

Supplementary Information

Photo-enhanced hydrolysis of bis(4-nitrophenyl) phosphate using Cu(II) bipyridine-capped plasmonic nanoparticles

Scott A. Trammell ^{a*}, Rafaela Nita ^b, Brett Martin ^a, Martin H Moore ^a, Jake Fontana ^a

Somayeh Talebzadeh ^b and D. Andrew Knight ^{b*}

Experimental

Materials and methods

3-(*N*-morpholino)propanesulfonic acid, Cu(NO₃)₂ and bis(4-nitrophenyl) phosphate (BNPP) were purchased from Aldrich and used as received. Cu[*S*-(6-(2,2'-bipyridinyl-5-carboxamido)hexyl)ethanethioate]Cl₂ (**1**), 1-mercaptohex-6-yl)tri(ethylene glycol) (**2**) and 10 nm AuNPs capped with **1** and **2** or both were prepared from previous studies.¹ 5-methyl-2,2'-bipyridine was prepared according to a literature procedure.² In brief, the catalyst loadings on capped AuNP with estimated using a combination of UV-vis spectroscopy and ICP-OES. From the ICP-OES, the mean concentrations of Cu from duplicate samples indicated a surface covering of 2,300 Cu ions/AuNP (assuming a 10-nm spherical particle). In addition, the coverage determined using the spectra of the AuNP and the extinction coefficient of Cu complex was determined to be 2,400 Cu/AuNP.

Preparation of [(5-methyl-2,2'-bipyridine)Cu]Cl₂ (**3**).

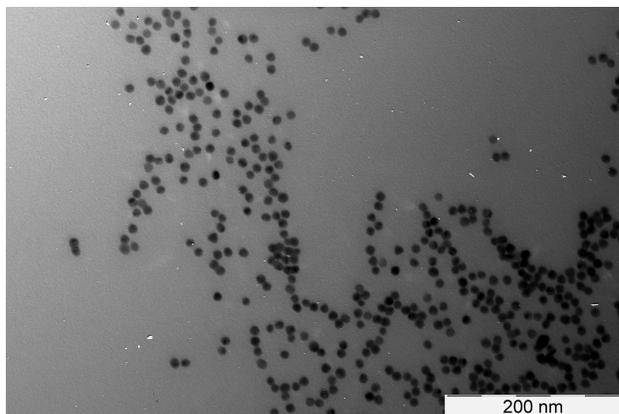
A screw-capped scintillation vial was charged with 5-methyl-2,2'-bipyridine (0.067 g, 0.50 mmol) and MeOH (5 mL) and was stirred for 5 min. Then, a solution of CuCl₂•2H₂O (0.078 g, 0.50 mmol) in MeOH (5 mL) was added dropwise and the brown-green solution was stirred for another 30 min. Stirring was discontinued, and after 2 hours the resulting precipitate was collected by filtration, washed with MeOH (ca. 5 mL) and dried under oil-pump vacuum to give **3** as a green solid. Yield: 0.087 g, 57%. Anal. Calcd for C₁₁H₁₀Cl₂CuN₂: C, 43.37; H, 3.31; N, 9.19. Found: C, 43.16; H, 3.40; N, 9.14.

Instrumentation

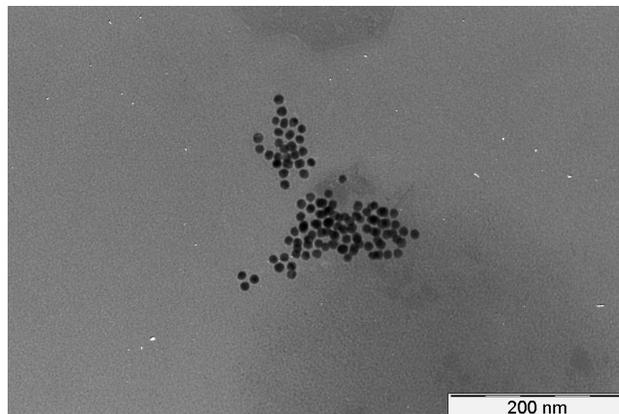
The kinetic UV-visible measurements were made with an Agilent 8453 diode array spectrometer and referenced against a solvent blank using a 50- μ l micro-cell cuvette (part number 5062-2496, Agilent Technologies). The solutions (50- μ l) were mechanically stirred with a PTFE shaft using a stirring system from Spectrocell, Inc. For the laser photolysis studies, the samples were irradiated with an Aries 100 532 nm green laser (beam width 1.5 mm, $1/e^2$) with an average sustained power of 120 mW (maximum power density of 13.88 W/cm²) or at 514 nm using a Coherent Innova 308 Argon ion laser at sustained powers of 400 and 800 mW (maximum power densities of 45.27 and 90.54 W/cm² respectively). The bulk temperature was measured as a function of laser illumination time using a USB TC-08 thermocouple (Pico Technology) mount inside the micro-cell cuvette. A small perturbation on the measurement (0.5 C) was observed upon laser illumination however no large changes in bulk temperature were recorded. The laser power was monitored with an optical power meter (Newport model 1830-C). To calculate the product formation as a function of time, [PNP]_t, the absorbance due to the AuNP at 405 nm was subtracted at each time point using the absorbance of the AuNP at 535 nm at each time point proportioned to the ratio of A_{405 nm}/A_{535 nm} at time = 0. The corresponding Δ 405 nm was converted to [PNP] using the extinction coefficient of $1.63 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ measured at pH 8. Non-linear regression analysis of the data was performed using the Excel macro Solver Statistics.³

Figure S1. TEM images for citrate stabilized 10 nm Au (a) before and (b) after exposure to 4-BNPP.

(a)



(b)



1. D. A. Knight, R. Nita, M. Moore, D. Zabetakis, M. Khandelwal, B. D. Martin, J. Fontana, E. Goldberg, A. R. Funk, E. L. Chang and S. A. Trammell, *J. Nanopart. Res.*, 2014, **16**, 1-12.
2. E. Zysman-Colman, J. D. Slinker, J. B. Parker, G. G. Malliaras and S. Bernhard, *Chemistry of Materials*, 2008, **20**, 388-396.
3. E. J. Billo, *Excel for chemists a comprehensive guide*, Hoboken, N.J. : John Wiley & Sons, 3rd edn., 2011.