

## Supporting information

### Ligand-assisted etching of silver nanoparticles to luminescent silver nanodots

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10 Methods

Chemicals. Silver nitrate (99.9999%), hydrogen peroxide, sodium borohydride, diethylenetriamine and poly(acrylic acid) were purchased from Sigma-Aldrich and used as received. DNA was purchased from IDT DNA.

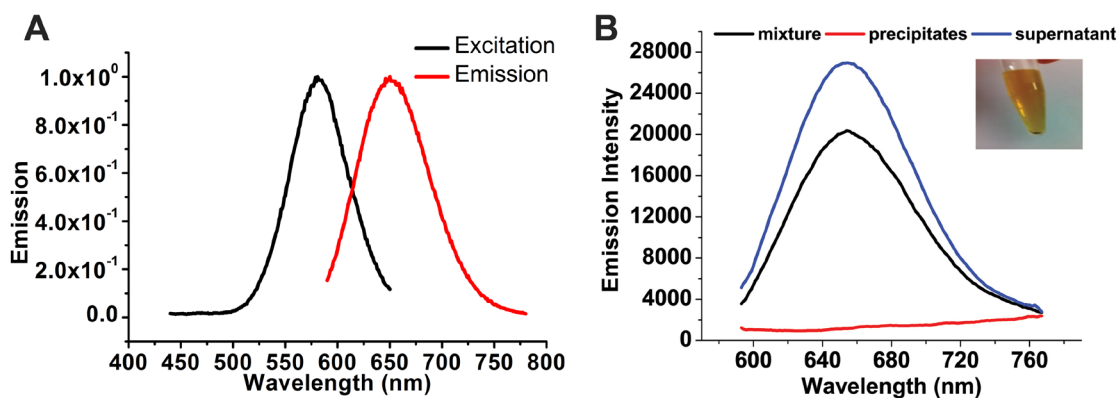
Preparation of silver nanoparticles. ssDNA and silver ions were mixed at a DNA base/Ag<sup>+</sup> ratio of 1:2.8, and reduced with sodium borohydride with silver:NaBH<sub>4</sub>=1:0.63.

15 HRTEM images were obtained on JEM 3010 high resolution transmission electron microscope. The size distribution of nanoparticles were obtained by counting the size of nanoparticles in multiple TEM images. UV-Vis absorption spectra and emission spectra were obtained on S-4100 (SCINCO) and QM-40 (Photon Technology International, Inc.), respectively.

Polyamines were stored in the absence of silver ions/silver nanoparticles, no emissions were observed.

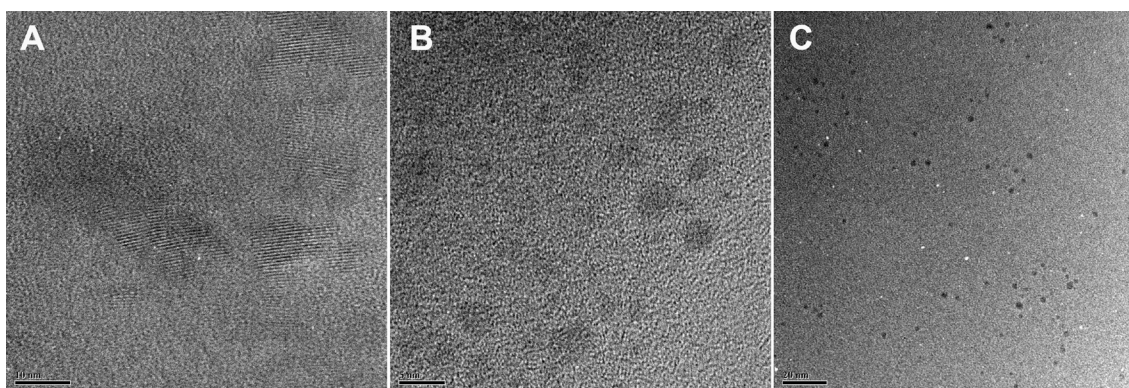
20 The 5'-CGCGCCCCCCCCCCCCGCG-3' (CGCGC12)-encapsulated silver nanodot shows 615 nm emission, whereas the 5'-ATATCCCCCCCCCCCCATAT-3' (ATATC12)-encapsulated shows 560 nm emission and the 5'-CCCTAACTCCCC-3' encapsulated shows 700 nm emission.<sup>1-2</sup>

Separation by centrifugation was done on Eppendorf 5415R at 16000 rpm.



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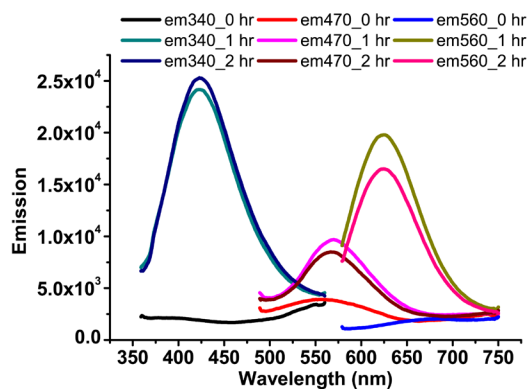
**Fig. 1S** Spectra of C12-etched silver nanoparticles. A. Typical excitation and emission spectra of silver nanodots prepared from the etching of silver nanoparticles. B. Emission spectra before and after centrifugation. The inset is a picture showing the spun mixture of C12-etched silver nanoparticles.



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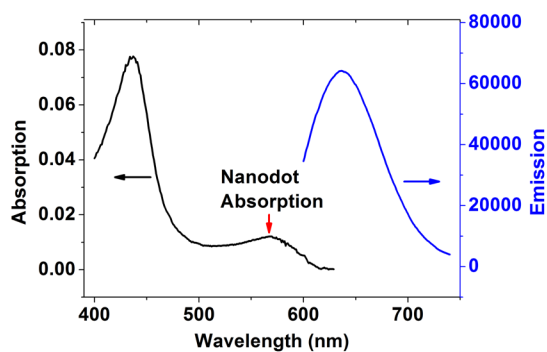
**Fig. 2S** TEM image of ssDNA stabilized silver nanoparticles. A. HRTEM image of C12-stabilized silver nanoparticle. B. HRTEM image of C20-stabilized silver nanoparticles that have been oxidized by hydrogen peroxide. C. TEM image of CGCGC12-stabilized silver nanoparticles that have been oxidized by oxygen and extra ssDNA molecules. Scale bar: A 10 nm; B 5 nm; C 20 nm.

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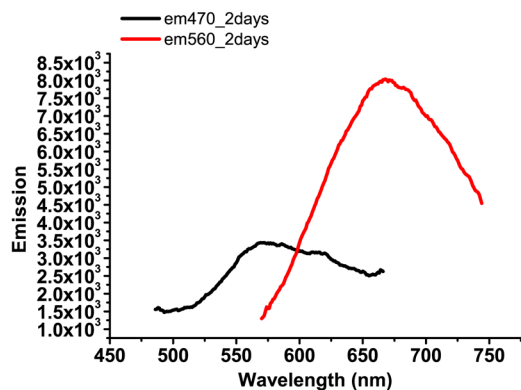
**Fig. 3S** Emission spectra of silver nanodots during hydrogen peroxide-enhanced etching of C12-stabilized silver nanoparticles at pH 7. Emxxx\_y hr stands for the emission spectrum excited at xxx y hrs after the addition of hydrogen peroxide ( 5 mM) and dEtA ( 30 mM).

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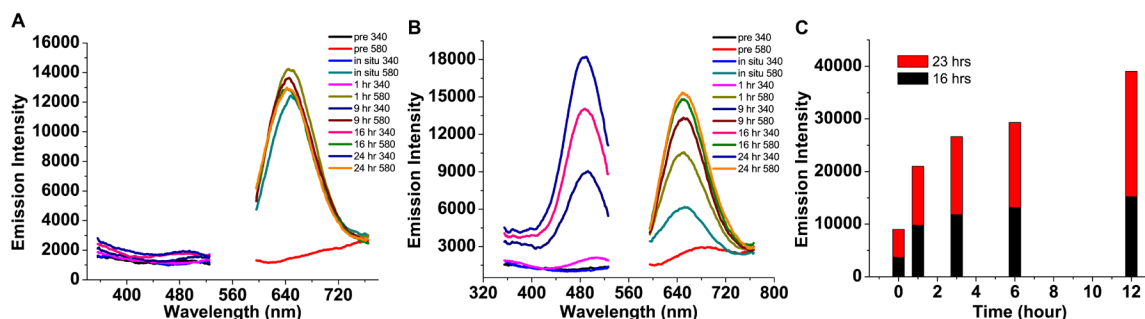
**Fig. 4S** Spectra of CGCG-encapsulated silver nanodots. It shows a similar emission intensity, but higher absorption peak compared to the silver nanodots shown in **Fig. 1A** and **1B**, indicating that the silver nanodots in **Fig. 1B** have a competitive quantum yield to the know silver nanodots. Be noted that we cannot distinguish a bump peak on the shoulder of the nanoparticle absorption peak, suggesting that the absorption from the resulting silver nanodots in **Fig. 1B** is very weak.

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**Fig. 5S** Hydrogen peroxide etching of poly(acrylic acid)-stabilized silver nanoparticles. The emission spectra of silver nanodots generated by the addition of hydrogen peroxide (10 mM) to poly(acrylic acid)-stabilized silver nanoparticles. Emxxx\_2days stands for the emission spectrum excited at xxx two days after the addition of hydrogen peroxide.

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**Fig. 6S** Impact of aging on the generation of silver nanodots. C12 was added to silver nanoparticles in a nitrogen-bubbled (A) or aerated solution (B). (C) shows silver nanoparticles after different aging time. "Pre" and "in situ" stand for the emission spectra before and right after the addition of C12, respectively. "340" and "580" are the excitation wavelengths. "16 hrs" and "23 hrs" indicate the aging time before the addition of C12 to silver nanoparticles and the emission intensities of silver nanodots at 650 nm are displayed.

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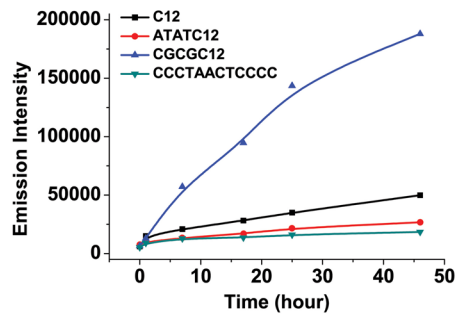


Fig. 7S Emission intensities of silver nanodots in the presence of various etching DNA sequences.

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1. Richards, C. I.; Choi, S.; Hsiang, J. C.; Antoku, Y.; Vosch, T.; Bongiorno, A.; Tzeng, Y. L.; Dickson, R. M. Oligonucleotide-stabilized Ag nanocluster fluorophores. *Journal of the American Chemical Society* **2008**, *130* (15), 5038-5039.
2. Choi, S.; Yu, J.; Patel, S. A.; Tzeng, Y.-L.; Dickson, R. M. Tailoring silver nanodots for intracellular staining. *Photochemical & Photobiological Sciences* **2011**, *10* (1), 109-115.

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