Electronic Supplementary Information

Correlation of photobleaching, oxidation and metal induced fluorescence quenching of DNA-templated silver nanoclusters

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Stability of AgNCs when stored in dark. In the paper we have described the fluorescence of DNA-templated AgNCs upon strong light exposure. The samples show fluorescence quenching even when stored in dark. Figure S1 shows the red peak of AgNCs templated by DNA1 and after reaching the maximal fluorescence, it shows ~1% decay of fluorescence every 30 min, which might be due to oxidation by oxygen. For comparison, when exposed to strong light, the fluorescence decays by more than 90% in 30 min.

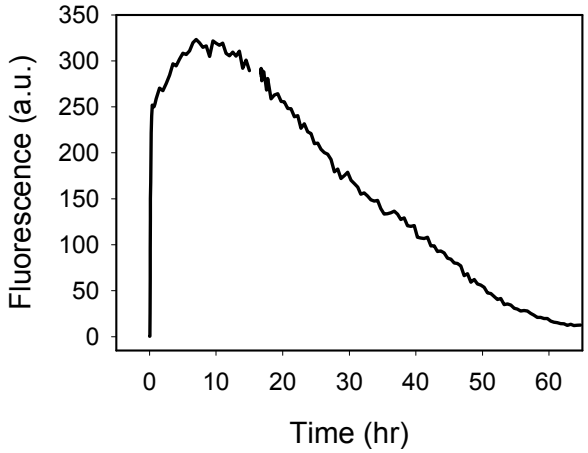

Figure S1. Time-dependent fluorescence intensity change of AgNCs templated by DNA1. $NaBH_4$ was added at time zero.

Effect of light exposure on DNA. To test whether the AgNC fluorescence quenching upon light exposure is due to DNA damage, we first exposed DNA to fluorescent tube light for 30 min. Such an exposure is sufficient to quench the fluorescence of AgNCs. As shown in Figure S2, the same fluorescence intensity was observed, regardless whether the DNA was initially exposed to light or not. Therefore, the fluorescence quenching of AgNCs cannot be attributed to DNA damage by light.

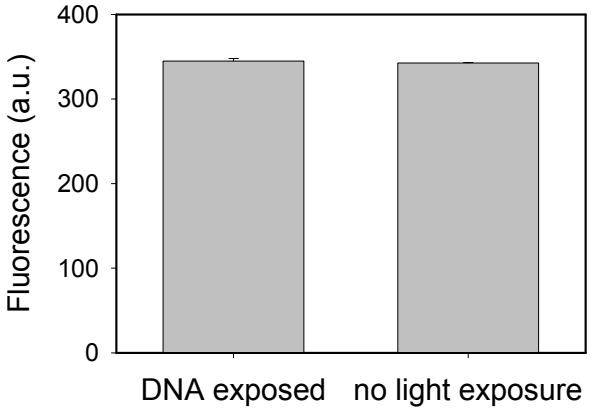

Figure S2. Fluorescence intensity of AgNCs templated by DNA4 as a function of DNA exposure time to light. One DNA was exposed for 30 min and the other for 0 min. Then both DNAs were mixed with $AgNO_3$ and $NaBH_4$ for 2 hr to produce AgNCs. The fluorescence of the samples at 620 nm was measured.

Reversibility tested by UV-vis spectrometry. We already showed that the fluorescence intensity (quenched by light exposure) recovered upon addition of $NaBH_4$, here we test the effect of $NaBH_4$ on the UV-vis spectrum. The black spectrum in Figure S3 is the AgNCs templated by DNA4 (freshly prepared). After 35 min exposure to light, the 560 nm absorption peak decreased significantly and the 420 nm peak increased (red spectrum). Adding $NaBH_4$ (1:1 $NaBH_4$ to Ag) resulted in the recovery of the 560 nm peak (green spectrum). This experiment further confirms that the 560 nm peak is responsible for the red fluorescence.

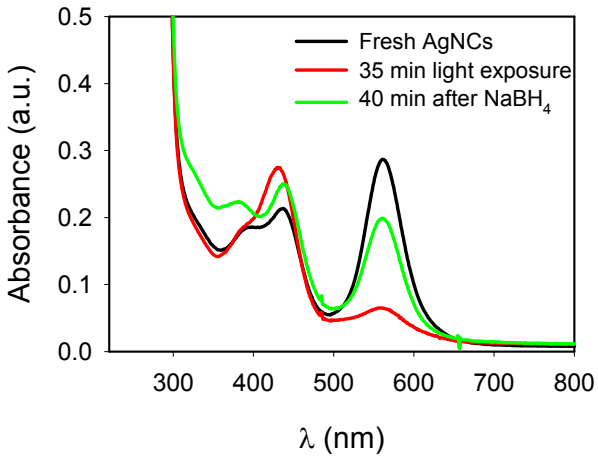

Figure S3. UV-vis spectra of AgNCs templated by DNA4 upon light exposure and then add $NaBH_4$.

Effect of EDTA. We further tested whether EDTA could recovery Hg^{2+} induced fluorescence quenching. Figure S4A shows the fluorescence spectrum of AgNCs templated by DNA4 and it was completely quenched by 300 nM Hg^{2+}. Addition of 2 mM EDTA failed to rescue the fluorescence. In Figure 4B, 2 mM EDTA was added first. Addition of 300 nM Hg^{2+} failed to quench fluorescence. This experiment indicates that EDTA has a high affinity for Hg^{2+}, and it can mask its effect (Figure S4B). At the same time, after reacting Hg^{2+} with AgNCs, subsequent addition of EDTA cannot pull mercury out and it supports our proposed oxidation mechanism.

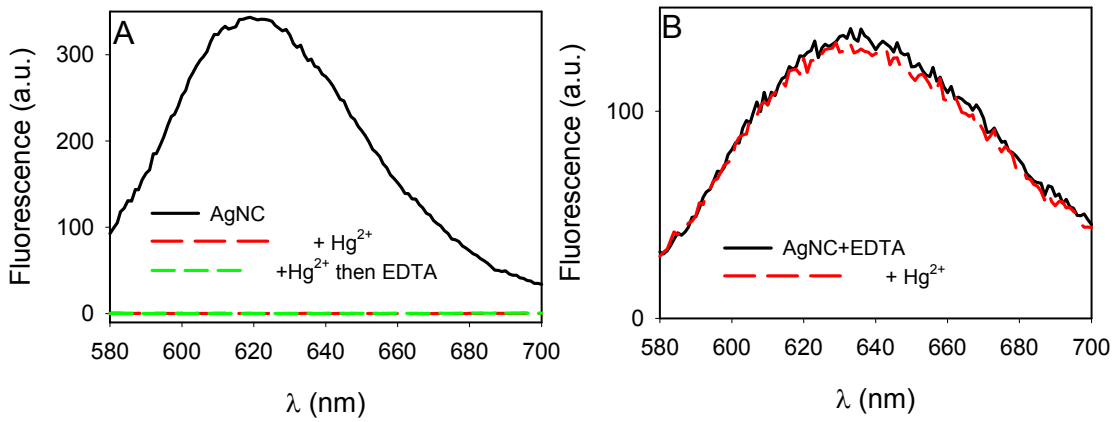

Figure S4. Fluorescence spectra of AgNCs templated by DNA4 and its reaction with 300 nM Hg^{2+} (A) 2 mM EDTA was added after Hg^{2+}. (B) 2 mM EDTA was added prior to Hg^{2+} addition.

Effect of sample drying. For many surface science tools, the sample needs to be dried. Dried samples have been commonly obtained for gold nanoclusters since they are quite stable against oxidation. On the other hand, few examples can be found in the literature regarding to dried silver nanoclusters. We herein prepared samples of AgNCs templated by DNA1 and monitored its red peak as a function of sample storage conditions. After overnight storage in dark, the fluorescence dropped by ~40%. When the sample was left in dark with cap open, the sample dried after overnight incubation. Upon re-hydration, the fluorescence was dropped by more than 80%. Even drying in vacuum still resulted in ~70% fluorescence loss (drying using Eppendorf Vacufuge plus Vacuum Concentrator). Therefore, the dried sample does not reflect the oxidation state of the sample in the solution phase.

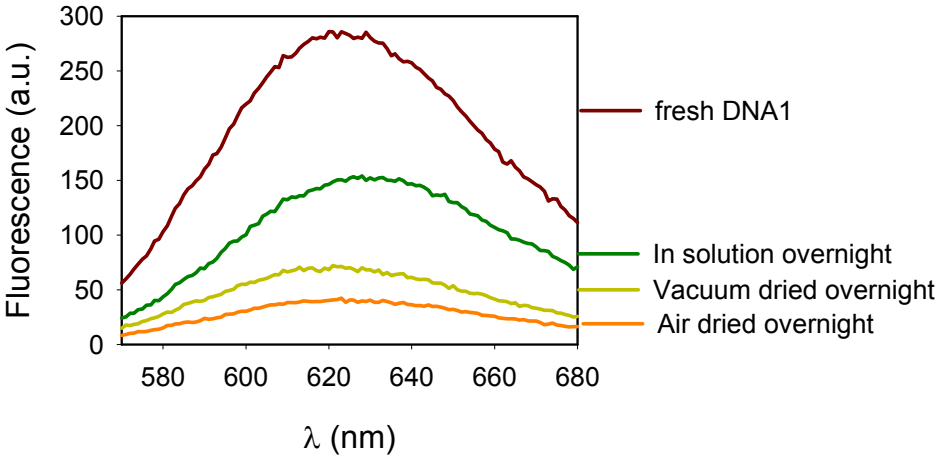

Figure S5. Effect of sample drying on the fluorescence intensity of the red peak of AgNCs templated by DNA1. Fluorescence of dried sample (dried from 5 μL) was measured after rehydration in water.