

Electronic Supplementary Information (ESI)

One-pot synthesis of responsive catalytic Au@PVP hybrid nanogels

Chuanfu Xiao,^a Shoumin Chen,^a Laiying Zhang,^a Shuiqin Zhou,^b and Weitai Wu*^a

^a State Key Laboratory for Physical Chemistry of Solid Surfaces, The Key Laboratory for Chemical Biology of Fujian Province, and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. E-mail: wuwtxmu@xmu.edu.cn

^b Department of Chemistry, College of Staten Island, and The Graduate Center, City University of New York, Staten Island, New York 10314, USA

SI 1. Experimental Procedures

1.1. Materials

Hydrogen tetrachloroaurate (III) hydrate (HAuCl₄·3H₂O, 99.9%), L-(+)-ascorbic acid (L-AA, 99+%), polyvinylpyrrolidone (PVP, *M_w* 58,000), 4-nitrophenol (4-NP, 99%), and sodium borohydride (NaBH₄, 98%) were purchased from Alfa Aesa. N,N'-Methylenebisacrylamide (MBAAm, 99%) was purchased from Sigma-Aldrich. Hydrogen peroxide (H₂O₂, 30%) was purchased from Guangzhou Jinhuada chemical reagent Co., Ltd. All chemicals were used as received without further purification. The water used in all experiments was of Millipore Milli-Q grade.

1.2. Synthesis of Au@PVP Hybrid Nanogels

HAuCl₄ aqueous solution (25.0 mM, 100.0 μL) and PVP (0.5 M, 1.0 mL) were dissolved in water (48.0 mL) in a 150 ml round-bottom flask equipped with a stirrer and a N₂ gas inlet. After stirring for 15 min at 25.0 °C, L-AA (6.3×10⁻¹ M, 1.0 mL) was rapidly injected into the mixture to initiate the reduction. The color of the solution became pink immediately, which further changed to red wine. The reduction reaction was continued for 1 h. Then, MBAAm (1.3×10⁻¹ M, 1.0 mL) was added. After stirring for 10 min, H₂O₂ (30 wt%) was injected into the reaction mixture. The reaction was allowed to proceed for another 90 min. The product was purified with 3 days of dialysis against very frequently changed water. The Au@PVP hybrid nanogels synthesized with 100.0 μL, 500.0 μL, and 5.0 mL of H₂O₂ were denoted as AP-1, AP-2, and AP-3, respectively.

1.3. Catalytic Reduction of 4-NP

NaBH₄ (150.0 μL, 0.1 M) was added into an Au@PVP hybrid nanogel dispersion in water (3.0×10^{16} Au-atom/mL) in quartz cuvette, and the mixture was stirred for 5 min at room temperature. 4-NP (10.0 μL, 0.01 M) was then added into the mixture, which was stirred until the deep yellow solution became red wine. During the course of reaction, the reaction progress was monitored by measuring UV-vis absorption spectra of the mixture.

1.4. Characterization

FTIR spectra were recorded with a Thermo Electron Corporation Nicolet 380 Fourier transform infrared spectrometer. The air-dried hybrid nanogels were redispersed in ethanol, which then dried on a KBr slice for FTIR measurements. TEM images were taken on a JEOL JEM-2100 transmission electron microscope at an accelerating voltage of 200 kV. The hybrid nanogels were air-dried on a carbon-coated copper grid for TEM measurements. UV-vis absorption spectra of the hybrid nanogel dispersions were recorded on a Shimadzu UV-2550 UV-Vis spectrometer. The pH value was measured on a EUTECH PH 700 instruments. Dynamic light scattering (DLS) was performed on a 90Plus multi angle particle sizing analyzer equipped with a BI-9000AT digital autocorrelator (Brookhaven Instruments, Inc.). A He-Ne laser (35 mW, 659 nm) was used as the light source. All samples were passed through Millipore Millex-HV filters with a pore size of 0.80 μm to remove dust before the DLS measurements.

SI2. Figures.

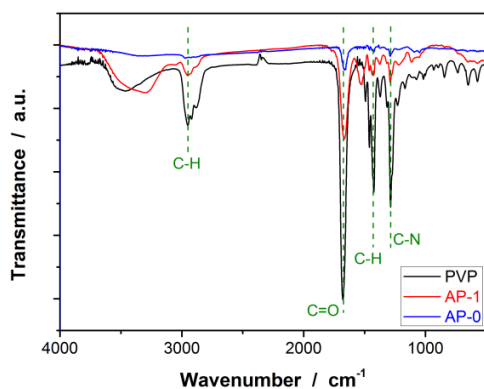


Fig. S1 IR spectra.

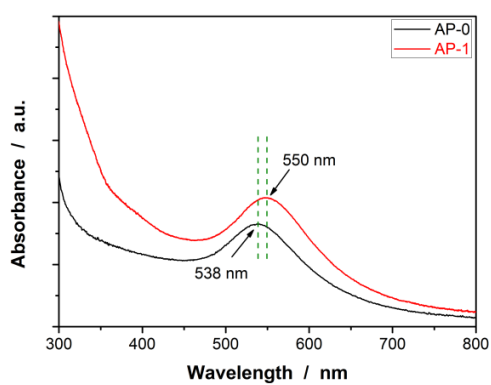


Fig. S2 UV-vis absorption spectra.

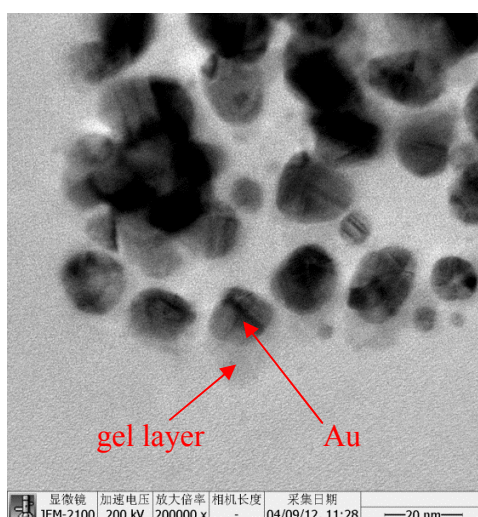


Fig. S3 TEM image of AP-1.

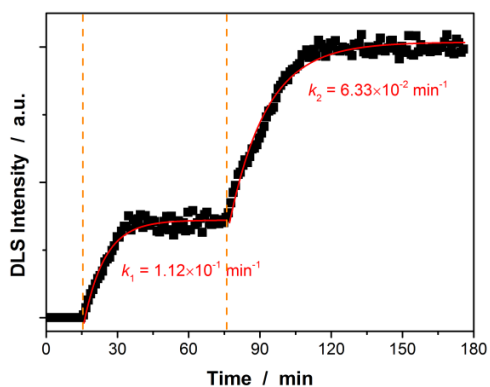


Fig. S4 Kinetic curves of Au@PVP hybrid nanogel AP-2's formation obtained from DLS studies. Solid lines: 1st-order kinetic fits.

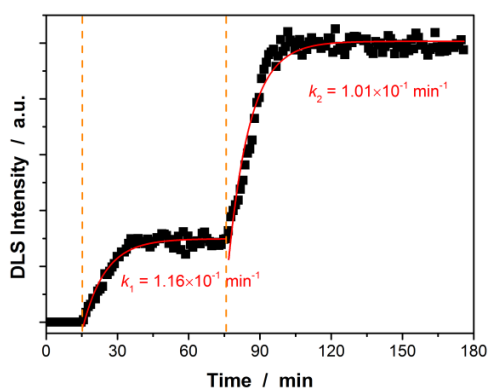


Fig. S5 Kinetic curves of Au@PVP hybrid nanogel AP-3's formation obtained from DLS studies. Solid lines: 1st-order kinetic fits.

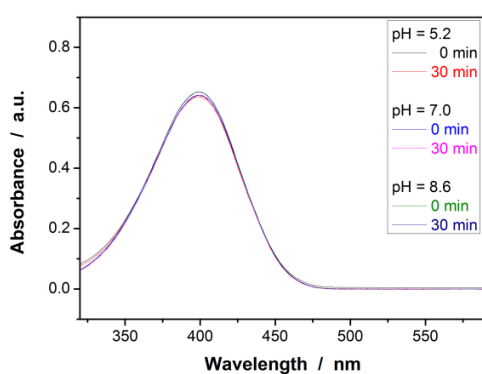


Fig. S6 The time-domain UV-vis spectra of the reaction mixture at different pH values, without the use of Au@PVP hybrid nanogels or any Au nanoparticles.

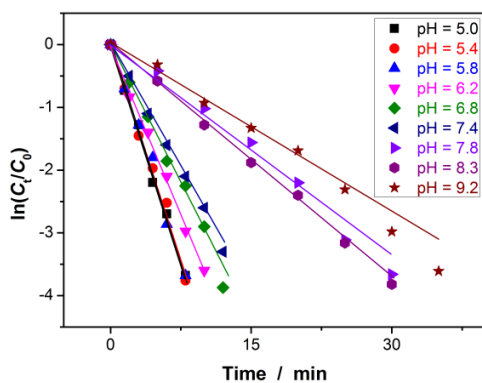


Fig. S7 The $\ln(C_t/C_0)-t$ plot, showing influence of solution pH value on the kinetic constant k_{4-NP} , measured with Au@PVP hybrid nanogels (AP-2)

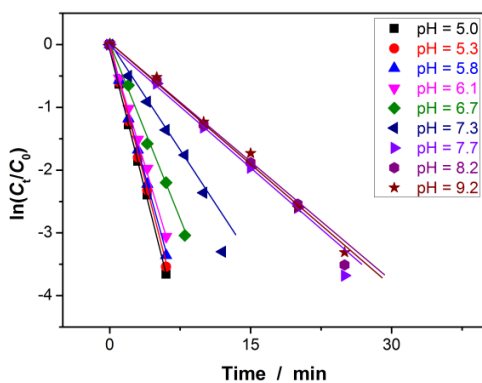


Fig. S8 The $\ln(C_t/C_0)-t$ plot, showing influence of solution pH value on the kinetic constant k_{4-NP} , measured with Au@PVP hybrid nanogels (AP-3)