Supplementary information for:

Opportunistic use of tetrachloroaurate photolysis in the generation of reductive species for the production of gold nanostructures

by

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S1-



Figure S1. Absorption spectra of AuNP prepared from air-saturated solutions of 0.33 mM HAuCl₄ and various concentrations of H_2O_2 upon 30 minutes photolysis in a 1 x 1 cm quartz cuvette in a Luzchem photoreactor.





Figure S2. Absorption spectra of AuNP prepared from Ar-purged (left) and air-saturated (right) solutions of 0.33 mM HAuCl₄ and 3.0 mM H_2O_2 upon 30 minutes photolysis in a 1 x 1 cm quartz cuvette in a Luzchem photoreactor.

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Figure S3. SEM images of AuNP prepared from 30 minutes UVA photolysis of 0.33 HAuCl₄ and 3.0 mM H₂O₂ under Ar-purged (left) and air-saturated (right) conditions.

S4-



Figure S4. Absorption spectra of AuNP prepared from an air-saturated solution of 0.33 mM HAuCl₄ and 3.0 mM H₂O₂ upon exposure to 30 minutes UVA, in the absence (♦) and presence (■) of 0.1 mM aqueous stabilizer, 4-hydroxyethoxy benzoic acid during photolysis.

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Figure S5 – (left) Benchtop view of the "Oxygen Uptake" apparatus mounted above an equilibrium water bath, and equipped with an EXPO panel positioned vertically against the left of the tank window. (right) View through the glass window, illustrating the foiled reference cell and the reaction vessel containing a pink solution of AuNP.

Quantifying the concentration of oxygen evolved:

The quantity of molecular oxygen in the synthesis of AuNP using H_2O_2 was measured using an *in-house* instrument donated from Professor Ross Barclay (Mount Allison, NB). Essentially, the change in pressure in a sealed pyrex reaction vessel equilibrated in a water tank at 30 °C is measured over time relative to a reference cell containing the same constituents, but wrapped in aluminum foil to prevent photolysis. Samples were irradiated using a Luzchem EXPO panel with five UVA lamps mounted against a glass window looking into the water tank.

The sample cell and reference cell were suspended in the water bath and attached to a shaker, ensuring fast diffusion of gas throughout the cell. A baseline measurement of the pressure in the reaction vessel was acquired for a minimum of five minutes prior to turning on the UVA panel. The electrical signal generated from the pressure changes in the vessel is transferred to a chart recorder pen, where the data was recorded on a paper feed. The output was also digitized using software developed using Labview v8.5. Initially, the sample cell and reference cell undergo a pressure check and baseline prior to sample loading, and each cell is specifically calibrated to its specific volume. Each reaction cell has been pre-calibrated with a known autooxidation reaction in order to convert the voltage detected to the concentration of oxygen generated.





Figure S6. Absorption of solutions before (left) and after (right) 30 minutes 350 nm photolysis. Samples prepared from 0.33 mM HAuCl₄ and 3.0 mM H₂O₂ in aqueous, aerated media where the pH was adjusted with HCl or NaOH. Samples were left to sit for 20 minutes prior to photolysis.

S7-



Figure S7. Absorption spectra of AuNP prepared from UVA photolysis of aqueous 0.33 mM HAuCl₄ and 50 mM 1,4-CHD in the presence (--) and absence (^{...}) of 17 mM CTAC. Inset: corresponding SEM images of the samples, where the scalebar represents 20 and 200 nm for CTAC and H₂O samples, respectively.