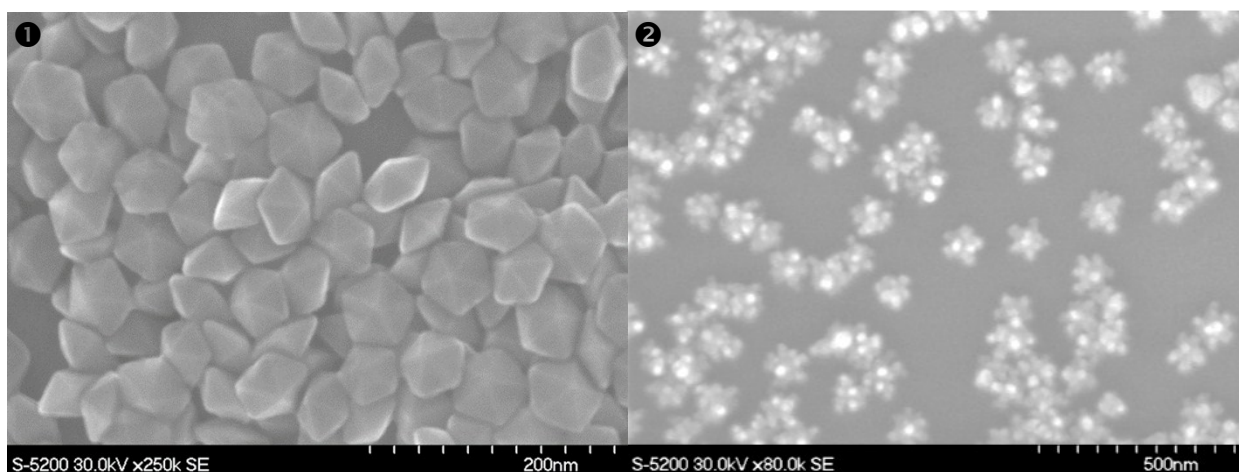


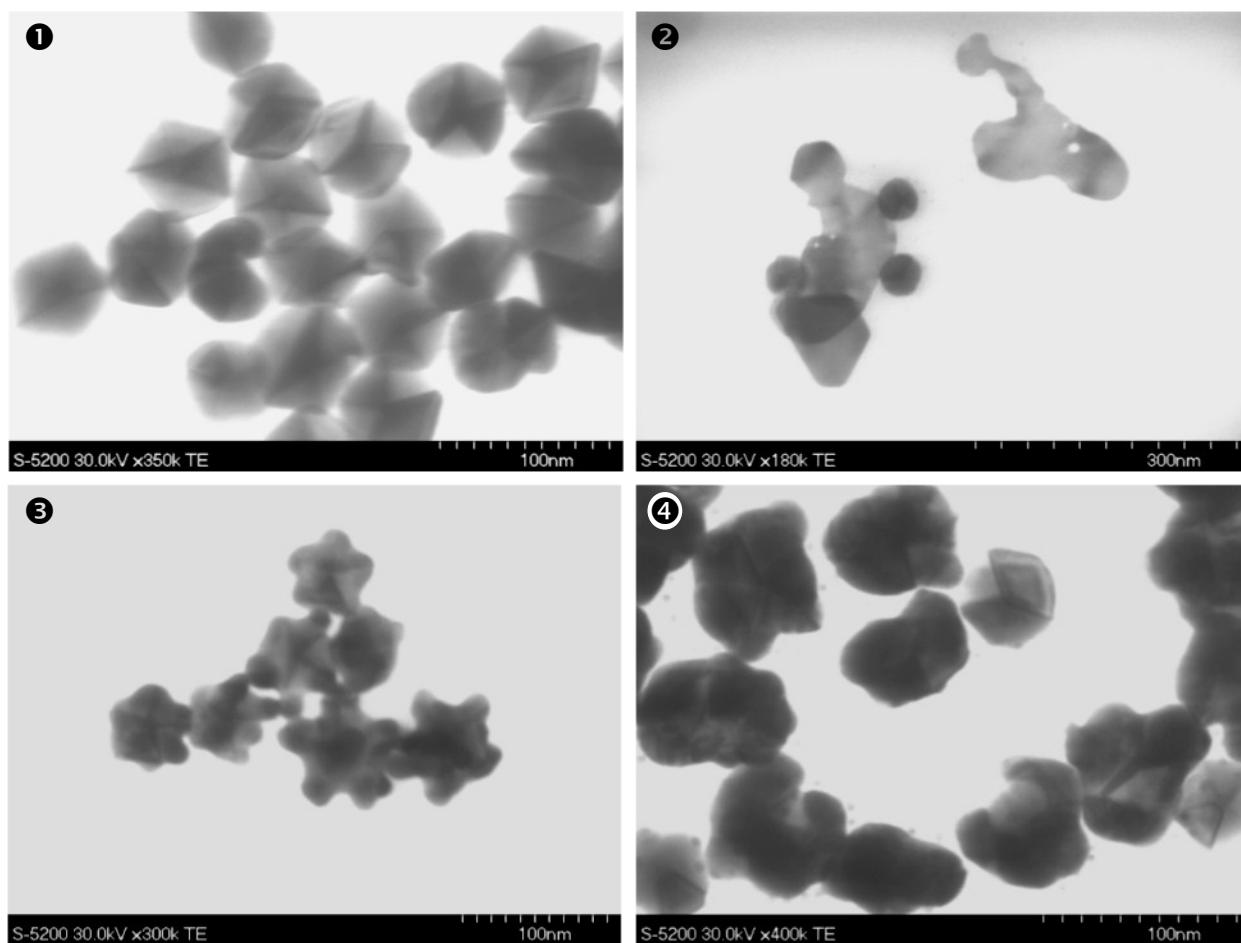
## Electronic Supplementary Information

### Synthesis and Sensing Properties of $D_{5h}$ Pentagonal Silver Star Nanoparticles

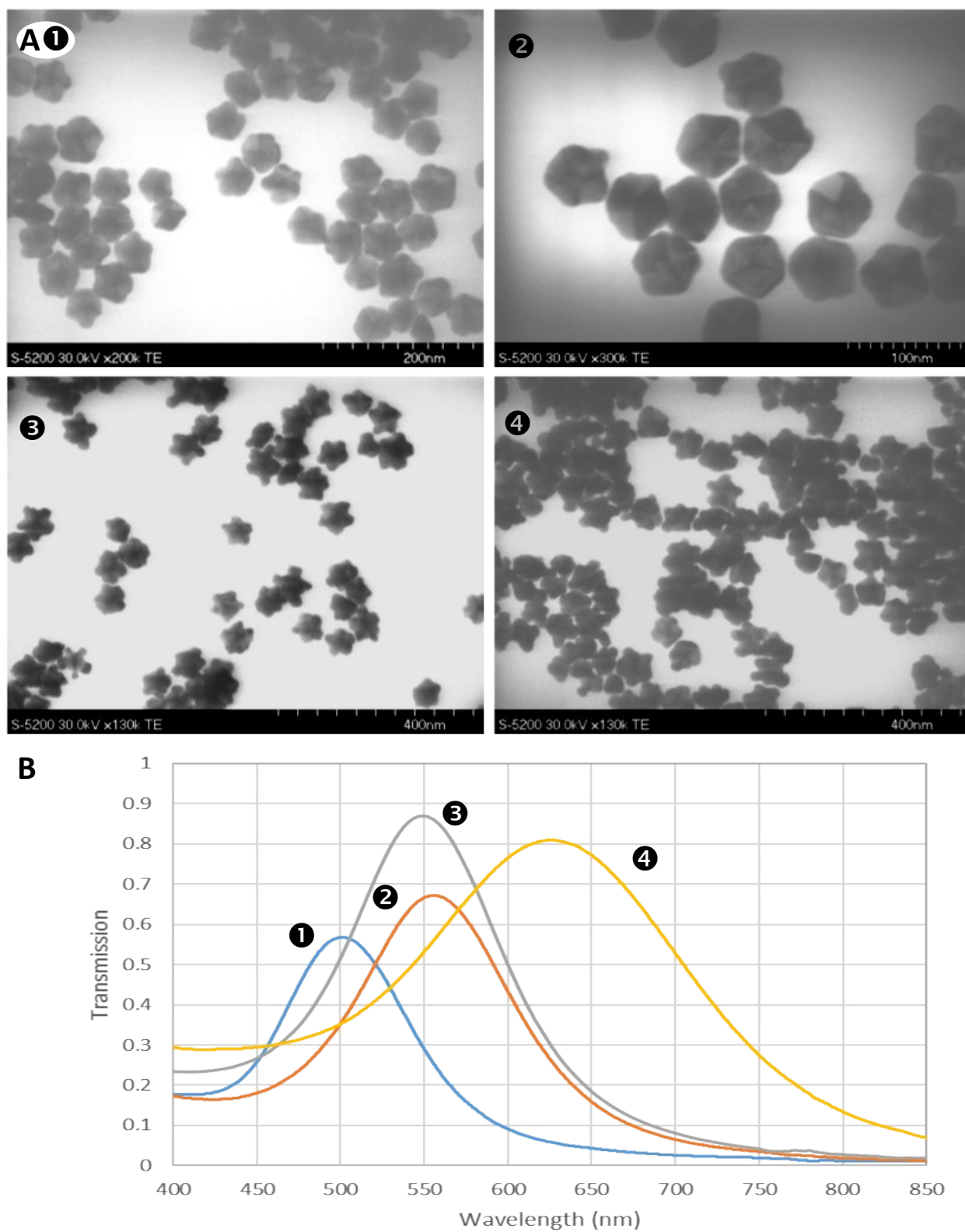
*Nicole Cathcart, Neil Coombs, Ilya Gourevich and Vladimir Kitaev*



**Figure S1.** Scanning electron microscopy (SEM) images of **1**) silver decahedral nanoparticles (AgDeNPs) and **2**) silver decahedral star nanoparticles (AgStDeNPs) prepared from AgDeNP seeds.

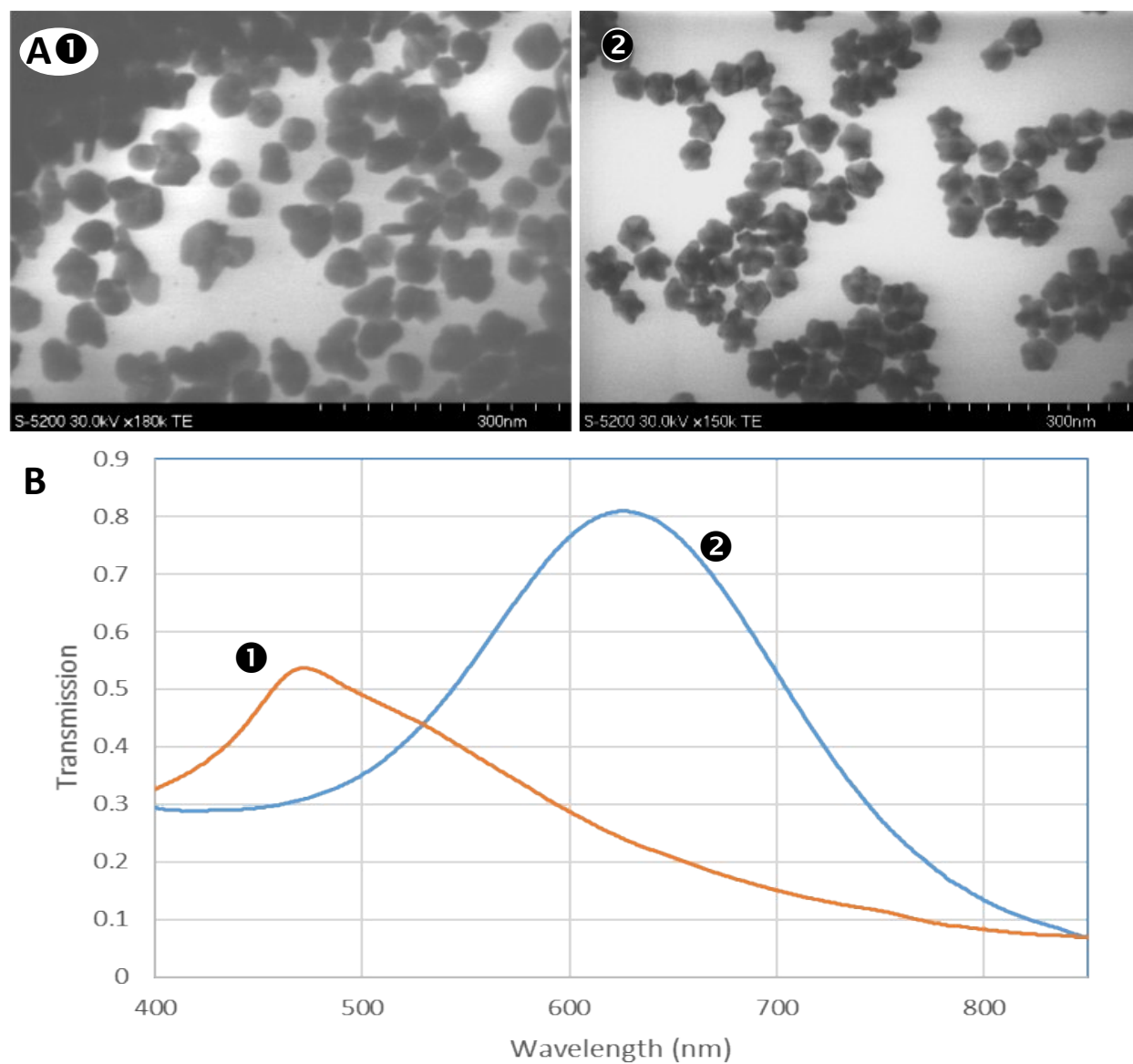


**Figure S2.** Transmission electron microscopy (TEM) images of AgStDeNP samples prepared at different pH ( $\pm 0.2$ ), **1**) 4.7, **2**) 5.3, **3**) 6.8, and **4**) 10.5; pH of the optimized procedure is 5.9. pH was varied by addition of either  $\text{HNO}_3$  or  $\text{KOH}$  to the synthetic preparation described in Experimental.

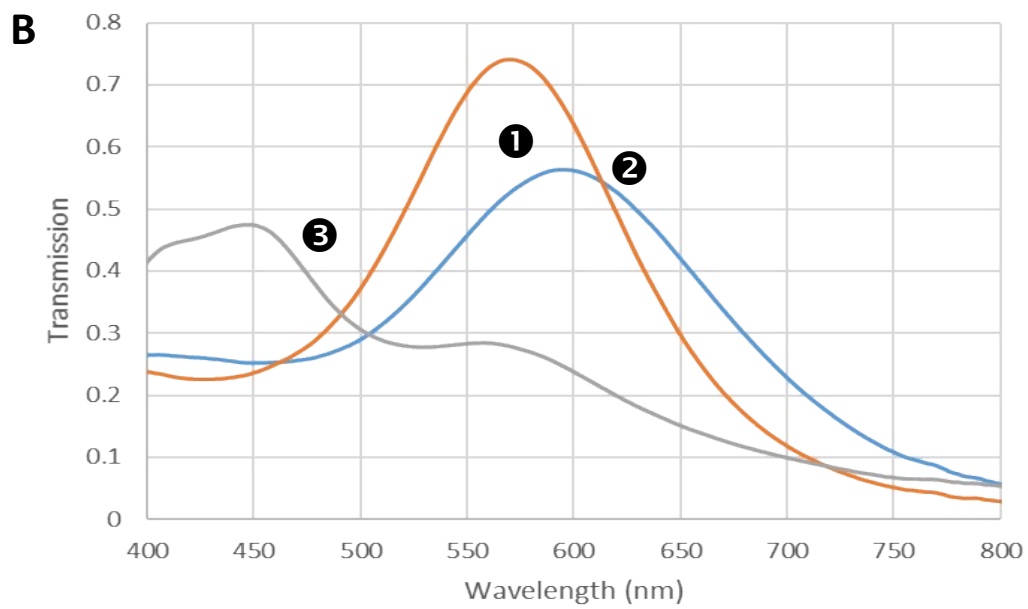
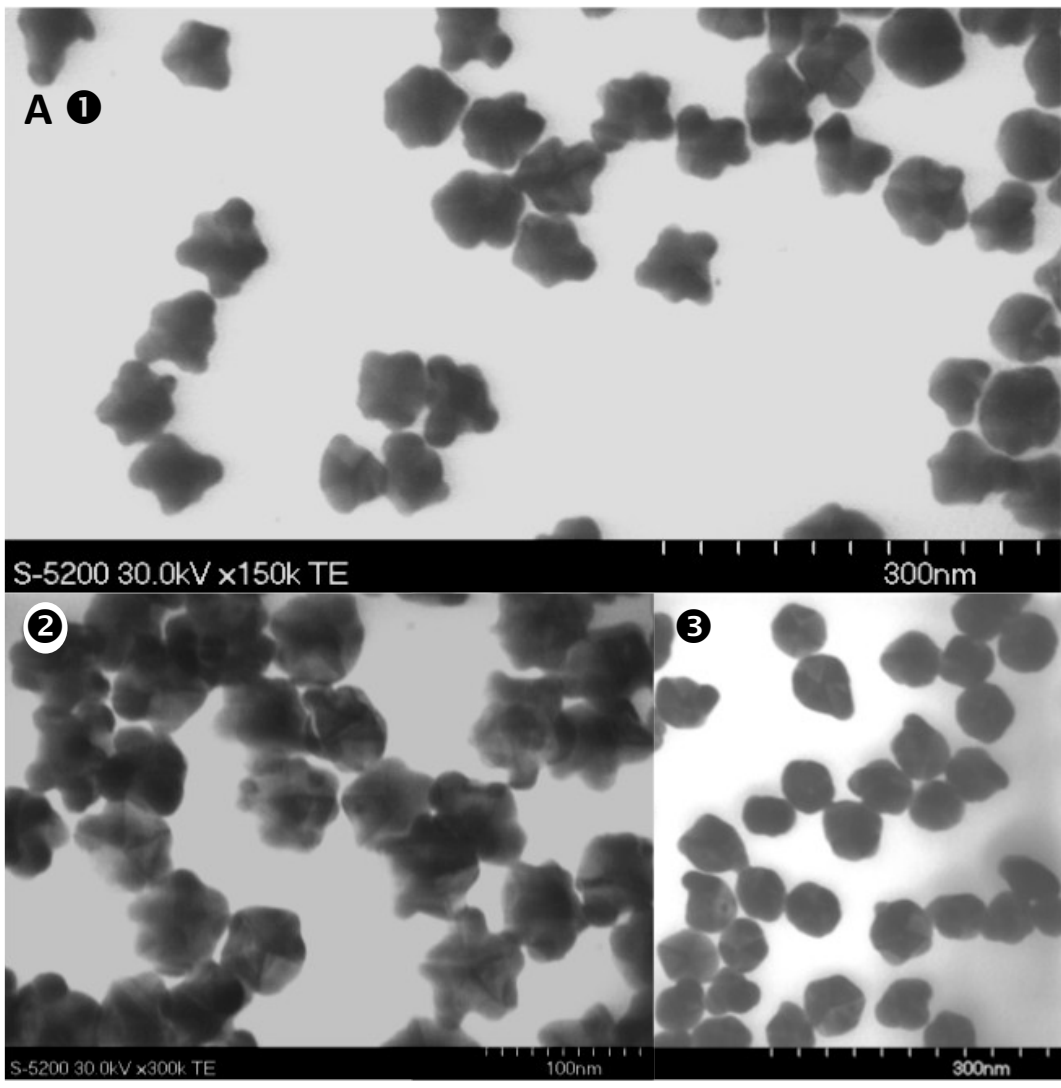


**Figure S3. A)** TEM images and **B)** UV-vis spectra of AgStDeNPs prepared with different amounts of added silver (presented as concentration of added silver in mM and ratio of new silver to silver in AgDeNP

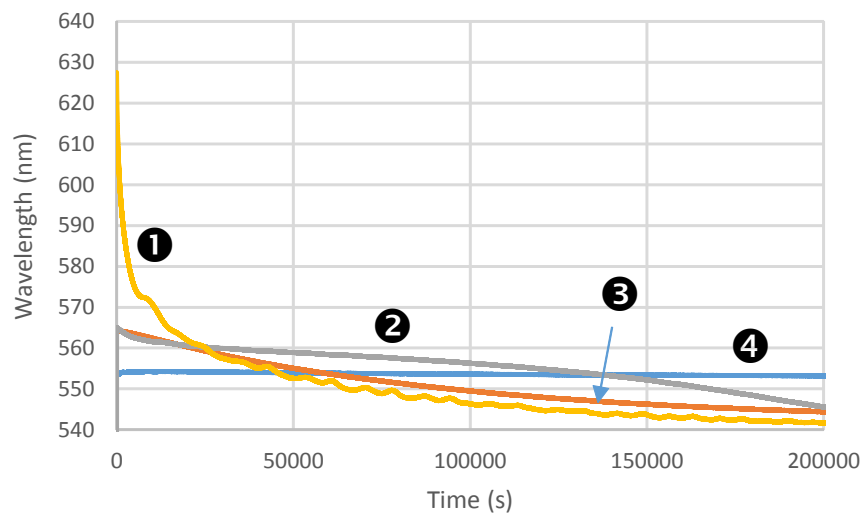
seeds, given in brackets), **1**) 0.034 mM (1:1), **2**) 0.051 mM (1.5:1), **3**) 0.067 mM (2:1), and **4**) 0.10 mM (3:1). Concentrations of reagents not varied were as follows: KOH – 0.61 mM, PANA – 0.37 mM, silver in AgDeNP seeds – 0.038 mM, and ascorbate – 0.76 mM.



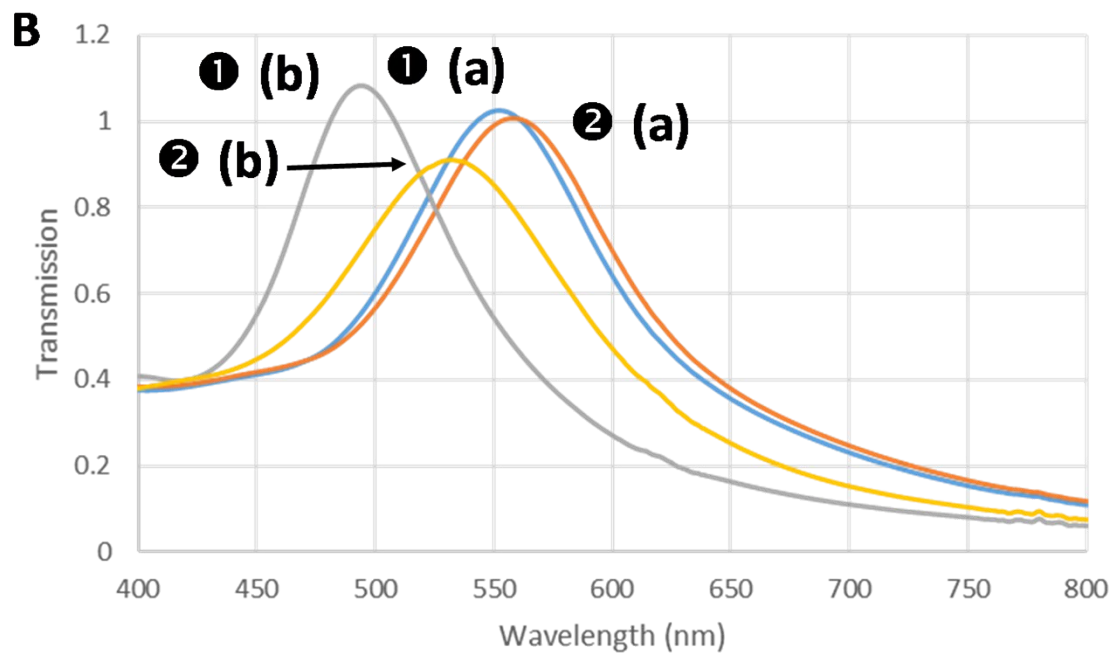
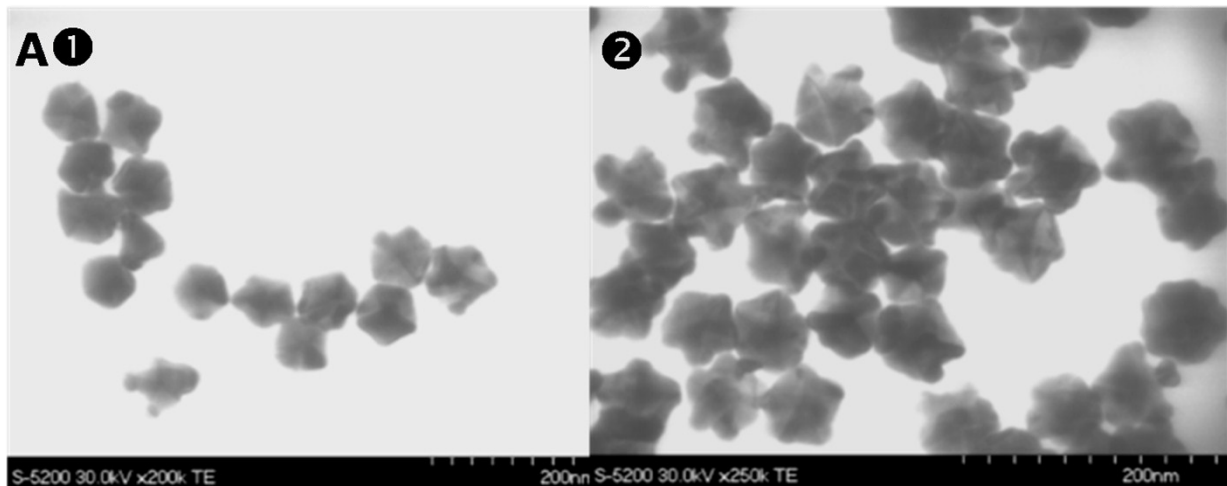
**Figure S4. A)** TEM images and **B)** UV-vis spectra of AgStDeNP samples prepared with **1**) slow stirring (200 rpm) and **2**) fast stirring (500 rpm) using a 3-mm stir bar.



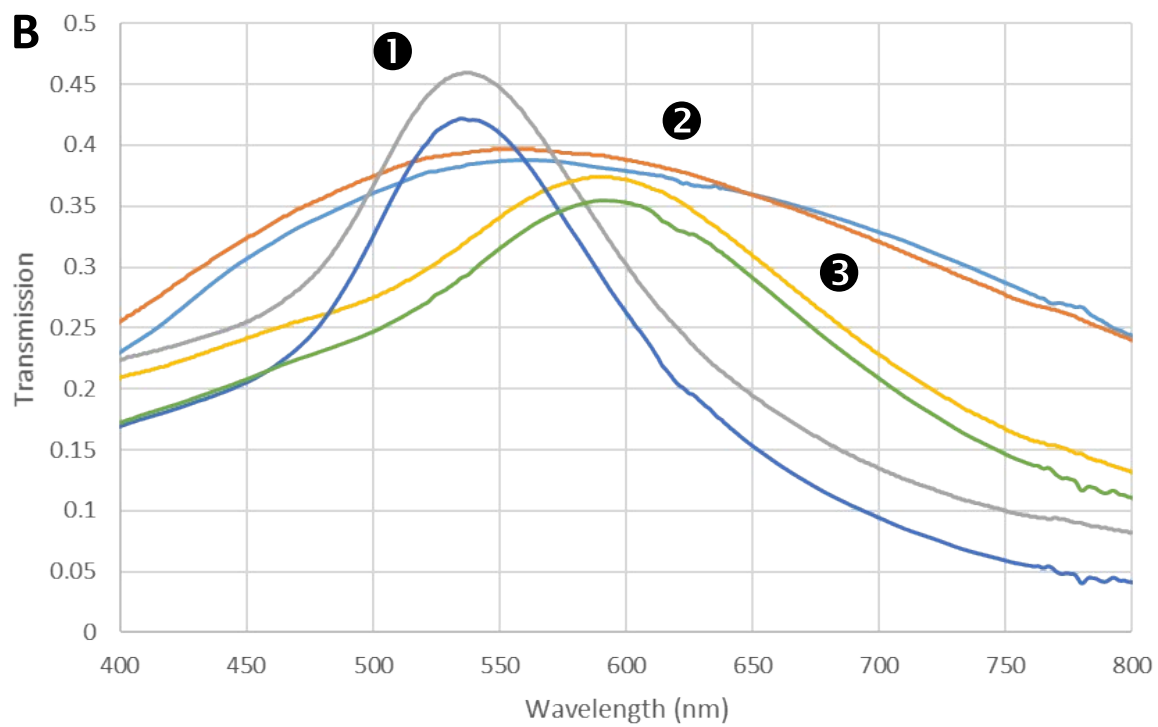
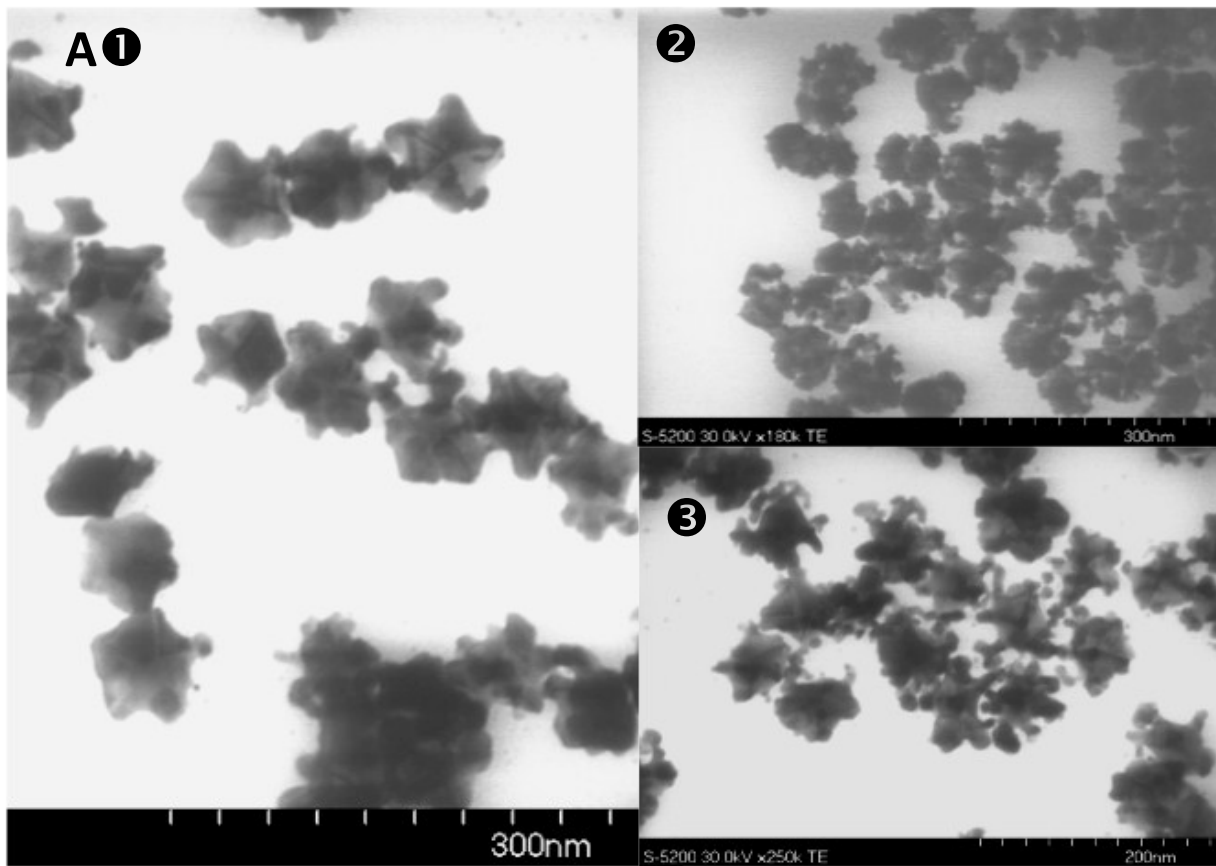
**Figure S5. A)** TEM images and **B)** UV-vis spectra of AgStDeNP samples prepared with ascorbate added over different periods of time: **1)** 1 second; **2)** two portions, 1 second each; 1 minute in between; and **3)** 1 minute.



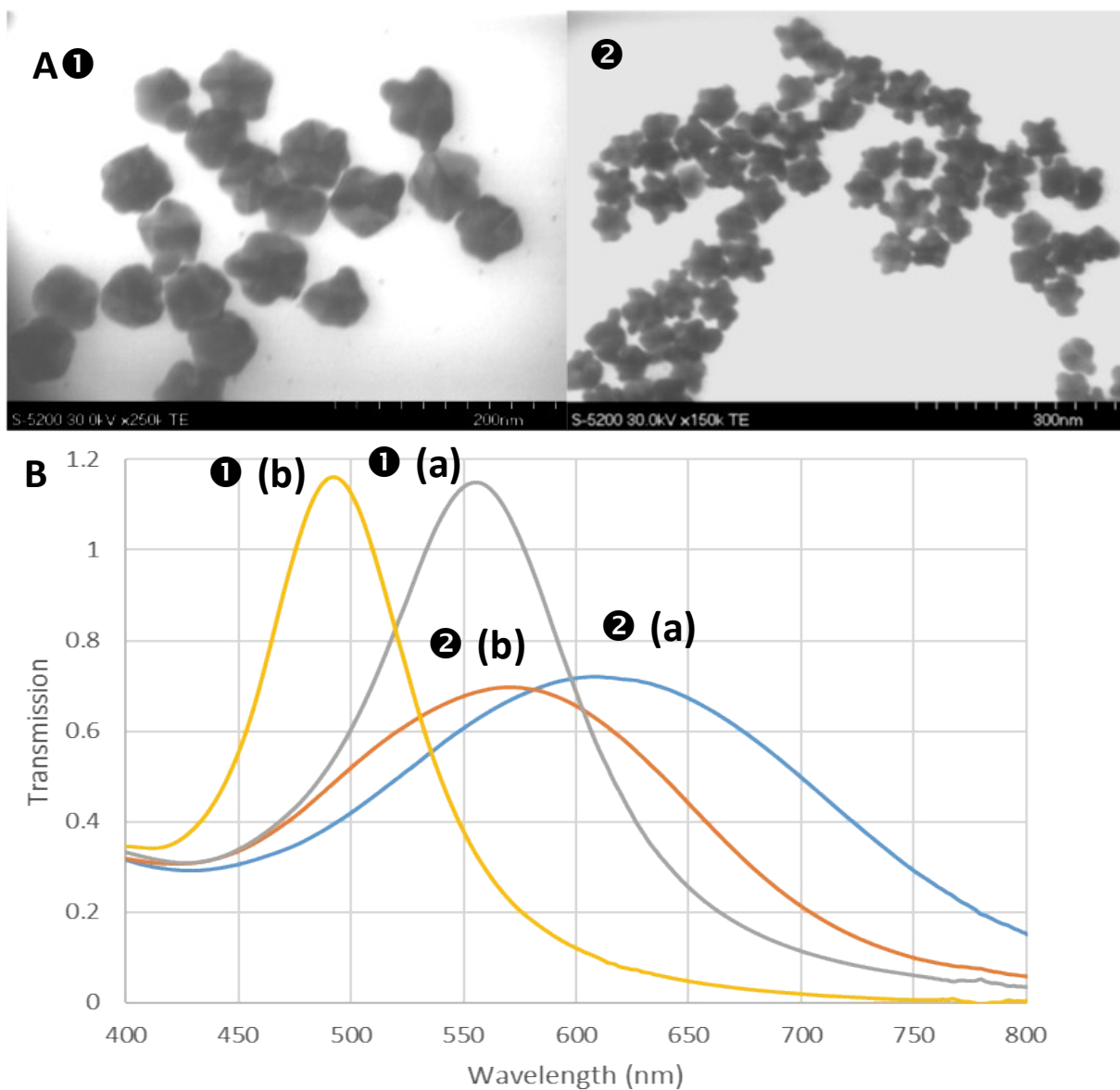
**Figure S6.** SPR response curve showing LSPR shift of AgStDeNPs over time: **1)** representative non-modified AgStDeNPs (280%  $R_{Ag/seed}$ ), **2)** AgStDeNPs (200 %  $R_{Ag/seed}$ ) with 0.27 mM ampicillin, **3)** AgStDeNPs (200 %  $R_{Ag/seed}$ ) with 0.18 mM cysteine, **4)** AgStDeNPs (200 %  $R_{Ag/seed}$ ) with gold coating (3% molar relative to silver).



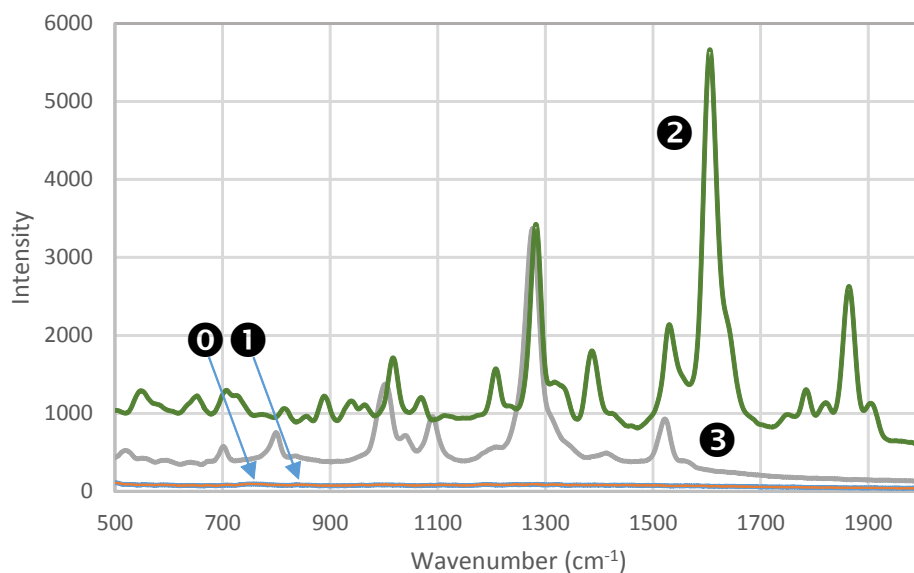
**Figure S7. A)** TEM images and **B)** UV-vis spectra of the same AgStDeNP sample, divided into two portions and aged 4 days. **1)** control sample, **2)** portion treated with  $10^{-4}$  M ampicillin. UV-vis spectra labeled (a) are measured for original, as prepared AgStDeNPs, (b) after 4 days.



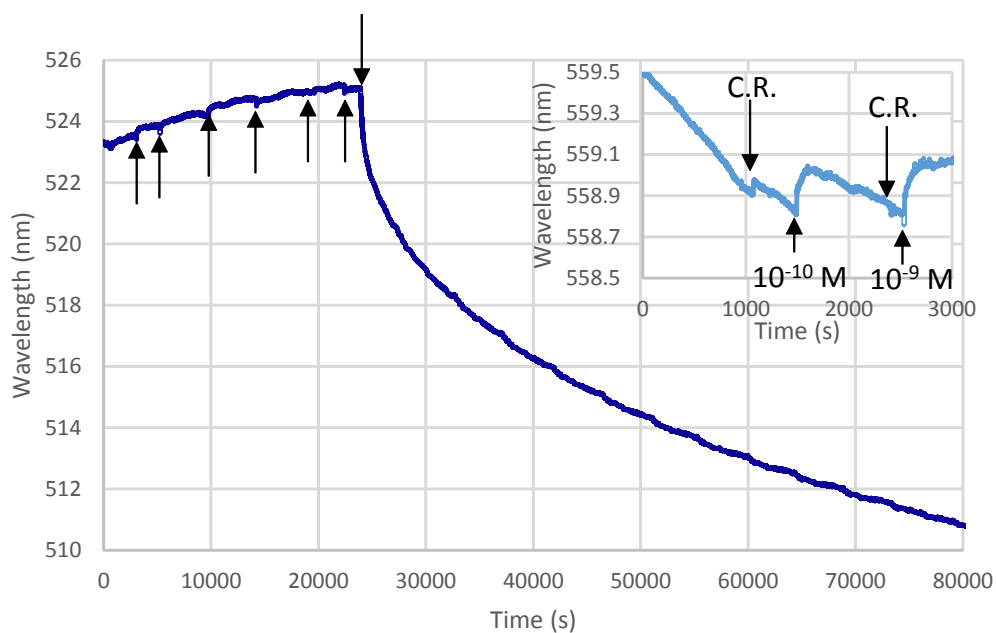
**Figure S8. A)** TEM images and **B)** UV-vis spectra of gold-coated AgStDeNP samples prepared with **1)** 4 %, **2)** 7 %, and **3)** 8 % of added gold, relative to total silver (molar ratio). Lower intensity spectra of each pair are measurements performed on original, as prepared, samples; higher intensity spectra are measured after one week for **1** & **3**, and after 5 months for **2**.



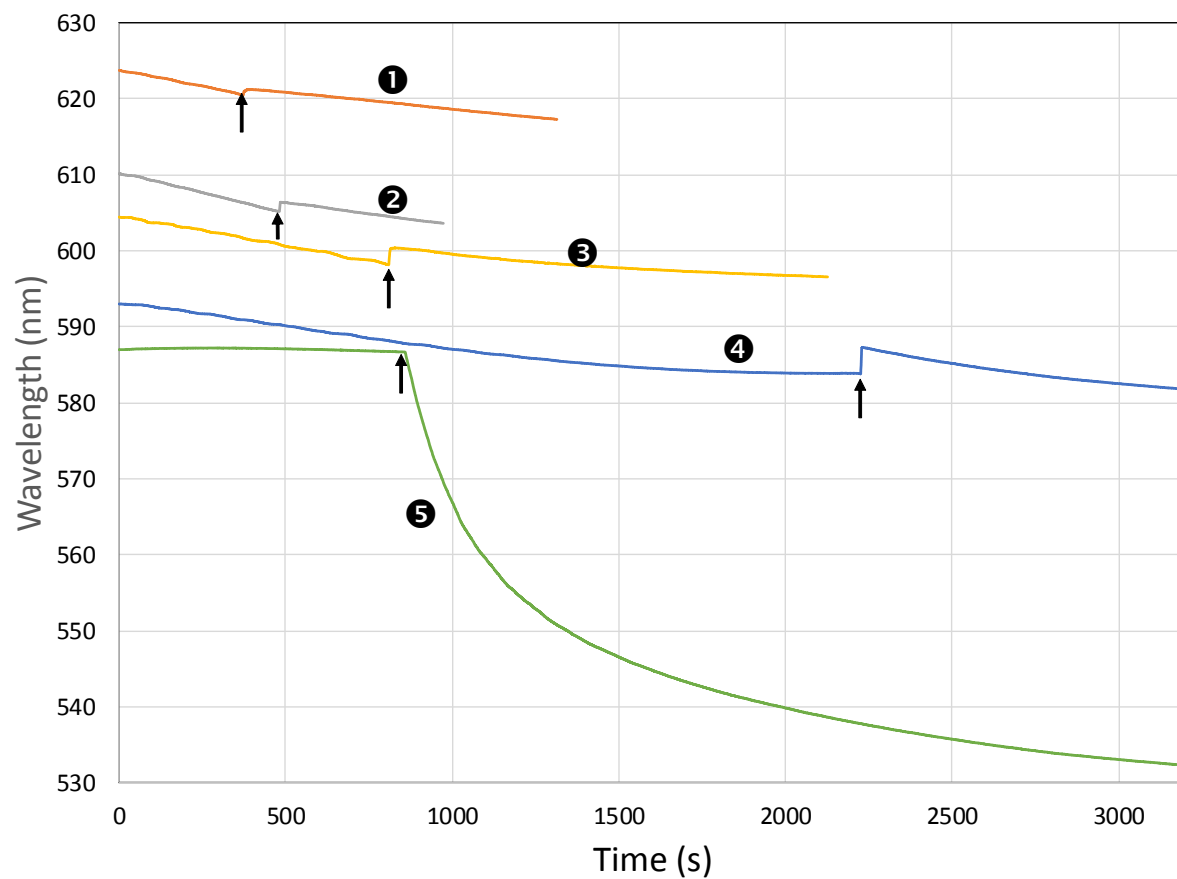
**Figure S9. A)** TEM images of aged AgStDeNP samples and **B)** UV-vis spectra of original and aged AgStDeNP samples prepared **1)** in absence of additional KOH, pH = 5.6 and **2)** with additional KOH (3 mM total), pH = 6.8. UV-vis spectra are labeled (a) for original AgStDeNP samples and (b) for these samples aged for 1 week.



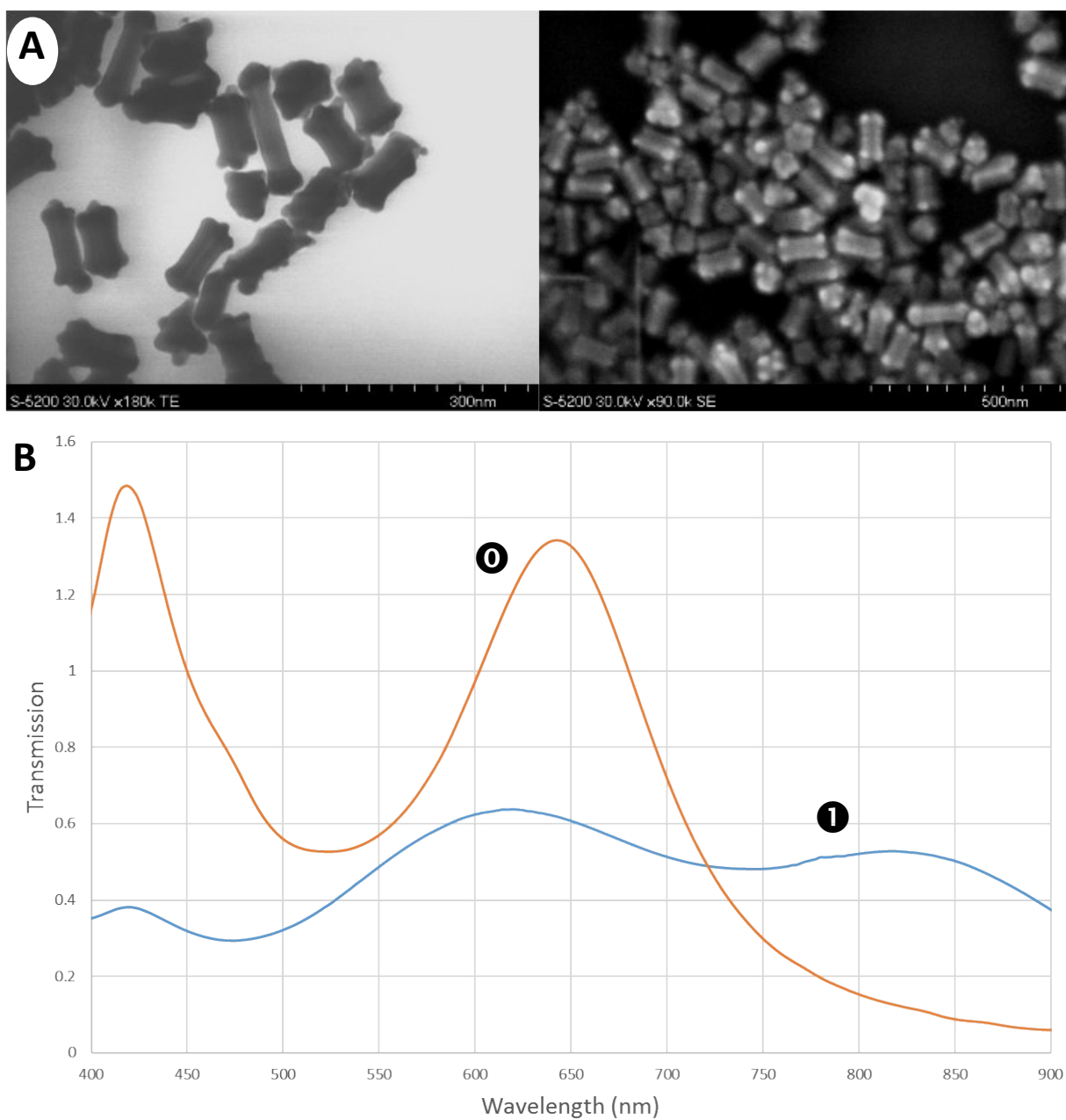
**Figure S10.** Raman spectra showing the effect of surface enhancement with AgStDeNPs. **0)** blank quartz, **1)** AgStDeNP film, **2)** AgStDeNPs with  $10^{-16}$  moles of 5',5'-dithiobis(2-nitrobenzoic acid) spread over 0.15  $\text{cm}^2$ , **3)**  $1.87 \times 10^{-5}$  moles of 5',5'-dithiobis(2-nitrobenzoic acid) spread over 1.8  $\text{cm}^2$



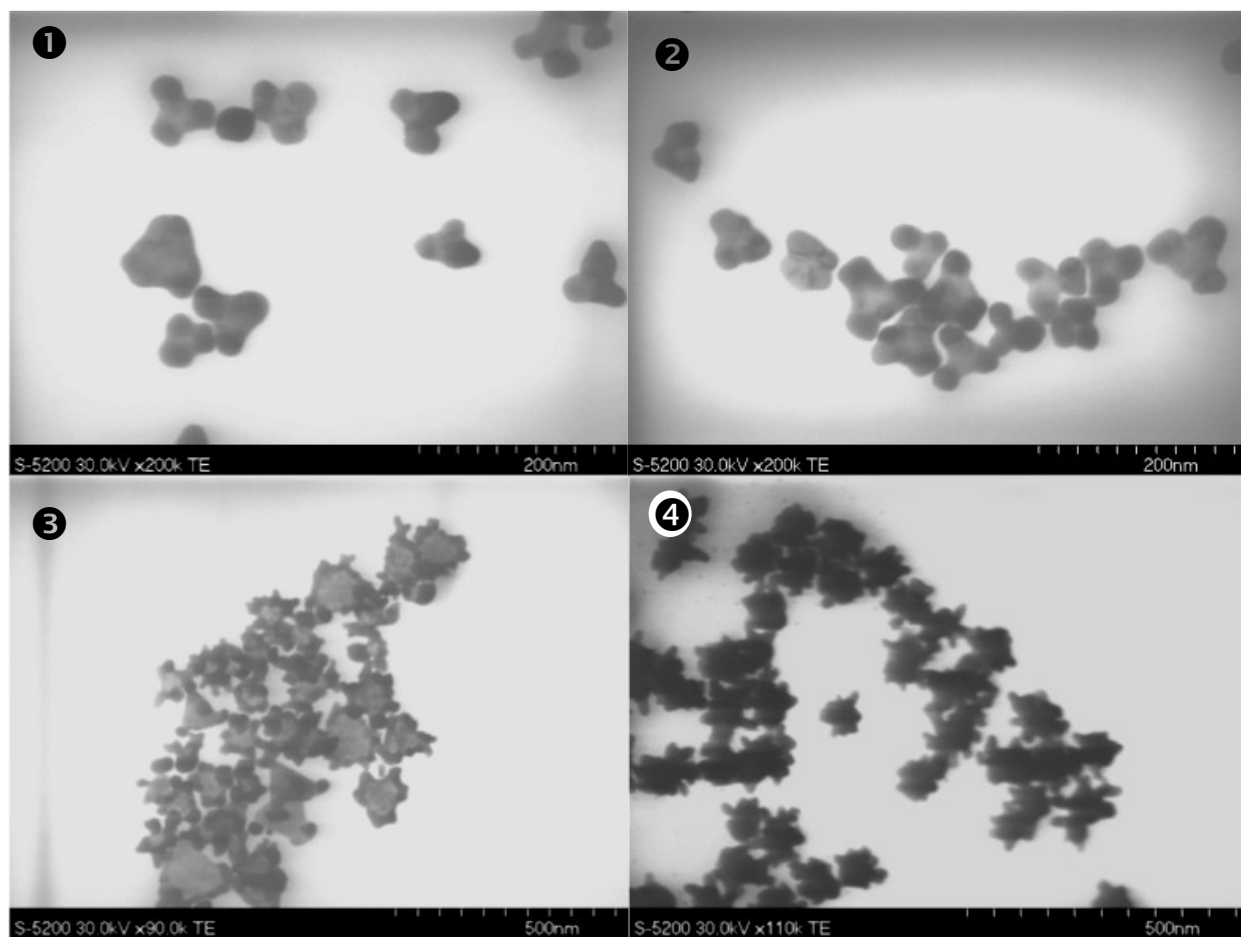
**Figure S11.** SPR response curve showing LSPR shifts of AgStDeNPs upon sequential exposure to KBr. Arrows represent additions of increasing concentrations of KBr in 10-times increments from  $10^{-10}$  M to  $10^{-4}$  M. Inset is SPR curve showing the effect of low concentrations upon addition of  $10^{-10}$  and  $10^{-9}$  M KBr. C.R. is where the cell cap was removed to represent the cell disturbance.



**Figure S12.** SPR response curve showing LSPR shifts of AgStDeNPs upon exposure to different concentrations of KBr performed for independent samples. Arrows represent additions of KBr of varying concentrations: **1)**  $10^{-9}$  M, **2)**  $10^{-8}$  M, **3)**  $10^{-7}$  M, **4)**  $10^{-6}$  M, and **5)**  $10^{-5}$  M.



**Figure S13.** Stellation pentagonal rods prepared with the developed procedure using silver pentagonal rods as seeds instead of AgDeNPs. **A)** TEM (left) and scanning electron microscopy (SEM) (right) images and **B)** UV-vis spectra of **0)** pentagonal rod seeds and **1)** stellated pentagonal rods.



**Figure S14.** TEM images of stellated prisms (1-3) and icosahedra (4) prepared with the developed procedure using silver prisms or icosahedra, respectively, as seeds instead of AgDeNPs.