nm cubes with A) 2.3 nm crystallites, B) 3.7 nm shell, and C) 17.6 nm shell; it is clear that there are no particles so large that they would not be seen in the TEM, and no large isolated particles are seen in the TEM.
Figure S4: XPS for 71 nm Ag nanocubes with 17.6 nm ceria shells. A) Ce 3d peaks, fit with 5 doublets, of which 3 are assigned to Ce$^{4+}$ (red) and 2 to Ce$^{3+}$ (green). \(^4\)–\(^7\) The area of the peaks was used to determine the relative abundance of the Ce$^{3+}$ to the Ce$^{4+}$ oxidation state (Table S2) by comparing the relative intensity of the areas ([Ce$^{3+}$] = \(\frac{\text{Area}_{\text{Ce}^{3+}}}{\text{Area}_{\text{Ce}^{3+}} + \text{Area}_{\text{Ce}^{4+}}}\)). B) O 1s peaks which show the presence of oxygen vacancies (Ce$_2$O$_3$, Ce$^{3+}$) and hydroxides.\(^4\)\(^5\)

Table S2: Results of Ce 3d peak fitting.

| Band | Position (eV) | FWHM  | Height | Area  | % Area | Assignment     |
|------|--------------|-------|--------|-------|--------|----------------|
| 1    | 881.19       | 2.46  | 3440   | 9001  | 1.82   | Ce$^{3+}$ (V$_0$) |
| 2    | 882.85       | 2.10  | 21255  | 47442 | 9.60   | Ce$^{4+}$ (V)   |
| 3    | 884.93       | 2.25  | 6553   | 15911 | 3.22   | Ce$^{3+}$ (V')  |
| 4    | 888.76       | 6.93  | 13073  | 117218| 23.71  | Ce$^{4+}$ (V'') |
| 5    | 898.52       | 2.66  | 26344  | 106426| 21.53  | Ce$^{4+}$ (V'') |
| 6    | 899.49       | 2.46  | 1614   | 6030  | 1.22   | Ce$^{3+}$ (U$_0$) |
| 7    | 901.15       | 2.10  | 14241  | 31786 | 6.43   | Ce$^{4+}$ (U)   |
| 8    | 903.23       | 2.25  | 4225   | 10660 | 2.16   | Ce$^{3+}$ (U')  |
| 9    | 907.06       | 6.93  | 9874   | 78536 | 15.89  | Ce$^{4+}$ (U'') |
| 10   | 916.82       | 2.99  | 16426  | 71306 | 14.43  | Ce$^{4+}$ (U'') |

\(^4\)\(^5\)
Figure S5: Refractive index sensitivity of the Ag cubes’ dominant corner mode determined by dispersing the cubes in water, ethanol, and ethylene glycol was found to be 310±70 nm/RIU and 310±30 nm/RIU for 47±7 nm and 71±9 nm cubes.

Figure S6: FDTD results: A) simulated absorption spectra for a 50 nm Ag nanocube in water with a shell of various thicknesses ($n_{\text{shell}}=2.2$) used to determine $\text{RIS}(t)$. B) $\text{RIS}(t)$ for the dominant corner mode (C-mode) and highest energy facial mode (F-mode) for different core sizes.
Figure S7: Raman spectra at 488 nm excitation of 47 and 71 nanometer cubes functionalized with 4-MBA, with and without ceria shell; and of CeO$_2$ nanoparticles in water at 785 nm excitation. The ceria Raman intensity is normalized to the F$_{2g}$ mode at 412 cm$^{-1}$.\textsuperscript{11} The 1415 cm$^{-1}$ peak indicative of charge transfer is not present in the absence of the ceria shell. The slight shift in the 1070 cm$^{-1}$ mode and intensity of the 1370 cm$^{-1}$ mode for Ag cubes coated with 4-MBA only are both explicable by different H-bonding relative to the ceria coated analogues.\textsuperscript{12} For assignment of the Raman peaks, see main text.
Figure S8: Probability (and uncertainty thereof, dashed lines) that an electron excited by the dephasing of the plasmon has sufficient energy to enter the 4-MBA LUMO (2.28 eV above the Ag Fermi level), calculated by comparing the area of the Fermi distribution for silver that would allow the transition to all allowed transitions. Generally, this supports the excitation wavelength dependency seen in the \( \rho_{CT} \) values.
Raman Spectrum Processing

While analyzing the data, it was found that the result of $\rho_{CT}$ could vary non-trivially depending on how the Raman spectra were baselined. To account for this, a robust baselining method is needed for quantitative analysis. Common approaches include use of derivatives, filters, or manual polynomial fitting. The latter approach was used to achieve this: a MATLAB script was made to algorithmically baseline the data through the `msbackadj` function, which estimates the baseline through a spline approximation of multiply shifted windows. To prevent calculating $\rho_{CT}$ for an incorrect baseline, the algorithm uses a loop for `msbackadj` step sizes of 2 to 250 data points, and then calculates the $\rho_{CT}$ for each baseline. Initialization of the script first allows for the calibration of the detector (convert pixel to wavenumber) using cyclohexane. All Raman data sets except for 785 nm excitation require this step.

The second step of the script is to import the remaining spectra of the set and then to begin treating the data. The script allowed for the removal of artifacts through the “zap” function, which removed the offending data point from the set of Raman spectra (in the processing, one set was all the spectra from a single excitation energy and measured on the same day). To calculate $\rho_{CT}$ the user is prompted to select a window in which the 1070 cm$^{-1}$ reference peak is, and then the window where the varying 1400 cm$^{-1}$ peak is. The 1070 cm$^{-1}$ peak is fit with a single Gaussian; while the reference peak was fit with two Gaussian peaks, as there is are two asymmetric modes present. This gives the area of the peaks from which $\rho_{CT}$ is calculated.

The choice of Gaussian, and not a mixed, or convoluted system was reached as the convoluted system requires knowledge, or manual parameterization of the ratio of Gaussian and Lorentzian peaks (which introduce bias), and the mixed system is a further fitting parameter which had neutral benefit. The mixed Gaussian-Lorentzian peak more correctly models the SERS peak, however the persistent error induced by the use of Gaussian fitting was countered by the systematic deconvolution of the doublet peak. That is, use of a mixed peak fitting would have necessitated either a reduction in the baseline accuracy, or an introduction of a user parameter and therefore a bias. Summarily the Gaussian fit was used, and the error induced by this fit is minimized by averaging over many baselines.

It was observed that the average of the set is approximately the same as the calculated $\rho_{CT}$ for very small step sizes. The method produces few outliers which varied considerably from the rest of the set of $\rho_{CT}$ found for a single Raman spectrum; the most extreme are cut from the data in a consistent manner: exclusion of $\rho_{CT}$ which are 3 times greater than the $\rho_{CT}$ for small step sizes ($\rho_{CT}$=0.2 was set if no $\rho_{CT}$ was calculatable). The calculated $\rho_{CT}$ for a spectrum is then averaged for all non-excluded baselines, with the standard deviation as the error.
Figure S9: A) The data from 488 nm excitation being treated. The upper plot shows the raw data (subtracting the average of the initial points), and the baseline corrected data for a step size of 100. B) The lower pane shows the calculated $\rho_{CT}$ for the set of data, and the legend overlaying both panes pertains to the lower. C) An average $\rho_{CT}$, and the standard deviation are determined from the output in B.
(1) Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? Angew. Chemie Int. Ed. 2009, 48 (1), 60–103. https://doi.org/10.1002/anie.200802248.

(2) Saitzek, S.; Blach, J.-F.; Villain, S.; Gavarrì, J.-R. Nanostructured Ceria: A Comparative Study from X-Ray Diffraction, Raman Spectroscopy and BET Specific Surface Measurements. Phys. status solidi 2008, 205 (7), 1534–1539. https://doi.org/10.1002/pssa.200723419.

(3) Sahoo, S. K.; Mohapatra, M.; Singh, A. K.; Anand, S. Hydrothermal Synthesis of Single Crystalline Nano CeO$_2$ and Its Structural, Optical, and Electronic Characterization. Mater. Manuf. Process. 2010, 25 (9), 982–989. https://doi.org/10.1080/10426914.2010.480995.

(4) Ma, R.; Jahurul Islam, M.; Amaranatha Reddy, D.; Kim, T. K. Transformation of CeO2 into a Mixed Phase CeO$_2$/Ce$_2$O$_3$ Nanohybrid by Liquid Phase Pulsed Laser Ablation for Enhanced Photocatalytic Activity through Z-Scheme Pattern. Ceram. Int. 2016, 42 (16), 18495–18502. https://doi.org/10.1016/j.ceramint.2016.08.186.

(5) Światowska, J.; Lair, V.; Pereira-Nabais, C.; Cote, G.; Marcus, P.; Chagnes, A. XPS, XRD and SEM Characterization of a Thin Ceria Layer Deposited onto Graphite Electrode for Application in Lithium-Ion Batteries. Appl. Surf. Sci. 2011, 257 (21), 9110–9119. https://doi.org/10.1016/j.apsusc.2011.05.108.

(6) Paparazzo, E. On the Curve-Fitting of XPS Ce(3d) Spectra of Cerium Oxides. Mater. Res. Bull. 2011, 46 (2), 323–326. https://doi.org/10.1016/j.materresbull.2010.11.009.

(7) Burroughs, P.; Hamnett, A.; Orchard, A. F.; Thornton, G. Satellite Structure in the X-Ray Photoelectron Spectra of Some Binary and Mixed Oxides of Lanthanum and Cerium. J. Chem. Soc. Dalt. Trans. 1976, No. 17, 1686-1698. https://doi.org/10.1039/dt9760001686.

(8) Kedenburg, S.; Vieweg, M.; Gissibl, T.; Giessen, H. Linear Refractive Index and Absorption Measurements of Nonlinear Optical Liquids in the Visible and Near-Infrared Spectral Region. Opt. Mater. Express 2012, 2 (11), 1588-1611. https://doi.org/10.1364/ome.2.001588.

(9) Sani, E.; Dell’Oro, A. Spectral Optical Constants of Ethanol and Isopropanol from Ultraviolet to Far Infrared. Opt. Mater. (Amst). 2016, 60, 137–141. https://doi.org/10.1016/j.optmat.2016.06.041.

(10) Sani, E.; Dell’Oro, A. Optical Constants of Ethylene Glycol over an Extremely Wide Spectral Range. Opt. Mater. (Amst). 2014, 37, 36–41. https://doi.org/10.1016/j.optmat.2014.04.035.

(11) Filtschew, A.; Hofmann, K.; Hess, C. Ceria and Its Defect Structure: New Insights from a Combined Spectroscopic Approach. J. Phys. Chem. C 2016, 120 (12), 6694–6703. https://doi.org/10.1021/acs.jpcc.6b00959.

(12) Wang, Y.; Ji, W.; Sui, H.; Kitahama, Y.; Ruan, W.; Ozaki, Y.; Zhao, B. Exploring the Effect of Intermolecular H-Bonding: A Study on Charge-Transfer Contribution to Surface-
Enhanced Raman Scattering of p-Mercaptobenzoic Acid. *J. Phys. Chem. C* **2014**, *118* (19), 10191–10197. https://doi.org/10.1021/jp5025284.

(13) Sun, K.; Su, H.; Yao, Z.; Huang, P. Baseline Correction for Raman Spectra Based on Piecewise Linear Fitting. *Spectroscopy* **2014**, *29* (2), 54–61.