

Supplementary Material:

Circular dichroism in the interband transitions of achiral metal nanoparticles: TiN and noble metals

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Experiments

Circular dichroism spectroscopy. CD spectra were collected using a Chirascan CD spectrometer (Applied Photophysics, Leatherhead, UK; operating range 163-900 nm). Temperature on the sample holder was maintained at 20 °C by a cooling system. A wavelength interval was 2 nm, and acquisition time per point was 0.5 second. Seven spectra were subsequently collected and averaged for each sample. Water was used as the background solution, and three spectra of water have been collected and averaged at every time before and after the spectra of a sample were obtained. The averaged background spectrum was smoothed by the Savitsky-Golay algorithm. The smoothed background spectrum was subtracted from the averaged sample spectrum, and it is important to ensure that a background drift does not cause artifacts during the spectra subtraction. Finally, the resulting raw spectrum of a sample was smoothed. The averaging, subtraction, and smoothing procedures were performed using the built-in Chirascan software. Smoothed spectra were used in calculating molar ellipticity at a wavelength of 320 nm. Since values of absorbance at 320 nm ranges 1.6-2.5, ellipticity values were normalized relative to absorbance of 1.8. The choice of a cuvette is important to avoid obtaining artifacts. A fluorescence cell (Hellma GmbH & Co. KG, model 111-10-40 QS, light path 10 mm, width 10 mm)

was used in this study. The CD signal of the individual nanoparticles is not strong enough to measure with a standard 1.0-mm cuvette. If the width of a cuvette is smaller than the diameter of the CD beam, the cuvette usually generates an artifact birefringence; a micro-volume cell and a 4-mm inner-width cell may produce artifacts. Whether or not a cuvette produces an artifact spectrum is readily verified by monitoring spectral reproducibility while placing a cuvette with dye solution contained in the opposite direction.

UV-vis extinction spectroscopy. UV-vis spectra of nanoparticle solutions were collected using a Cary 5000 UV-Vis-NIR spectrophotometer (Varian, Palo Alto, CA).

Scanning electron microscopy (SEM). SEM images of nanoparticles were obtained by a Zeiss SUPRA 40VP scanning electron microscope. SEM images were used for determination of the size of Cu nanoparticles.

Dynamic light scattering (DLS). Average diameters of spherical Au nanoparticles were determined by DLS using a Malvern ZetaSizer.

Materials. All chemicals were used without further purification. Gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, >99.9%), copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 99.995%), sodium citrate tribasic dihydrate ($\text{Na}_3\text{Citrate} \cdot 2\text{H}_2\text{O}$, $\geq 99.0\%$), sodium hydroxide (NaOH , $\geq 98\%$), poly(acrylic acid) (M_w 1800), hydrazine hydrate solution (78 – 82%) were obtained from Sigma-Aldrich. TiN nanoparticles (average size 50 nm) were obtained from PlasmaChem GmbH. Water was purified by a Barnstead Nanopure system (17.8 $M\Omega/\text{cm}$). All glassware was washed with aqua-regia (3:1, HCl/HNO_3). *Caution! The aqua-regia solution are highly corrosive. It should be handled with extreme care and appropriate safety precautions.* The aqua-regia cleaned glassware was rinsed thoroughly with water. Purified water was used as the solvent unless otherwise stated.

Preparations of Au nanoparticles. Citrate stabilized Au nanoparticles were synthesized by the Turkevich method.^[1] Four milliliter of 10 mM $\text{Na}_3\text{Citrate}$ stock solution was added to 100 mL of 0.30 mM HAuCl_4 solution while boiling, and this yielded about 47-nm spheres estimated by SEM and the

plasmon wavelength of 531 nm in the UV-vis extinction spectrum (DLS mean peak: 49 nm \pm 15 nm, DLS z-average: 26 nm).

Preparations of Cu nanoparticles. Spherical copper nanoparticles were synthesized by a method in the literature.^[2] Both 0.0125 g of CuSO₄·5H₂O and 0.025 g of poly(acrylic acid) (PAA, M_w 1800) were dissolved in 10 mL water, and this resulted in the PAA concentration of 1.33 mM. The mixture solution was stirred at around 60 °C. After 20 minutes, pH of the solution was adjusted to 10.0 by adding dropwise 0.5 M NaOH. Ten minutes later 1.28 μ L of the hydrazine reagent, which was diluted with 1 mL of water, was added to the CuSO₄/PAA solution. The reaction was stopped within 30 minutes before bluish color from Cu oxide nanoparticles appeared. Average diameter measured by SEM is 56 nm \pm 18 nm.

Table S1. Molar ellipticities of 5 – 88 nm gold spheres at a wavelength of 320 nm

Diameter (nm)	Abs at SPs [†]	Molarity (mole/L)	Abs at 320 nm [†]	Ellipticity [†] (mdeg)	Normalized ellipticity w.r.t. Abs 1.8 at 320 nm	Molar ellipticity [‡]
20	3.05	3.7×10^{-9}	2.44	0.05	0.04	1.08×10^9
32	3.20	8.3×10^{-10}	2.55	0.22	0.16	1.93×10^{10}
47	3.19	3.0×10^{-10}	2.39	0.48	0.36	1.20×10^{11}
55	2.91	1.7×10^{-10}	1.72	0.92	0.96	5.65×10^{11}
60	2.95	1.3×10^{-10}	1.84	1.03	1.00	7.69×10^{11}
65	2.95	1.0×10^{-10}	1.84	1.15	1.13	1.13×10^{12}
69	3.05	8.5×10^{-11}	1.79	1.40	1.41	1.66×10^{12}
80	3.09	5.6×10^{-11}	1.67	1.70	1.83	3.27×10^{12}
88	3.18	4.5×10^{-11}	1.92	1.87	1.75	3.89×10^{12}

[†]obtained from CD and UV-vis spectra in Ref. 3.

[‡]unit: [mdeg·M⁻¹·m⁻¹]

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