Supplementary Information

One-Step Catalytic Reduction of 4-Nitrophenol through the Direct Injection of Metal Salts into Oxygen-Depleted Reactants

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1. Supplementary Information Video S1. Accompanying this Supplementary Information document is a video showing the reaction described in Fig. 3 in which Ag nanoparticles, formed after the injection of 1 mL of 500 µM AgNO$_3$ into a 500 mL aqueous solution containing 4-NP (1 mM) and NaBH$_4$ (100 mM), catalytically reduce the 4-NP to 4-AP in 55 s.

2. Experimental Section

(i) Chemicals. Au, Pd, Cu, and Ag nanoparticles were formed using hydrogen tetrachloroaurate(III) trihydrate (HAuCl$_4$·3H$_2$O), palladium nitrate (Pd(NO$_3$)$_2$), copper(II) nitrate trihydrate (Cu(NO$_3$)$_2$), and silver nitrate (AgNO$_3$), respectively (Sigma Aldrich). 4-Nitrophenol and sodium borohydride (NaBH$_4$), were sourced from Fluka. All aqueous solutions were prepared using deionized (DI) water derived from a Milli-Q system (18.2 MΩ·cm at 25 °C). Gas purging utilized ultra-high purity Ar or N$_2$ (Airgas). All chemicals were used as received.

(ii) Purging Reactants with Ar Gas. The catalytic reduction of 4-NP was carried out using aqueous solutions containing dissolved oxygen at the ambient value (8.3 mg·L^{-1}) and at values below our detection limit (0.03 mg·L^{-1}). The procedures used to obtain and maintain dissolved oxygen levels below the detection limit are described in detail elsewhere.[1] For the cuvette-based catalytic reactions presented in Figs. 1 and 2, 4 mL aqueous solutions of (i) 4-NP (300 µM), (ii) NaBH$_4$ (30 mM), and (ii) metal salts (3–150 µM) were separately purged with Ar gas at a flowrate of 250 ccm for 10 min. Control experiments monitoring the aqueous liquids show that the dissolved oxygen concentration falls below the detection limit in less than 150 s (Fig. S1a). The purging period used to obtain data was, however, extended well beyond this time interval to further ensure that the influence of dissolved oxygen on catalysis is minimized. In another control experiment we purged reactants with N$_2$ gas instead of Ar and found no significant differences in the rate at which dissolved oxygen is removed (Fig. S2a) or in the catalytic reduction of 4-NP (Fig. S2b). The high concentration measurements presented in Fig. 3 required the use of a 500 mL 4-NP/NaBH$_4$ solution and, as a consequence of this greater volume, the solution was purged with Ar gas for 30 min, but where values below the detection limit were achieved in 20 min (Fig. 1Sb). The metal salt solutions (500 µM, 4 mL) used in these high concentration measurements were purged for 10 min.
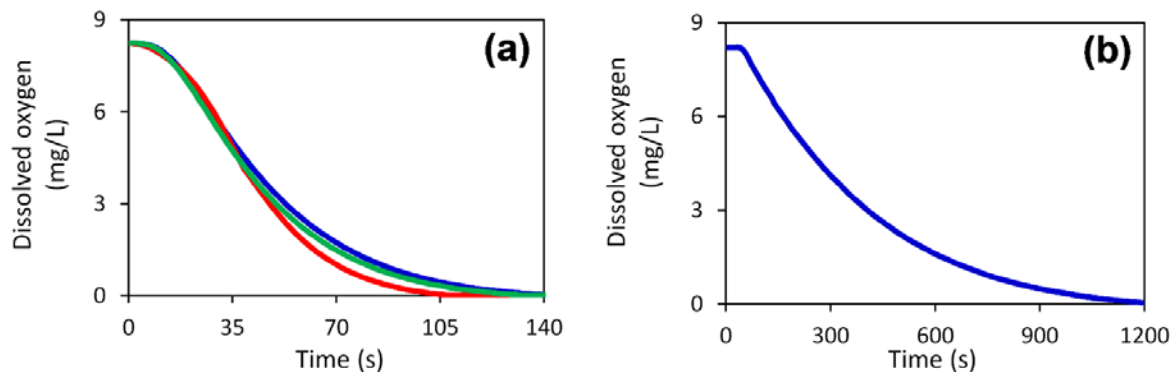
Fig. S1. (a) Time-dependence of the dissolved oxygen concentration of 4 mL aqueous solutions of (i) 4-NP (100 µM) (blue), (ii) HAuCl$_4$ (10 µM) (green), and (iii) NaBH$_4$ (10 mM) (red). (b) Time-dependence of the dissolved oxygen concentration for a 500 mL aqueous solution of 4-NP (1 mM) and NaBH$_4$ (100 mM).
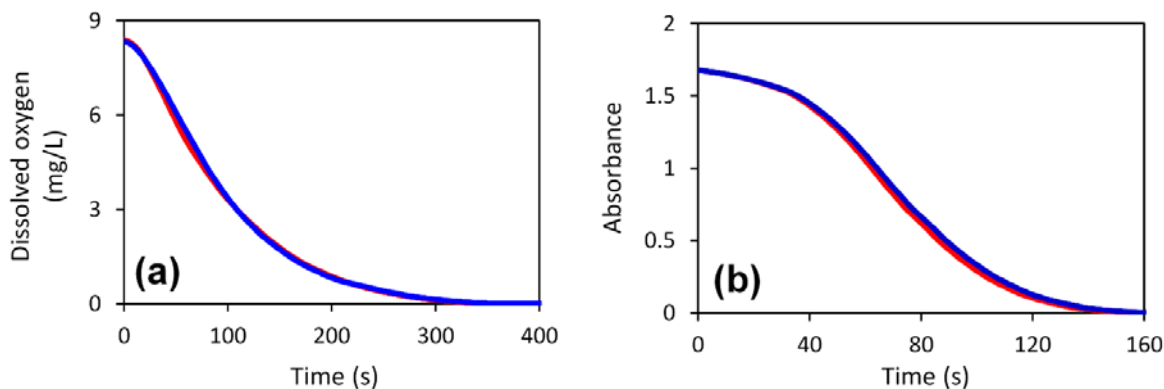

Fig. S2. (a) Comparison of the time-dependency of the dissolved oxygen concentration within an 8 mL solution of 4-NP as it is purged with Ar (red) and N$_2$ (blue) gas. (b) Absorbance measurements monitoring the 400 nm 4-NP absorbance as 3 mL of 100 µM 4-NP solution is reduced to 4-AP using 1 mL of 1 µM AgNO$_3$ for reactants purged with Ar (red) and N$_2$ (blue) gas. Note that the measured quantities are insensitive to the purging gas used.

(iii) Cuvette-Based Catalysis Measurements using 100 µM 4-NP. The catalysis data shown in Fig. 1 and 2 were obtained by spectroscopically monitoring reactants contained within a 1 cm path length quartz cuvette with a 3.5 mL volume. Spectral dependencies (Fig. 1a) were used to monitor (i) the fall in the 400 nm 4-NP absorbance and the concomitant rise at 300 nm associated with the 4-AP reaction product and (ii) the localized surface plasmon peaks (LSPR) for Au, Ag, and Cu (Fig. 1c–f). The apparent reaction rate constants (k_{app}) reported in Fig. 2 were obtained by continuously monitoring the absorbance at 400 nm (see Fig. 1d) and then analyzing the data using standard procedures.[2] Reactions were initiated by injecting 1 mL of aqueous metal salt into a cuvette containing 2 mL of aqueous 4-NP and NaBH$_4$. For these measurements the 4-NP and NaBH$_4$ concentrations contained within the combined 3 mL solution were 100 µM and 10 mM, respectively, while the concentration of the various salts was varied between 1 and 50 µM. Reactions were carried out using aqueous solutions containing dissolved oxygen and those where the dissolved oxygen was purged. For the former case, salts were injected immediately after aqueous solutions of 4-NP and NaBH$_4$ were added to the cuvette where efforts were made to keep the timing constant in order to ensure reproducibility.

(iv) High Concentration Catalysis Measurements using 1 mM 4-NP. The catalytic reduction of large volumes (500 ml) of high concentration 4-NP (1 mM) by borohydride (100 mM) were carried out in a stoppered flask through which a glass tube (5 mm) is inserted to facilitate Ar gas purging (Fig. 3a). The spent gas is exhausted through the side arm of the flask, which is connected to a gas washing bottle whose purpose is to limit the backflow of air to the reactants. Once the Ar purging process was complete, the reaction was initiated through the injection of 1 mL of 500 µM metal salts using a syringe that penetrated through the stopper. The salts were injected over a 10 s period where stirring was used to ensure the dispersal of the formed nanoparticles. Once the reaction was complete, a 0.1 mL sample was removed from the reaction product that was used to prepare TEM samples.

Spectroscopic monitoring of the high concentration measurements (Fig. 4c) required the use of a 0.7 mL quartz cuvette (LabShops, NJ, USA) with a 2 mm path length. The smaller path length allowed for detectable levels of light to reach the detector throughout the entire reaction. Measurements were carried out that compared the k_{app} values for reactions where the nanoparticles were formed in the presence and absence of 4-NP for all four metal salts under investigation. For the former case, 0.2 mL of aqueous metal salt was pipetted into a cuvette containing 0.4 mL of aqueous 4-NP and NaBH$_4$. For the latter case, 0.2 mL of aqueous metal salt was pipetted into 0.2 mL of NaBH$_4$ in order to initiate nanoparticle formation. After a 1 min interval, in which nanoparticles were allowed to form, the reaction was initiated through the addition of 0.2 mL of 4-NP. For all cases, a 0.6 mL solution was formed within the cuvette where the metal salt, 4-NP, and NaBH$_4$ concentrations at the beginning of the reaction are 1 µM (0.1 mol%), 1 mM, and 100 mM, respectively.

(v) Instrumentation. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM 2011 transmission electron microscope. The samples were prepared by drop casting freshly formed nanoparticle solution onto a TEM grid (carbon Type A on 400 mesh Cu – Ted Pella, Inc.). TEM images were taken immediately after the sample dried. A Jasco V–730 Spectrophotometer was used to monitor the catalytic reduction of 4-NP. An optical sensor was used to measure the dissolved oxygen concentration (Vernier Software and Technology – Beaverton, OR, USA).

3. Nanoparticle Formation at Low 4-NP Concentrations. Figure 1c–e shows the LSPR peak observed for Au, Cu, and Ag nanoparticles. For the case of Pd there was no observable LSPR peak. Nanoparticles were, however, observed, in the reaction product for all four metal salts. Images of these structures are shown in Fig. S3. Note that in all cases individual nanoparticles as well as agglomerates can be observed.
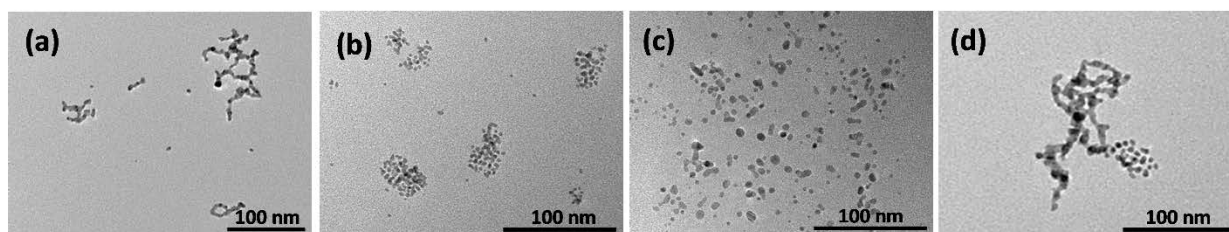

Fig. S3. TEM images of the (a) Au, (b) Pd, (c) Cu, and (d) Ag nanoparticles formed through the direct injection of 10 µM aqueous salts into a solution containing 100 µM 4-NP and 10 mM NaBH$_4$.

4. Induction Time Data. Figure 2 shows the k_{app} values obtained when salts of Au, Pd, Cu, and Ag of varying concentrations are injected into aqueous reactants in both the presence and absence of dissolved oxygen. Figure S4 shows the corresponding induction times for each of these reactions. The data is consistent with our previous study that shows a mechanistic connection between the dissolved oxygen concentration and the duration of the induction time.[1] The substantial induction times observed for the 1μM concentration likely occur because dissolved oxygen is still present in concentrations of significance when compared to the quantity of catalyst present. It is also possible that induction times are attributable to the time required for catalytic nanoparticles to form.
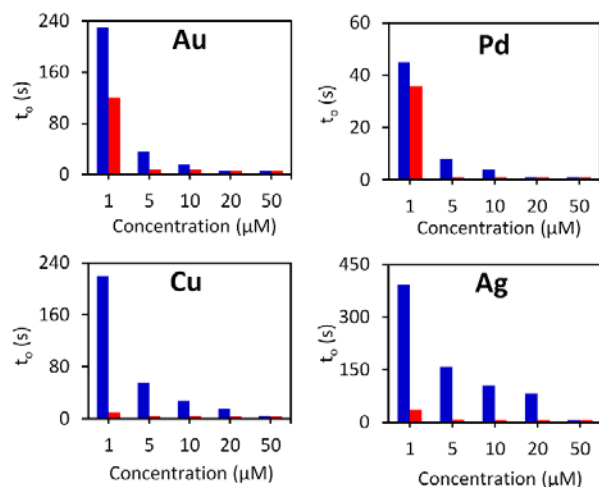

Fig. S4. Dependency of the induction time (t_0) on the concentrations of metal salt injected into reactants in both the presence (blue) and absence (red) of dissolved oxygen.

Nanoparticle Formation at High 4-NP Concentrations. Figure 4 shows schematics and kinetic data for high concentration 4-NP reactions in which (a) the single-step injection method is used and (b) for an alternative procedure where nanoparticles are first formed in NaBH$_4$ followed by the addition of 4-NP after 1 min. Fig. S5 shows TEM images of the nanostructures observed in the reaction product. It also noted that nanostructures synthesized in the presence and absence of dissolved oxygen showed no observable differences.
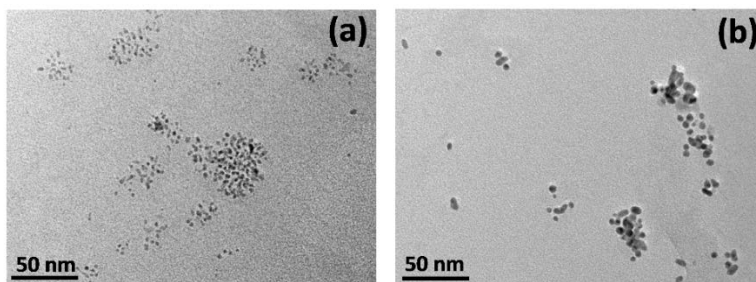

Fig. S5. TEM images of the Ag nanoparticles formed in the (a) presence and (b) absence of 4-NP.

[1] Menumerov E.; Hughes R. A.; Neretina S. The Catalytic Reduction of 4-Nitrophenol: A Quantitative Assessment of the Role of Dissolved Oxygen in Determining the Induction Time. *Nano Lett.,* 2016, **16**, 7791.

[2] Hervés P.; Pérez-Lorenzo M.; Liz-Marzán L. M.; Dzubiella J.; Lu Y.; Ballauff M. Catalysis by Metallic Nanoparticle in Aqueous Solution: Model Reactions. *Chem. Soc. Rev.,* 2012, **41**, 5577.