Supporting Information for: Plasmon-Enhanced Photocleaving Dynamics in Colloidal MicroRNA-Functionalized Silver Nanoparticles Monitored with Second Harmonic Generation

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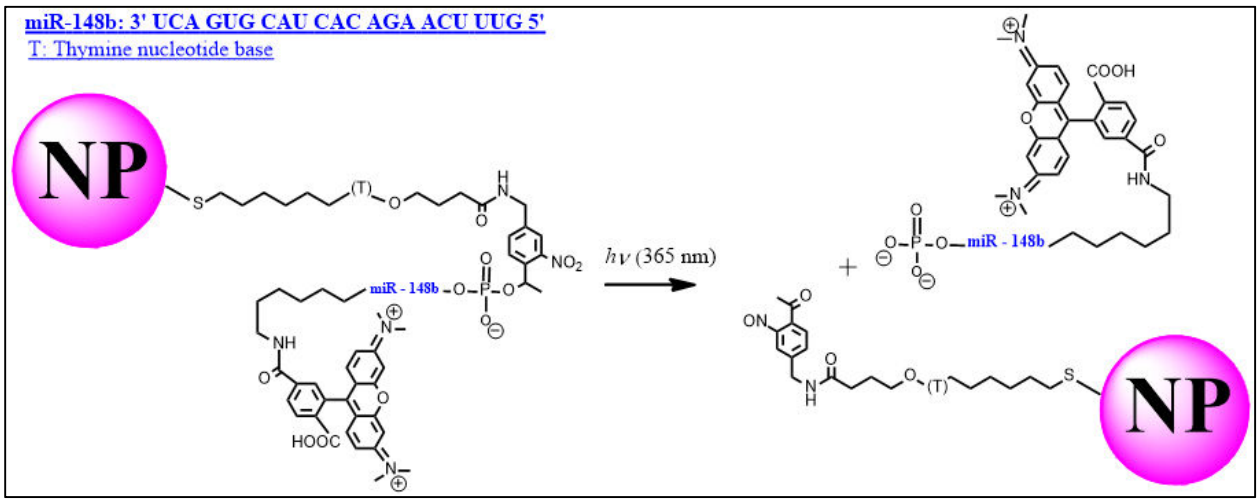
The nitrobenzyl photocleaveable linker is a commonly used linker utilized for its high cleaving efficiency under UV irradiation.[1-3] The photolytic mechanism is understood to follow the nitro group reduction to nitroso and oxidation of the benzylic carbon through the *aci*-nitro anion intermediate to release the phosphate ester.[4] Scheme 1 shows the structure of the photocleavable (PC) miRNA-148b functionalized nanoparticles before and after UV irradiation.



Scheme 1: Details of the sequences and the photocleaving process. The alkyl thiol linker attaches to the nanoparticle surface and connects through the PC-linker to the miRNA that is labeled with the 6-TAMRA fluorophore.

Additional fluorescence measurements are taken on the colloidal silver nanoparticles (SNPs) and the miRNA-functionalized SNPs labeled with the 6-TAMRA fluorophore. When excited with 531 nm, negligible emission is observed from the SNP sample. However, a strong emission peak centered at 572 nm is observed from the miRNA-functionalized SNPs due to the labeled 6-TAMRA fluorophore, as shown in Figure SI1.

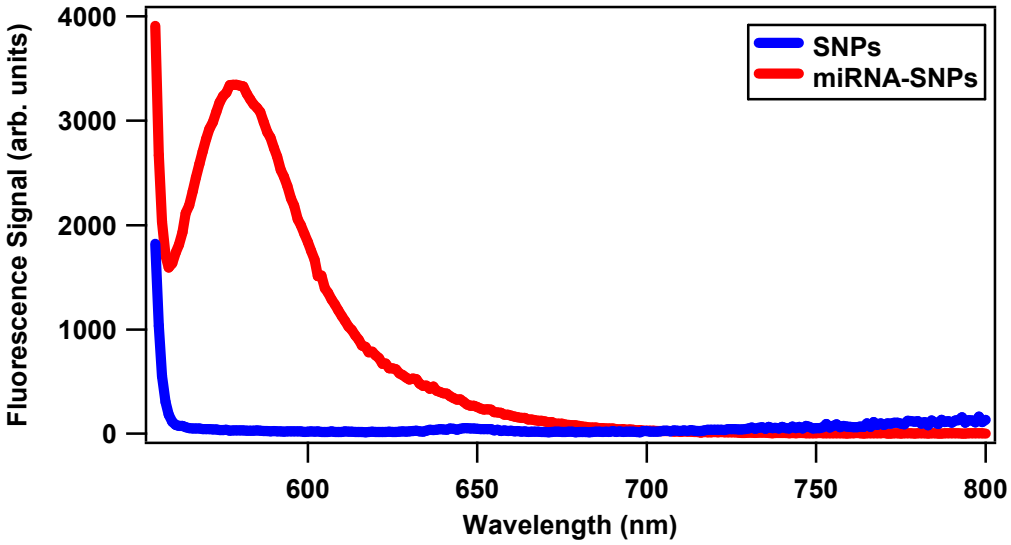


Figure SI1: Fluorescence signal of the SNPs before and after miRNA functionalization.

MiRNA-functionalized PSNPs are irradiated at different laser powers at 365 nm and the time-dependent SHG electric fields are shown in Figure SI2. The rate constants from the miRNA-functionalized PSNPs obtained at the laser powers of 15, 25, 35, 60, and 85 mW are $(0.9 \pm 0.3) \times 10^{-3}$ s^{-1}, $(1.3 \pm 0.3) \times 10^{-3}$ s^{-1}, $(1.8 \pm 0.2) \times 10^{-3}$ s^{-1}, $(3.5 \pm 0.3) \times 10^{-3}$ s^{-1} and $(4.5 \pm 0.3) \times 10^{-3}$ s^{-1}, respectively. These power-dependent photocleaving rates are much lower than the corresponding rates from the miRNA-functionalized SNP sample shown in the manuscript.

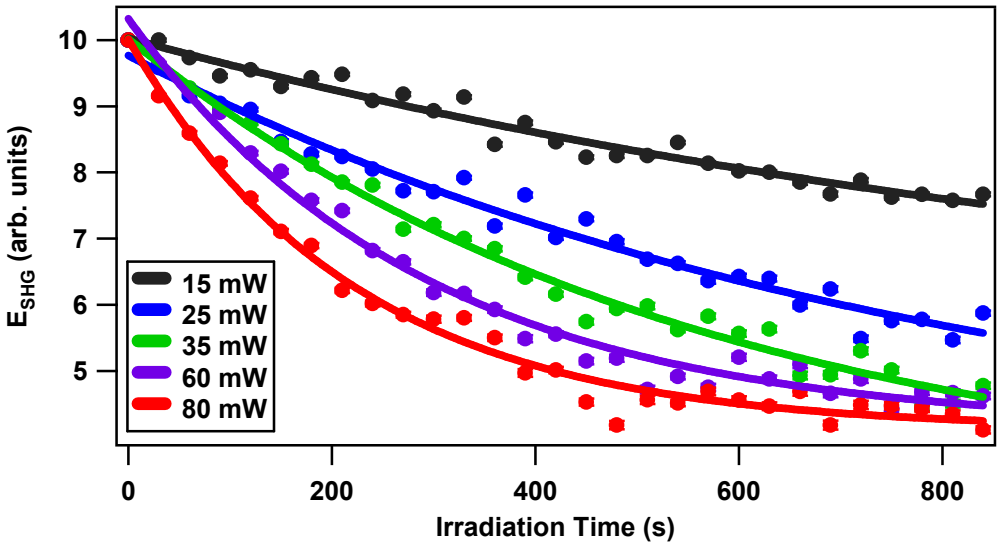


Figure SI2: Measured SHG electric fields from miRNA-functionalized PSNPs as a function of irradiation time with 365 nm at different UV laser average powers with corresponding exponential fits.

The controlled release of miRNA from the surface of the SNPs as a function of UV irradiation time is studied using a zeta potential measurements. The zeta potential of the miRNA-SNPs increases to less negative values under increasing UV irradiation times, as shown in Figure SI4 (a) and (b). Figure SI4 (a) shows electrophoretic mobilities of the miRNA-functionalized SNPs at different UV irradiation times using 365 nm irradiation at an average power of 20 mW. The electrophoretic motilities at 0 min, 0.5 min and 14 min are $(3.9 \pm 0.6) \times 10^{-8}$ m^2/Vs, $(3.5 \pm 0.5) \times 10^{-8}$ m^2/Vs and $(2.5 \pm 0.5) \times 10^{-8}$ m^2/Vs, respectively. The corresponding zeta potentials are –74.8 ± 11.4 mV, –66.7 ± 9.6 mV and –48.3 ± 10.3 mV for 0 min, 0.5 min and 14 min of UV irradiation, respectively, using Huckel's aproximation. The zeta potential of the miRNA-functionalized SNPs after 14 min of photolysis is equal to the zeta potential of the original SNPs sample, −49.8 ± 10.2

mV, to within experimental uncertainty. Figure SI4 (b) shows the zeta potential of the miRNA-functionalized SNPs as a function of UV irradiation time.

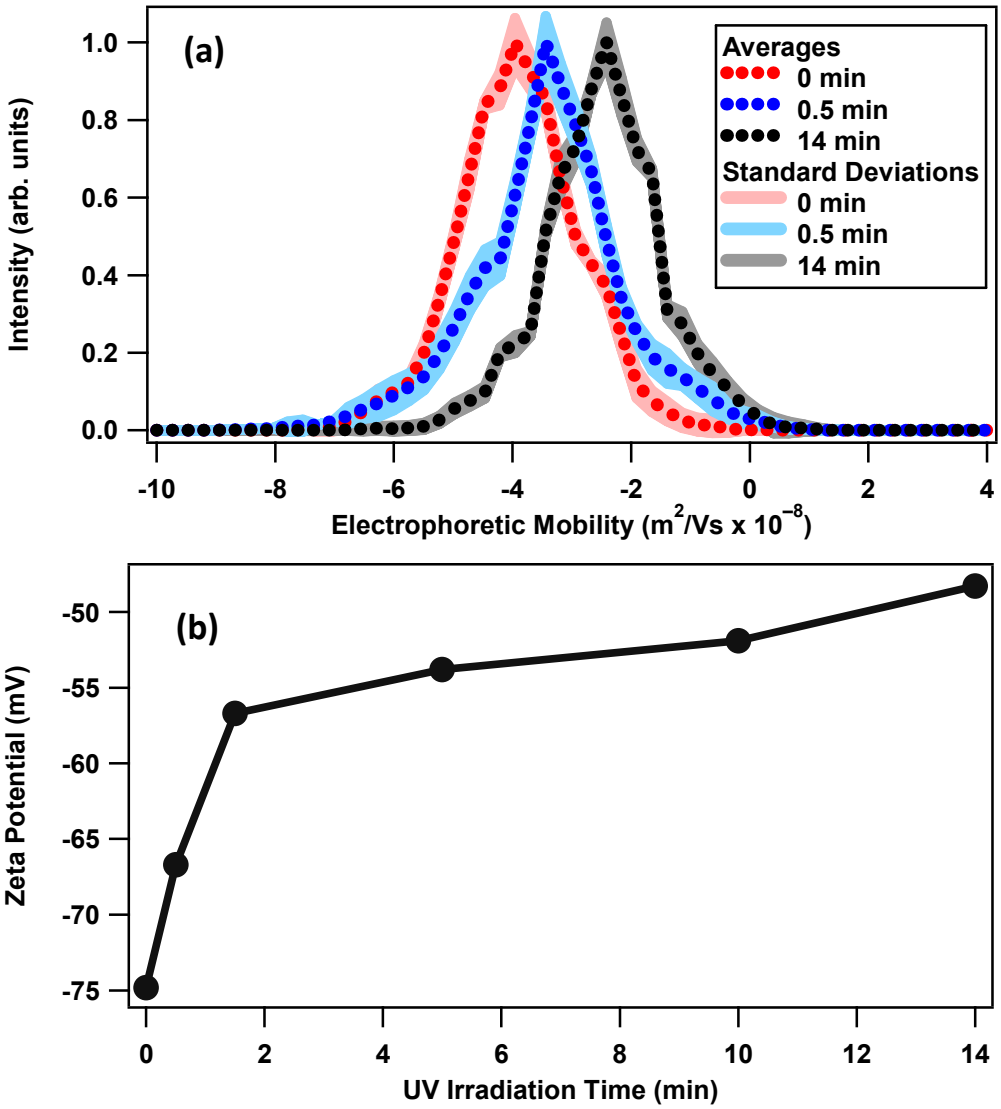


Figure SI4: (a) The electrophoretic mobility of the miRNA-functionalized SNPs under different UV irradiation times. (b) Zeta potential of the miRNA-functionalized SNPs under varying UV irradiation times.

References

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4. McCray, J. A.; Trentham, D. R. Properties and Uses of Photoreactive Caged Compounds. *Annu. Rev. Biophys. Biophys. Chem.* **1989,** *18*, 239-270.