Improving Fluorescence Emission of Graphene Quantum Dots through Surfactant-Assisted Stabilization

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ABSTRACT

Graphene quantum dots (GQDs) exhibit size-dependent visible and near-infrared fluorescence, high aqueous dispersibility, and biocompatibility, making them promising candidates for bioimaging and optoelectronic applications. However, interfacial interactions with water and aggregation-induced effects can introduce nonradiative decay pathways that limit emission efficiency. Inspired by the role of surfactants in preserving fluorescence in single-walled carbon nanotubes, we investigate surfactant-mediated modulation of GQD photophysics using five structurally distinct surfactants: sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS), sodium deoxycholate (SDC), sodium cholate (SC), and Pluronic F127. Two structurally and electronically distinct GQD systems—nitrogen-doped GQDs synthesized via a bottom-up approach and reduced graphene oxide-derived GQDs prepared through top-down fragmentation—were examined across a wide range of surfactant-to-GQD mass ratios. Fluorescence spectroscopy in both the visible and near-infrared regimes was combined with dynamic light scattering (DLS), zeta potential measurements, and transmission electron microscopy (TEM) to correlate optical behavior with changes in particle size distribution, surface charge, and interfacial organization. Complementary theoretical modeling of surfactant-coated GQDs was employed to elucidate structure-dependent encapsulation and dielectric effects.

INTRODUCTION

Graphene Quantum Dots (GQDs) fluoresce (glow) under specific wavelengths of light.

This study focuses on two types of GQDs:

- NGQDs (nitrogen-doped): graphene sheets with nitrogen and oxygen-containing groups.
- rGQDs (reduced): similar structure, but without nitrogen—only graphene and oxygen

Hypothesis: Surfactants influence fluorescence by interacting with GQDs hydrophobic ends face the GQDs, and hydrophilic ends face water, enhancing light emission.

Surfactants tested:

- Sodium dodecyl sulfate (SDS)
- Sodium deoxycholate (SDC)
- Sodium dodecylbenzene sulfonate (SDBS)
- Pluronic F127 (P-F127)
- Sodium cholate (SC)

METHODS

- Batches of NGQDs were synthesized through a microwave-assisted hydrothermal process then were dialyzed using MWCO 500–1000 Da tubing for 24 hours then filtered through 0.22 µm syringe filters then air-dried to reach desired concentration
- Batches of rGQDs were synthesized through an oxidative fragmentation process then were dialyzed using MWCO 500–1000 Da tubing for 24 hours then filtered through 0.22 µm syringe filters then air-dried to reach desired concentration
- Surfactants were added to 5 mL aliquots at mass ratios of 0, 0.5, 1, 5, 10, 50, 100, 500, and 1000 relative to GQD concentration
- Samples were tip sonicated for 1 minute to promote dispersion and surfactant encapsulation
- Samples were transferred into cuvettes for fluorescence measurements
- Particle size and hydrodynamic diameter were measured via dynamic light scattering (DLS). Zeta potential was measured via electrophoretic light scattering

RESULTS

FIGURE 1:

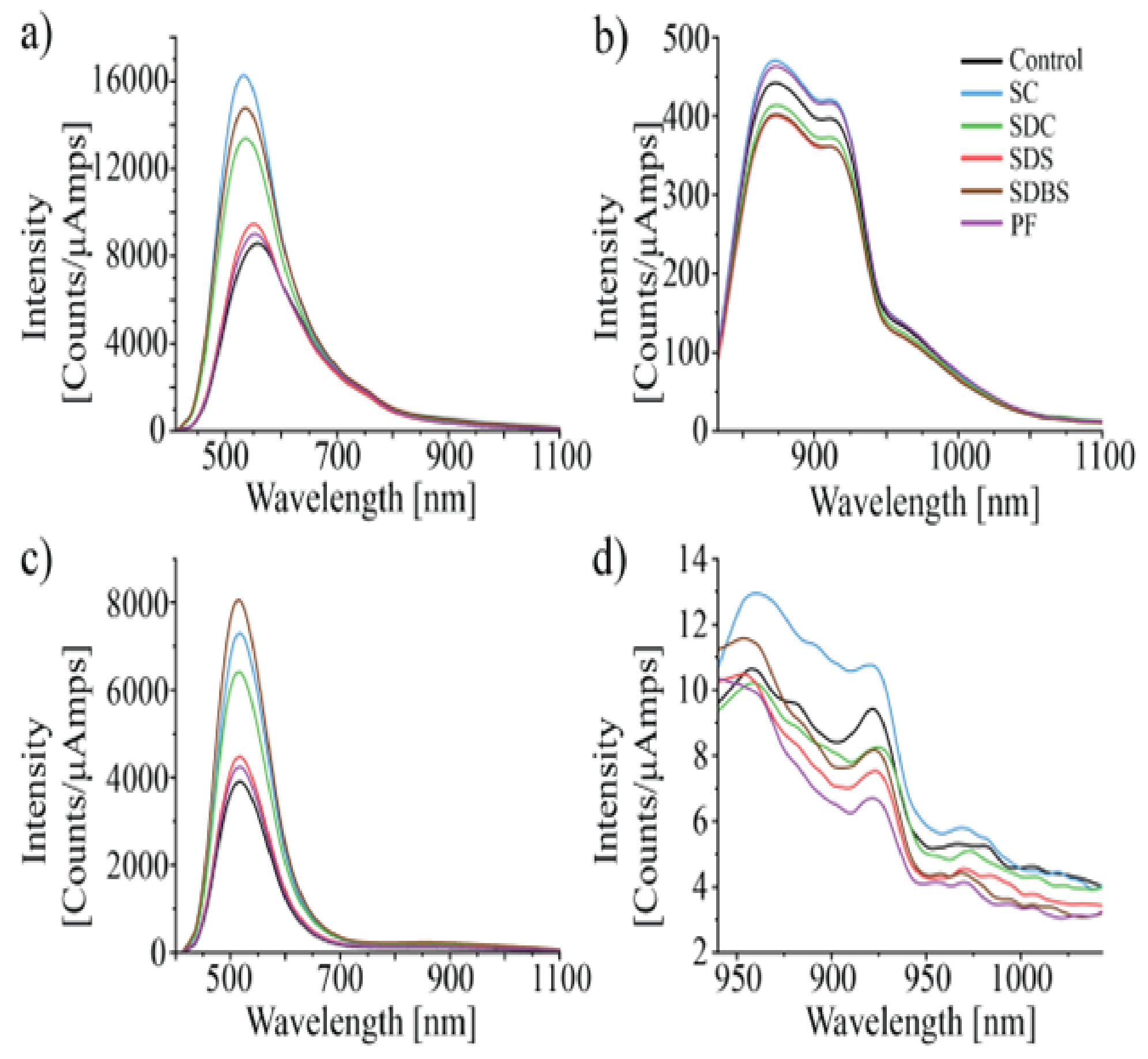
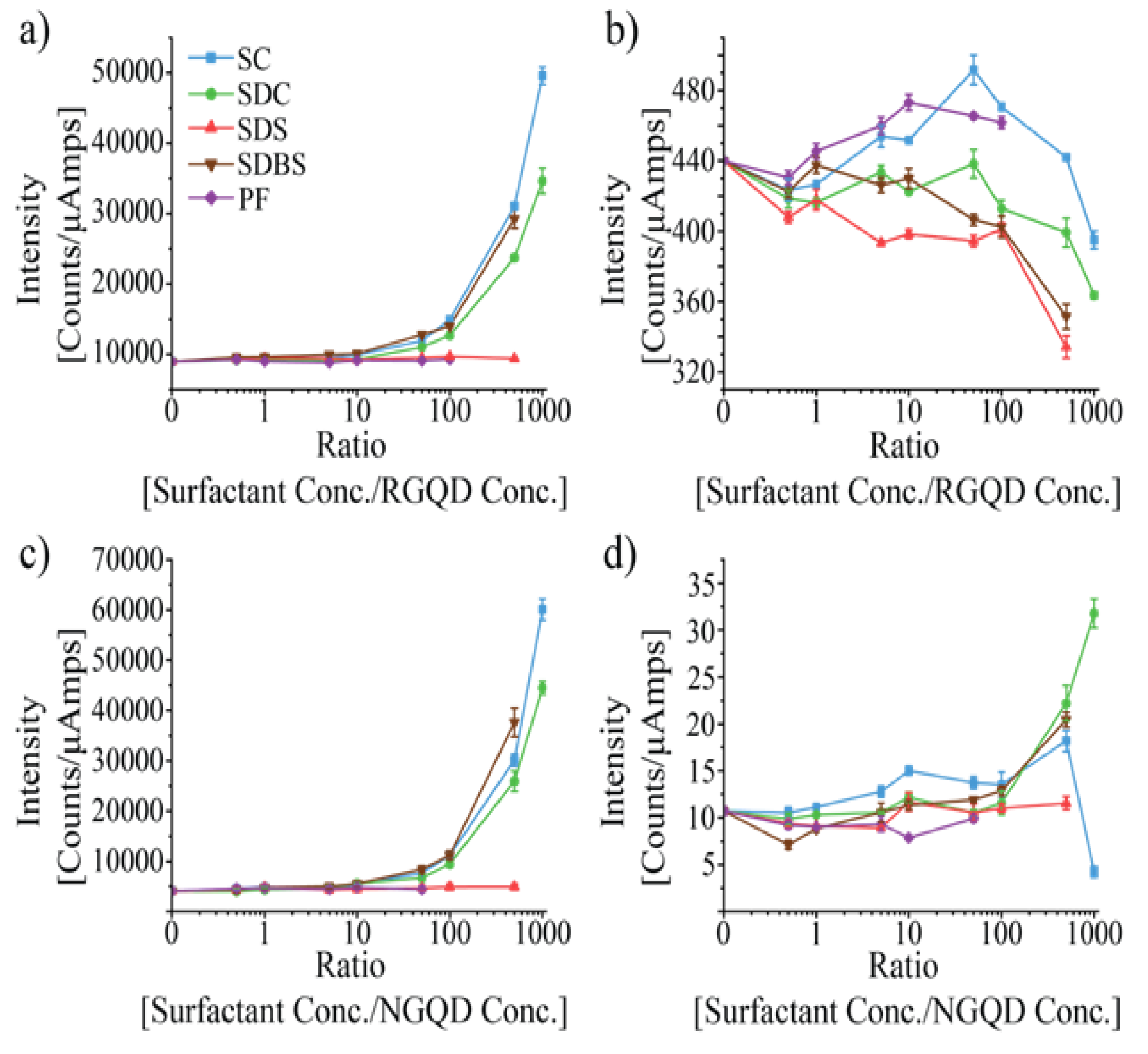


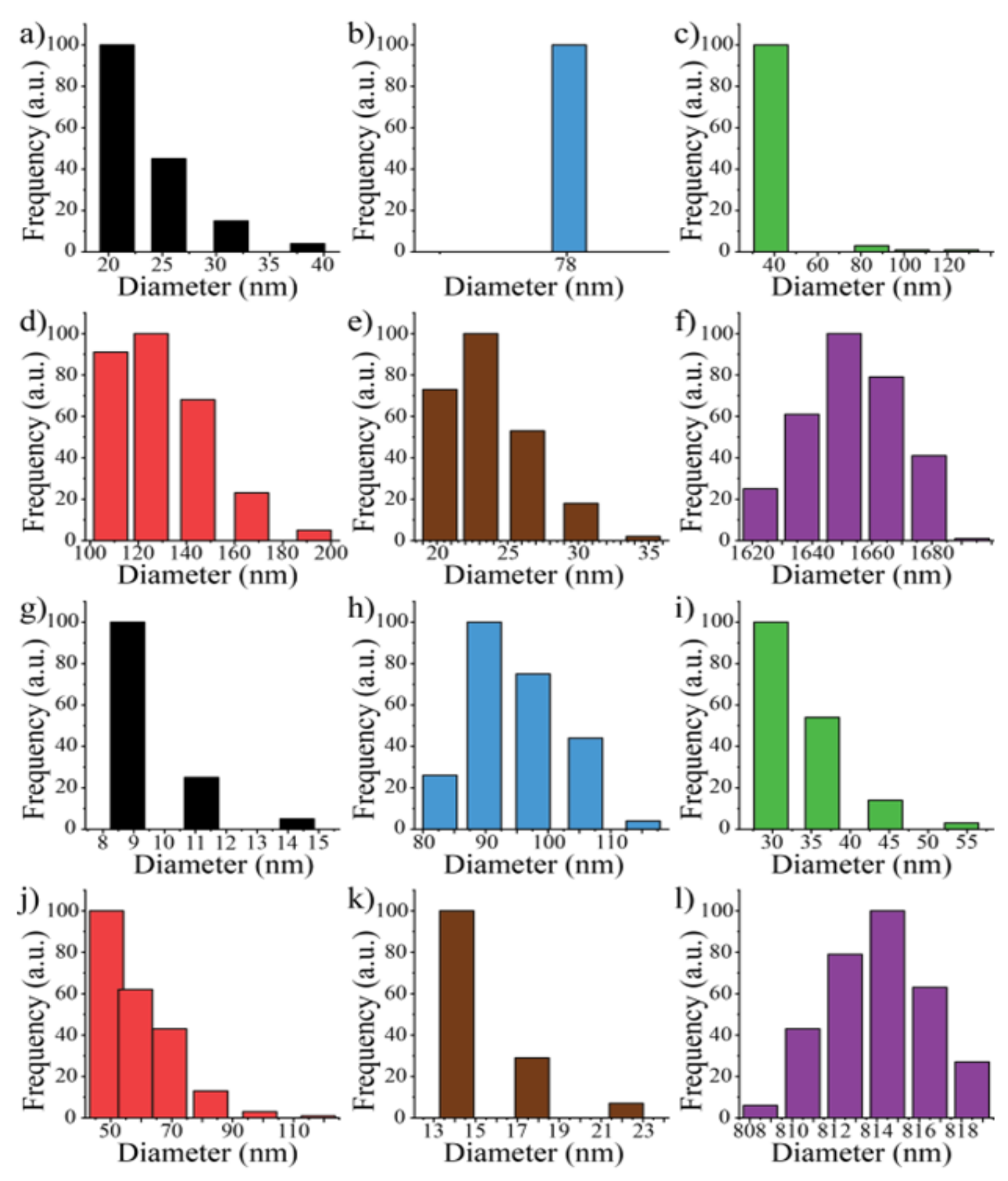
Figure 1(a) is the visible emission spectra of RGQDs suspended with various surfactants at a 100:1 ratio of surfactant to RGQD by mass (14.07 mg/mL of surfactant). Presented in Figure 1(b) is the NIR emission spectra of RGQDs suspended with various surfactants at the same concentration of surfactant. Presented in Figure 1(c) is the visible emission spectra of NGQDs suspended with various surfactants at a 50:1 ratio of surfactant to NGQD by mass (7.963 mg/mL of surfactant). Presented in Figure 1(d) is the NIR emission spectra of NGQDs suspended with various surfactants at the same concentration of surfactant.

FIGURE 2:



Presented in Fig. 2 is the peak fluorescence at values chosen as the peak fluorescence of the control GQDs as they vary with addition of surfactant. Presented in Figure 2(a) is the fluorescent peak visible emission of RGQDs suspended with various surfactants at increasing concentrations based on the ratio of surfactant to RGQDs taken at 562 nm. Presented in Figure 2(b) is the peak NIR emission of RGQDs suspended with the same varying concentrations of surfactant taken at 866 nm. Presented in Figure 2(c) is the peak visible emission spectra of NGQDs suspended with various surfactants at increasing concentrations based on the ratio of surfactant to NGQDs taken at 515 nm. Presented in Figure 2(d) is the peak NIR emission spectra of NGQDs suspended with the same varying concentrations of surfactant taken at 854 nm

FIGURE 3:



Presented in Figure 3 is the DLS readings for the surfactant-GQD suspensions. Figure 3(a-f) represent the RGQD and surfactant mean diameter at a ratio of 100:1 surfactant to RGQD. (a) no added surfactant, (b) SC, (c) SDC, (d) SDS, (e) SDBS, (f) PF. Figure 3(g-l) represent the NGQD and surfactant mean diameter at a ratio of 50:1 surfactant to NGQD. (g) no added surfactant, (h) SC, (i) SDC, (j) SDS, (k) SDBS, (l) PF. The frequency of each diameter is shown in the distribution graphs, and the mean diameter is present in Table 1.

TABLE 1:

GQD type	Surfactant	Zeta Potential (mV)	Mean Diameter (nm)
RGQD	Control	-3.29	23.51829268
	SC	-4.7	77.9
	SDC	-14.2	41.19238095
	SDS	-17.47	129.0989547
	SDBS	-25.25	23.56341463
	PF	-2.45	1653.178827
NGQD	Control	-18.26	9.47307692
	SC	-4.17	94.67871486
	SDC	-46.15	33.51754386
	SDS	-4.73	58.25810811
	SDBS	-22.51	15.28455882
	PF	-16.47	814.0849057

Zeta Potential (mV) and Mean Diameter (nm) of the particles in the surfactant and GQD suspensions based on the mass ratios present in the spectra graphs above. RGQD tests have a ratio of 100:1 surfactant to RGQD while NGQD tests were run at a ratio of 50:1 surfactant to NGQD ratio

CONCLUSIONS

Our results suggest that visible emission in graphene quantum dots (GQDs) is primarily associated with surface states and edge/dopant effects, while near-infrared (NIR) emission is more strongly linked to core electronic structure, including π-conjugation and sp² graphitic domains, though both likely arise from a combination of mechanisms. Reducing water interactions at the surface appears to decrease quenching and enhance visible emission in a relatively direct manner, whereas NIR emission is more sensitive to the surrounding dielectric environment, showing concentration-dependent behavior with an optimal surfactant level followed by decreased emission at higher concentrations. Surfactant structure significantly influences GQD organization and optical response: rigid bile salt surfactants (SC and SDC) promote tighter, more ordered packing, with SDC exhibiting the greatest packing density, while SDS forms more flexible, less ordered micelles and provides weaker NIR enhancement. SDBS, containing an aromatic ring, appears to uniquely affect emission through interactions with graphitic electronic states, and PF likely induces larger aggregates with minimal enhancement to optical properties. Differences in aggregation and stability, supported by DLS and zeta potential measurements, indicate that mean particle diameter can serve as a qualitative indicator of packing density when accounting for surfactant size, highlighting the combined importance of surface chemistry and local environment in governing GQD emission behavior.

Overview

We studied how soap-like molecules (surfactants) affect the glow (fluorescence) of ti-ny carbon particles called graphene quantum dots (GQDs). These dots can be used in things like medical imaging or sensors. We found that different surfactants can either make the dots glow more or less depending on how they inter-act. Understanding this helps us control the glow, which is important for future uses in sci-ence and technology.

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