

Supporting Information

P22 Virus-like Particles Constructed Au/CdS Plasmonic Photocatalytic Nanostructures for Enhanced Photoactivity

Ziyou Zhou, Gregory J. Bedwell, Rui Li, Ningzhong Bao, Peter E. Prevelige, Jr., and Arunava Gupta**

Materials: CdS and gold nanostructures were synthesized using commercially available reagents. Cadmium chloride (CdCl_2 , 99.99%) and thioacetamide ($\text{C}_2\text{H}_5\text{NS}$, $\geq 99\%$) were purchased from Acros Organics (New Jersey, US). Auric chloride (HAuCl_4 , 99.99%) and sodium borohydride (NaBH_4 , 98%) were purchased from VWR (Pennsylvania, US). Sodium Hydroxide (NaOH , 99%) was purchased from Fisher Scientific (Pennsylvania, US), and Tris(hydroxymethyl)aminomethane (Tris, 99%) was purchased from VWR (Pennsylvania, US). All the chemicals were used as-received without any further purification.

Plasmids construction, protein expression and CdS synthesis: followed exactly a previously reported procedure.¹

Gold nanoparticle synthesis: After the confined synthesis of CdS inside P22 VLP, the resultant solution was centrifuged using a centrifuge filter device (MOCO 3000) to remove residual reactants and any other molecules with molecular weight smaller than 3000. P22 VLP with CdS collected in the centrifuge filter tube was re-suspended in DI water (1 mL), into which NaBH_4 (5 mM, 50 μL) was added and then auric chloride solution was added drop wise to synthesize the gold nanoparticles. To synthesize different size gold nanoparticles, varying concentration of gold precursor (35 μM , 70 μM , 105 μM , 140 μM , and 175 μM) was used while the concentration of

VLP was kept constant (0.1mg/mL), with corresponding ratio of gold precursor to coat protein being approximately 20:1, 40:1, 80:1, 100:1, and 120:1, respectively. It is worth noting that the NaBH₄ should be added before addition of HAuCl₄, otherwise the acidic gold precursor interacts with the CdS and destroys its integrity. For gold nanoparticles synthesized using only P22 VLP without CdS, the amount and ratio of protein and gold precursor used were exactly the same, as well as the synthesis procedure except for the centrifuge filtering step. To achieve the size controllability it is important to control the reaction rate by drop wise addition of the gold precursor solution. When the gold precursor is all added at one time, the size range of resultant gold nanoparticles remains between 2 - 5 nm, but a large amount of gold nanoparticles nucleate and grow in the solution rather than on the VLP template.

Photoactivity measurements: The photocatalytic activities of P22 VLP, VLP-CdS, Au-VLP, and Au-VLP-CdS were evaluated by measuring the photodegradation of methylene blue (MB). An optical glass cuvette containing water (1 mL), MB (10 μM) and either P22 VLP or mineralized P22 VLP was illuminated using a solar simulator with an illumination intensity of 1 sun (AM 1.5, 100 mW/cm²). Before illumination, the cuvette was placed in the dark for 24 hours, allowing the plasmonic photocatalyst and dye to reach absorption equilibrium. The photodegradation was monitored by the decrease in absorbance at 660 nm using a UV-Vis spectrometer.

Materials Characterization: The morphology and structure of the products were studied using TEM (transmission electron microscopy) with high resolution (HR) (Tecnai F-20) equipped with a CCD camera for STEM, HAADF detector, and EDX. 2% uranyl acetate was used as a negative

staining agent for imaging the assembled P22 VLP. The optical measurements were carried out using a UV-Vis spectrometer (Beckman DU 800).

1. Z. Zhou, G. J. Bedwell, R. Li, P. E. Prevelige and A. Gupta, *Sci. Rep.*, 2014, **4**, 3832.

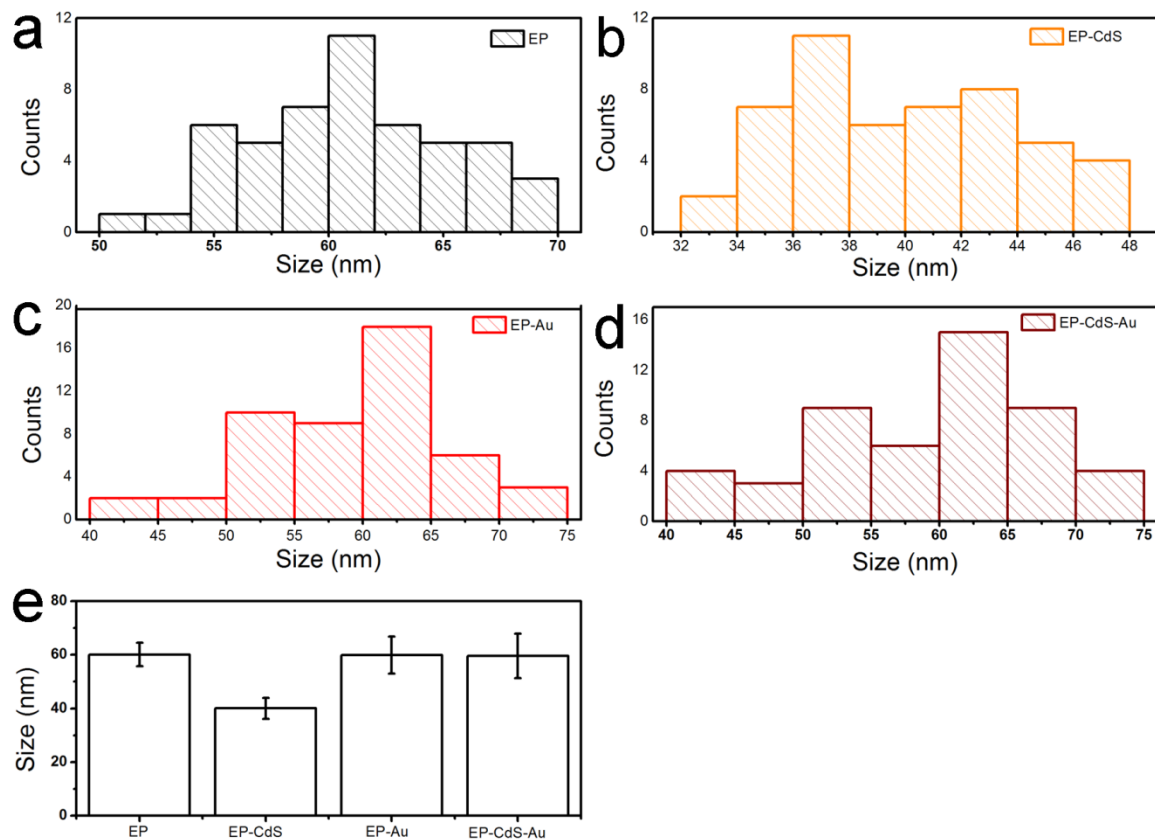


Figure S1. Size distribution of engineered P22 VLP (EP) as determined from TEM results. a) EP by itself, b) EP with CdS, c) EP with Au, d) EP with both CdS and Au, and e) size comparison of different EP-based particles.

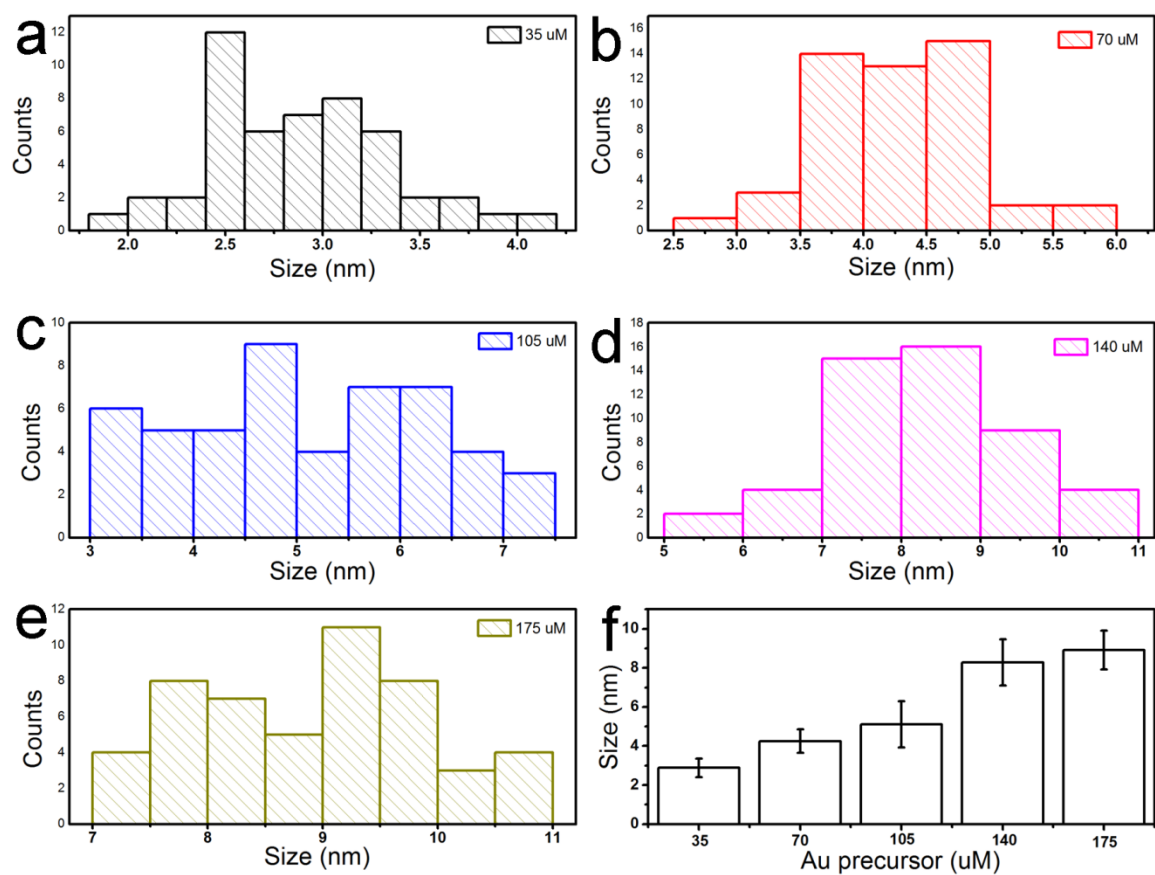


Figure S2. Size distribution of gold nanoparticles obtained using different concentrations of gold precursor as determined from TEM results. a) 35 μM , b) 70 μM , c) 105 μM , d) 140 μM , and e) 175 μM . f) Average size of gold nanoparticles as a function of gold precursor concentration.

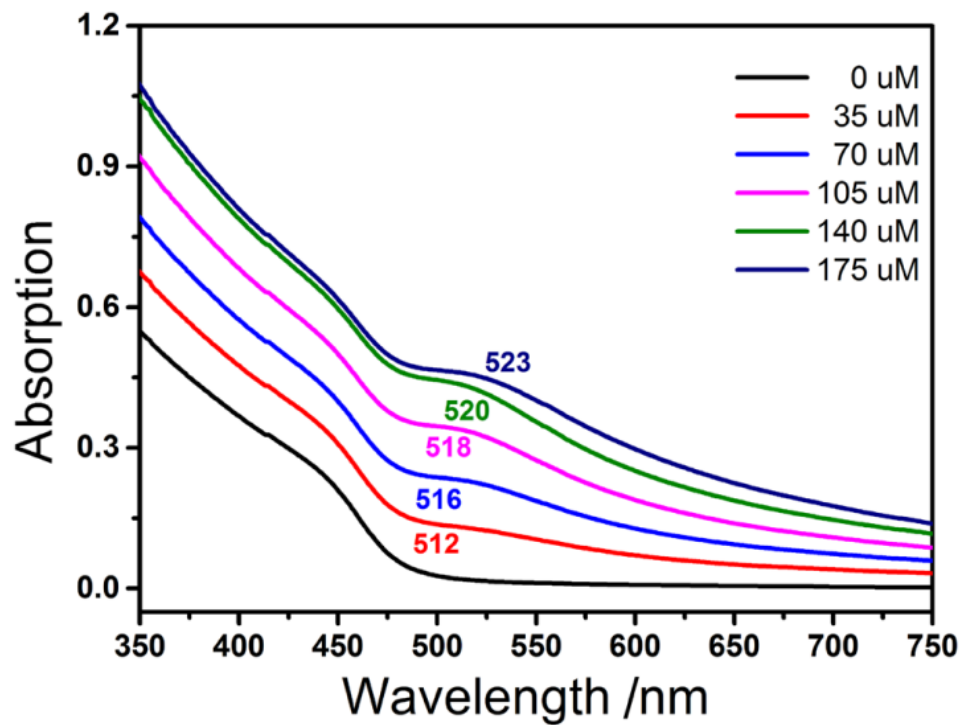


Figure S3. In-situ observation of the changes in the plasmon absorption peak of gold nanoparticles on the surface of P22 VLP with encapsulated CdS as measured by UV-vis spectroscopy. Spectra are obtained one minute after addition of AuHCl₄ into VLP - CdS solution with an excess amount of NaBH₄.

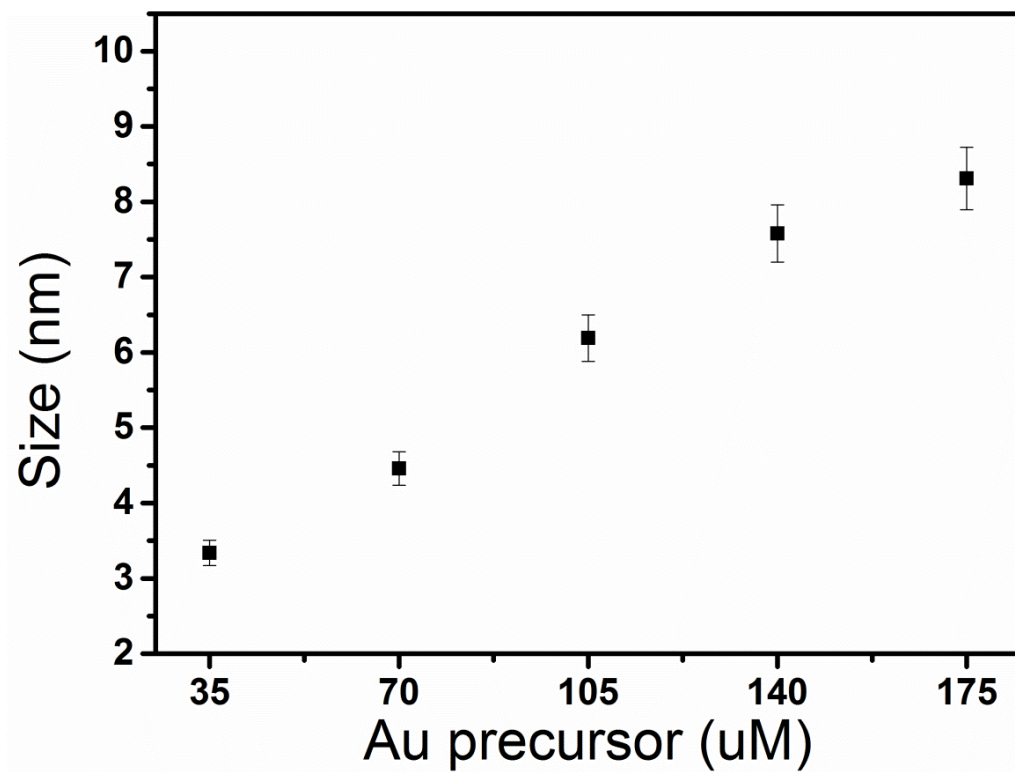


Figure S4. Average size of gold nanoparticles as a function of precursor concentration as calculated from the UV/Vis absorption spectra.

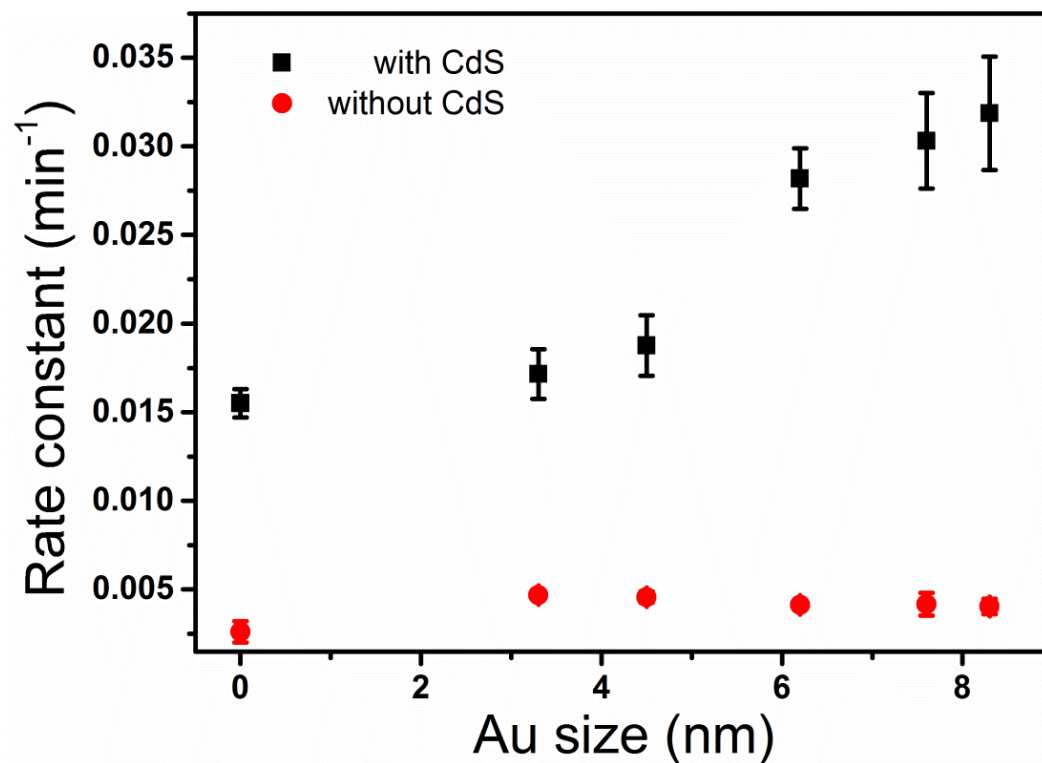


Figure S5. Au size-dependent photodegradation rate of methylene blue, both with and without CdS (n=3 independent experiments, error bars represent \pm S.D).