

pH-mediated nanoparticle dynamics in hydrogel nanocomposites

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Supplemental Information

I Quantum dot characterization

Prior to single particle tracking (SPT) measurements, the poly(ethylene glycol) modified quantum dots (QDs) must be characterized. A transmission electron microscopy (TEM) image of the bare core/shell CdSe/ZnS nanoparticles used in this study can be seen in Figure S1. Image analysis is used to determine the diameter of the bare core/shell QDs (Fiji/ImageJ).¹ For SPT measurements, the particle length scale calculate is the hydrodynamic diameter of the PEG modified QDs to account for the added length due to the hydrated PEG brush. To calculate the hydrodynamic diameter, the diffusion coefficient of PEG-QDs is measured for various ratios of glycerol/water solutions of known viscosity. Specifically, four glycerol/water solutions of 80, 85, 90 and 95 wt% are used with a corresponding viscosity at 30C° of 0.0339, 0.058, 0.109 and 0.237 Pas. In a homogeneous fluid, the diffusion of a spherical probe can be modeled by the Stokes-Einstein relationship,

$$D = \frac{k_B T}{6\pi\eta r_h} \quad (1)$$

where k_B and T , η , and r_h are Boltzmann's constant, temperature, the solvent viscosity, and the particle hydrodynamic radius respectively. The mean squared displacement (MSD), measured by SPT, of a probe moving linearly throughout time can be defined as,

$$MSD = 2nD\tau \quad (2)$$

where n is the dimensionality of diffusion process, which in this work is 2. The example of the 90 wt% glycerol/water solution is shown, where the black line indicates the ensemble average MSD and the red line a linear fit to the data. The agreement of the data to a linear fit indicates that the probe is diffusive. Using Eq 1, the PEG-QD nanoparticle hydrodynamic diameter is calculated to be 8 nm, with a 3 nm CdSe/ZnS QD and a 5 nm PEG brush (Figure S1, inset).

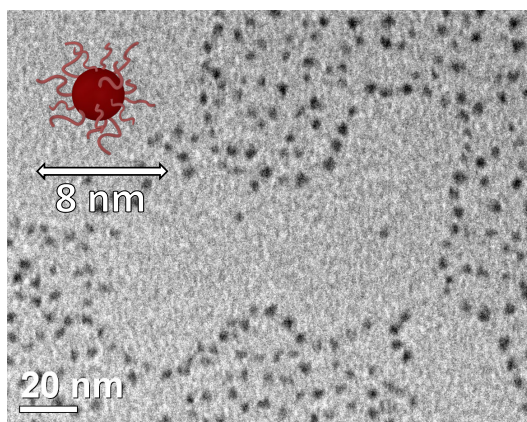


Figure 1: TEM image of core-shell CdSe/ZnS QDs prior to modification with PEG. Inset represents the added dimension due to the surface modification with PEG.

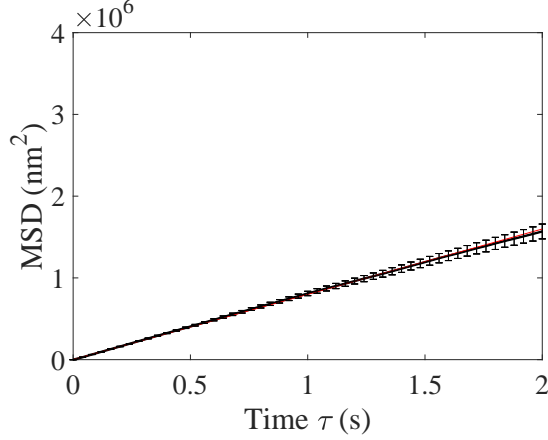


Figure 2: Ensemble average MSD curve from 1978 PEG-QD trajectories in 90% glycerol water at 30C° with a viscosity of 0.109 Pas². Error bars represent the standard error.

Furthermore, the van Hove correlation distribution function can be used to determine the homogeneity of the PEG-QD particles. In the case of a homogeneous probe diffusing through a purely viscous fluid, such as a glycerol/water solution, the ensemble average displacements will follow a Gaussian distribution. The van Hove correlation distribution is plotted in Figure S2 for multiple lag times, τ , spanning an order of magnitude. For all τ , the displacements are well fit with a Gaussian indicating that the PEG-QDs probes are homogeneous in size post PEG modification.

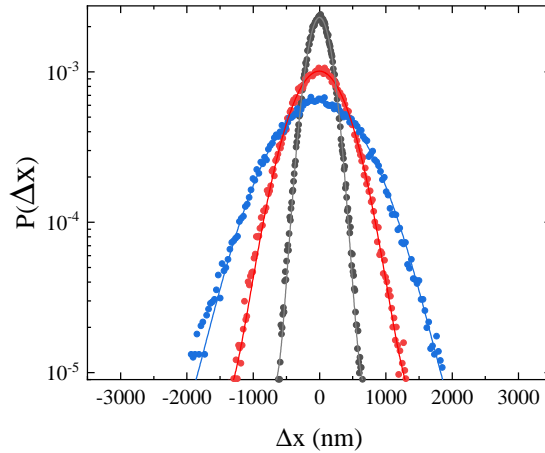


Figure 3: van Hove distribution function for PEG-QDs in 90% glycerol water solution at times 0.08 (grey), 0.4 (red) and 1 (blue) seconds. Fitted lines represent a Gaussian fit.

II Hydrogel Characterization

The elastic blob model estimates the mesh size of a network based on the number of elastically effective chains, defined as the strands between cross links which contribute to the modulus.

$$G'_{(0)} = \rho_{el} k_b T \quad (3)$$

where ρ_{el} is the density of elastic blobs, k_b is the Boltzman constant, and T is the absolute temperature.³ Assuming a cubic lattice, the mesh size relates to ρ_{el} as

$$\zeta_{el} = \rho_{el}^{-1/3} \quad (4)$$

The modulus measurements for this study are obtained immediately after polymerization and are representative of the hydrogel modulus in a prepared state rather than the swollen state. The as-prepared and swollen modulus are related by the volumetric swelling ratios,

$$\frac{G_s}{G_r} = \frac{Q_s^{-1/3}}{Q_r^{-1/3}} \quad (5)$$

where G_s is the swollen modulus, G_r is the as-prepared modulus, and Q is the swelling ratio.⁴ The swelling ratio can also be described as the inverse of the polymer volume fraction, v_p

$$Q = \frac{1}{v_p} \quad (6)$$

which can be achieved by measuring the weight of the swollen gels at equilibrium, lyophilizing the hydrogels to remove the water, and measuring the resulting polymer volume fraction. To calculate the zero-shear as-prepared modulus, a frequency sweep from 1 rad/sec to 20 rad/sec is conducted in the linear regime (1% strain), and a fit is used to extrapolate from 1 rad/sec to 2 rad/sec to 0. For the neat polyacrylamide gel, $\Phi = 0$, the average mesh size, $\langle \zeta \rangle$ is determined to be 25 nm.

A key finding of this paper is the ability to create nanocomposite hydrogels with homogeneously distributed static silica particles at low loadings. As noted in the manuscript, this is attributed to the use of a photoinitiator, lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP) rather than the traditional ammonium persulfate (APS) and tetramethylethylenediamine (TEMED). While the network formation for traditional photopolymerization takes less than a minute (see manuscript), the traditional method takes much longer (minutes) for hydrogels with a similar mesh size, allowing for the silica particles to be mobile aggregate in and at the surface of the hydrogel (Figure S4). This not only create a non-uniform dispersion of silica within the hydrogel, but prevents QDs from infiltrating into the hydrogel due to the crust of silica particles on the surfaces of the hydrogel. Additionally, using appropriate length scales aids in the immobilization of silica particles. To create a system in which the PEG-QD probes are mobile but the silica particles are not, the average mesh size of the polyacrylamide hydrogel needed to be around 30 nm; larger than the hydrodynamic diameter of the PEG-QD probe (8 nm) while smaller than the immobilized silica particles (66 nm). To determine the optimal acrylamide concentration for this system, a series of polyacrylamide gels are synthesized with various starting acrylamide concentration. The average mesh sizes are determined determined through rheology ($G'_{(0)}$) and lyophilization (v_p) and are summarized below in Table 1.

Table 1: The average mesh size of neat polyacrylamide hydrogels for varying starting acrylamide concentrations. All hydrogels are synthesized with the same concentration of bisacrylamide (crosslinker) and LAP (photoinitiator).

Acrylamide Concentration (wt%)	Mesh Size, $\langle \zeta \rangle$ (nm)
7	69.7
8	47.6
10	25.1
12	23.0

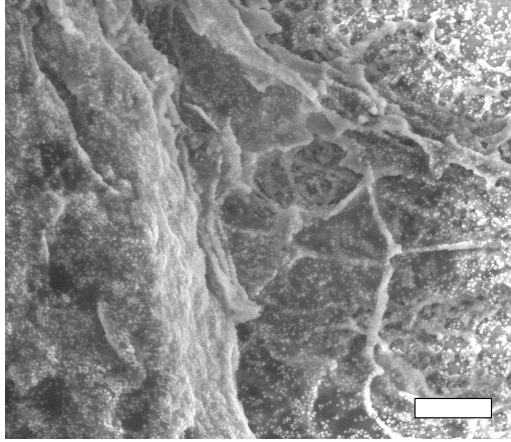


Figure 4: Scanning electron microscopy (SEM) of the surface of a $\Phi = 0.01$ SiO_2 polyacrylamide hydrogel polymerized using APS and TEMED.

III Supplemental Particle Tracking Data

Along with the particle tracking data presented in the manuscript, we have provided additional data to showcase the ensemble average and dispersity of all probe tracks and mobile probe tracks. Specifically, the means of the log-normal MSDs (see Figure 4, bottom, in main text) for all PEG-QDs and the mobile PEG-QDs are reported. Percent error is calculated as follows:

$$\text{PercentError}(\%) = \frac{\sigma}{\mu} \quad (7)$$

where σ is the standard deviation of the log-normal distribution of MSDs and μ is the mean of the log-normal distribution. This metric is included to give a sense of the breadth of the distributions of probe MSDs. For example, in the neat polyacrylamide hydrogel there is negligible change between the mean, μ , whether examining all probe MSDs or the mobile population. However, in the $\Phi = 0.005$ composite, the addition of silica leads to the emergence of two probe populations, localized and mobile. The two populations lead to a decrease in the mean MSD when examining all probe tracks, as well as an increase in the percent error which is expected.

Table 2: Additional single particle tracking analysis.

Silica volume fraction (Φ)	Percent Mobile Particles	Percent Localized Particles	Log-normal Mean, All tracks (log[MSD(nm ²)])	Standard Deviation (STD)	Percent Error	Log-normal mean, Mobile population (log[MSD(nm ²)])	STD of log-normal mean	Percent Error
0	92%	8%	5.479	0.6637	12.1	5.5546	0.5319	9.6
0.005	63%	37%	4.7395	1.0314	21.8	5.3352	0.5387	10.1
0.01	60%	40%	4.8017	1.0332	21.5	5.4842	0.5121	9.3
0.1	63%	37%	4.8889	0.9735	19.9	5.4504	0.6025	11.1

IV Supplemental Quartz Crystal Microbalance with Dissipation Data

Quartz crystal microbalance with dissipation (QCM-D) is used to determine the attraction between the PEG-QDs and the surface of silica. Figure S5 shows QCM-D data for all overtones. The overtones follow the expected trends, with a larger change in frequency corresponding with smaller overtones.

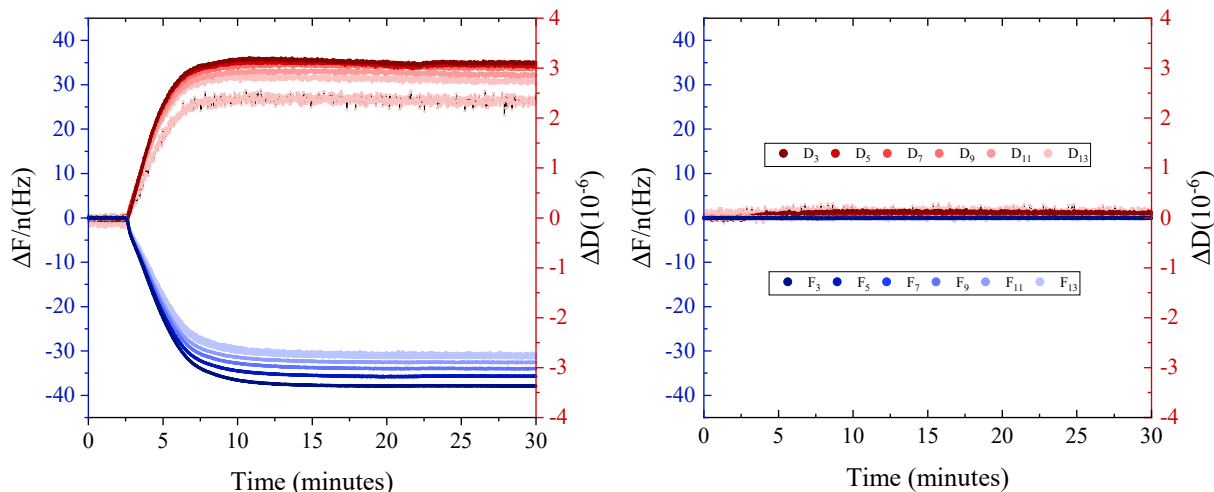


Figure 5: Change in frequency (ΔF , blue) and dissipation (ΔD , red) as a silica coated QCM-D crystal is exposed to a PEG-QD solution (top). Experiments are conducted in solutions with pH 5.8 (left) and pH 9.2 (right). Overtones 3 through 13 are shown.

References

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