Supporting Information

Measuring Temperature Heterogeneities during the Solar-Photothermal Heating Using Quantum Dot Nanothermometry

Stephanie K. Loeb^{a,b}, Haoran Wei^{a,c}, Jae-Hong Kim^{a*}

^aDepartment of Chemical and Environmental Engineering and Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment (NEWT), Yale University, 17 Hillhouse Ave, New Haven, Connecticut, USA, 06511

^bDepartment of Civil Engineering, McGill University, 817 Rue Sherbrooke Ouest, Montreal, QB, H3A 0C3 Canada

^eDepartment of Civil and Environmental Engineering and Environmental Chemistry and Technology Program, University of Wisconsin–Madison, Madison, WI, 53706 USA

Supporting Information includes the following figures and tables, as cross reference throughout the main article:

| Figure S1: Experimental set-up for measuring QD fluorescence | 2 |
|---|---|
| Alternative Methods Tested for Attaching QDs to Au NR-Si | 2 |
| Figure S2: TEM images for alternative Au NR-Si method tested | 3 |
| Figure S3: Dynamic light scattering curves for different Au NR structures | 4 |
| Figure S3: Example fluorescence spectra for each Au NR-QD structure | 5 |



Figure S1: Experimental set-up for measuring QD fluorescence

Methods Tested for Attaching QDs to Au NR-Si

Several methods were tested to attach QDs to the Au NR-Si. The most successful was a cocondensation approach in which a small amount of APMTS was added to the Au NR-Si suspension to further grow the silica shell followed quickly by the addition of the QDs in Traut's Reagent. This resulted in the QDs being incorporated into the additional layers of silica shell. The cocondensation method is described in detail in the manuscript.

The first alternative method tested was the addition of 5X QD:Au NR particle concentration ratio directly in the Stöber process. 5 mL of as-synthesized Au NRs were washed twice by centrifugation and resuspended in 1 mM CTAB and the pH of the Au NR suspension was adjusted to ~10.5 by dropwise addition of 0.1 M NaOH. TEOS was diluted in anhydrous methanol to make a 10% v/v solution. 50 μ L of the TEOS solution followed immediately by the amine-functionalized QDs were added to the Au NR suspension. The resultant mixture was vortexed briefly, followed by shaking overnight on an orbital shaker. The structures, shown in **Figure S2a**, resulted in the separate encapsulation of Au NR and QDs, rather than a combined structure that co-located the QD and the Au NR. TEM elemental mapping indicating the presence of Au, Si, Cd, and Se is shown in the Figure S2 insert.



Figure S2: TEM images for alternative Au NR-Si method tested. (a) Structures resulting from the addition of amine functionalized QDs directly into the Stöber process. (b) Structures resulting from initiating QDs attached with Au NRs partially coated in silica.

A second alternative method explored employed, as a starting material, a suspension of Au NRs that has been partially coated in silica, i.e., dumbbells, as described previously.¹ Partially coated Au NRs were stabilized with SH-PEG-NH₂ using the Tween assisted ligand exchange protocol described in the manuscript. Briefly, aliquots of the as-synthesized partially coated Au NRs were pelleted by centrifugation and the supernatant was removed. Small amounts of a concentrated SH-PEG-NH₂ solution were added to the pellet and vortexed thoroughly for 20 s followed by resuspension in 0.01% Tween-20 (v/v) such that the final solution had a concentration of 10 μ M SH-PEG-NH₂. This process was repeated a minimum of 4 times. After the final washing step, Au NRs were resuspended in 0.01% Tween-20 to remove excess PEG. Meanwhile, amine-functionalized CdSe/ZnS QDs were added to a freshly prepared solution of 1 mM Traut's Reagent in DI water that had been adjusted to pH ~9.5 by dropwise addition of 0.1 M NaOH. The resultant solution was thoroughly vortexed for 1 min, then left to react for 15 min. The suspension of QDs in Traut's Reagent was then combined with partially Si stabilize by SH-PEG-NH₂ and vortexed thoroughly for 2 min. The resultant structures, shown in **Figure 2b**, had reduced colloidal stability and resulted in aggregated QDs.



Figure S3: Dynamic light scattering curves for different Au NR structures before and after QD attachment.



Figure S4: Example fluorescence spectra for each Au NR-QD structure during 2 Sun illumination with simulated solar light passed through a 750 nm longpass filter.

References

1. L. R. Rowe, B. S. Chapman and J. B. Tracy, *Chemistry of Materials*, 2018, 30, 6249-6258.