

Pickering Emulsions of Self-Assembled Lead Sulfide Quantum Dots with Janus-Ligand Shells as Nanoreactors for Photocatalytic Reactions

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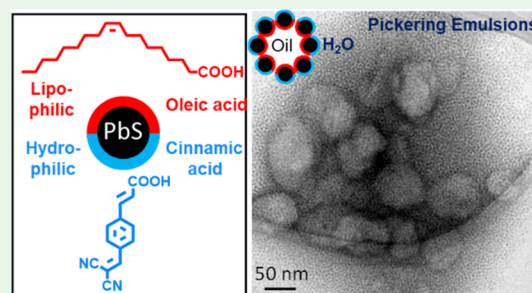
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Supporting Information

ABSTRACT: Here we prepare Pickering emulsions with semiconductor quantum dots (QDs). Amphiphilic PbS QDs are prepared by constructing Janus-ligand shells comprised of lipophilic oleic acid and hydrophilic 4-(2,2-dicyanovinyl)cinnamic acid ligands. Upon homogenization, the QDs with Janus-ligand shells self-assemble at the water–dichloromethane interface, forming stable Pickering emulsions. The photocatalytic properties are evaluated by the photodegradation reaction of methyl orange (MO) dye molecules. Under the same conditions, MO was significantly degraded when photocatalyzed by the QD Pickering emulsions, while no degradation was observed when PbS QDs without Janus-ligand shells were employed. This work provides a guide to designing QD-based nanoreactors.

KEYWORDS: Pickering emulsions, semiconductor nanocrystals, Janus-ligand shells, nanoreactors, PbS QDs, photocatalytic reactors



Pickering emulsions^{1,2} are a type of emulsion that is stabilized by solid particles bound at the interface between oil and water (or between two nonmiscible liquids). Compared with molecular surfactants or amphiphilic polymers, solid particles as emulsion stabilizers possess a few advantages, such as higher stability against coalescence, lower toxicity with food-grade particles, ease of recycling, and the introduction of additional functionality through solid nanoparticle characteristics. In view of these properties, Pickering emulsions have potential applications in a number of industries, e.g., biomedicine, food, catalysis, petroleum, cosmetics, etc.^{3–5} So far, a series of solid particles have been used as emulsifiers for Pickering emulsions and can generally be classified into two categories: inorganic nanoparticles such as SiO₂ and Fe₃O₄ with surface chemical modifications, and polymer nanoparticles with amphiphilic surfaces.

While a variety of solid particles have been used to stabilize emulsions, few studies have been reported on the construction of Pickering emulsions with semiconductor quantum dots (QDs).⁶ With unique optical and electronic properties, QDs can endow Pickering emulsions with multiple interesting characteristics, such as strong photoluminescence for labeling, and the transfer of charges or energy to substrates in different phases for photocatalytic reactions. One example reported by Burdyny et al.⁷ has shown that Pickering emulsions stabilized by TiO₂ nanoparticles can catalyze the degradation reaction of methylene blue dye molecules. The reaction rate is 2.2-fold higher compared with that of a fixed photocatalyst reactor, and the photocatalyst retention is ~100% in a continuous reactor. Another example is the 1-methylnaphthalene degradation

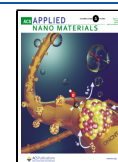
reaction photocatalyzed by titania-nanoparticle-stabilized Pickering emulsions. The reaction yield reaches 95% in 24 h, compared with only 25% in the nonemulsified system.⁸ Therefore, Pickering emulsions stabilized by semiconductor QDs should provide unique opportunities for photocatalytic properties for a variety of organic reactions,^{9,10} especially for heterogeneous reactions. In this work, we report the formation of Pickering emulsions through the self-assembly of PbS QDs with Janus-ligand shells, and the resulting enhanced photocatalytic properties were studied by the photodegradation of methyl orange (MO) dye molecules. We found that the yield of photodegradation catalyzed by the Pickering emulsions was significantly higher compared with that of the heterogeneous reaction in which PbS QDs without Janus-ligand shells and MO were suspended in different phases. This work provides a guide to the design of efficient nanoreactors and microemulsions for heterogeneous photocatalytic reactions.

With the idea of constructing QD-stabilized Pickering emulsions, the challenge lies in their synthesis. The formation of stable Pickering emulsions requires nanoparticles to be amphiphilic in oil and water phases, and Janus nanoparticles are great candidates as stabilizers because of the different

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chemistry on the two sides of the QD. For example, Haney et al.¹¹ reported the synthesis of Janus microparticles with a lipophilic side consisting of a cross-linked polymer and a hydrophilic side consisting of a hydrogel, and both oil-in-water and water-in-oil millimeter-sized Pickering emulsions were prepared with those Janus particles. Considering this, we propose Pickering emulsions utilizing QDs with Janus-ligand shells. Bronstein et al.¹² shows that the nearest-neighbor coupling energy between ligands, ΔJ , determines the pattern of the ligand shell during ligand exchange. Patchy or Janus-ligand shells can be formed when $\Delta J < -0.44 k_B T$, which means new 4-(2,2-dicyanovinyl)cinnamic acid (CAH) ligands tend to exchange with the oleic acid (OA) ligands next to the existing CAH ligands on the QD surfaces. As shown in Figure 1,

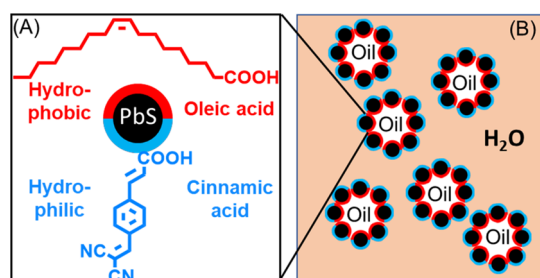


Figure 1. Illustrations of the use of PbS QDs capped with oleate–cinnamate Janus-ligand shells (A) to construct oil-in-water Pickering emulsions (B).

amphiphilic PbS QDs are prepared through a partial ligand-exchange reaction with CAH. There are a few reasons for using CAH as the ligand. First, Bronstein et al.¹² have shown that ligand–ligand interactions can drive a cooperative ligand-

exchange reaction, yielding ligand patterns on the surface of PbS QDs. Thus, the ligand exchange of OA-capped PbS QDs with dipolar CAH can form Janus-like ligand shells due to the beneficial interaction of the dipolar CAH ligands on the surfaces of PbS QDs. Second, the dicyanovinyl group in CAH makes the QD hydrophilic. Third, CAH-capped PbS QDs retain high colloidal stability, allowing for solution processing of the QDs without irreversible aggregation. Upon homogenization of the mixture of oil and water, the amphiphilic PbS QDs with Janus-ligand shells are bound to the oil–water interface and then self-assembled to form stable Pickering emulsions (Figure 1B).

The conditions to produce Janus-ligand shells on PbS QDs can be determined through the study of a OA-to-CAH ligand-exchange isotherm recorded through spectrophotometric titrations.^{12,13} Attaching conjugated ligands to QDs leads to an absorption enhancement due to QD ligand electronic coupling;^{14–16} i.e., maintaining the same concentration of PbS QDs, while increasing the amount of CAH results in an enhanced absorption (Figure 2A), as well as a red-shifted excitonic absorption peak due to exciton delocalization. The absorption enhancement is quantitatively correlated with the CAH/QD ligand loading:¹⁶ the number of bound CAH ligands is proportional to the absorption enhancement $(\Delta\alpha/\alpha_0)^2$, where α_0 is the integrated absorption for PbS/OA and $\Delta\alpha$ is the difference of the integration between ligand-exchanged PbS QDs and PbS/OA. The ligand-exchange isotherm of CAH ligand adsorption on PbS QDs is presented in Figure 2B. In the low concentration regime where the CAH/PbS ratio (in ligand exchange) is less than 100, nominal enhancement is observed. The enhancement then undergoes a sharp increase with increasing CAH/PbS equivalents, indicating the transition from OA-dominated to CAH-dominated

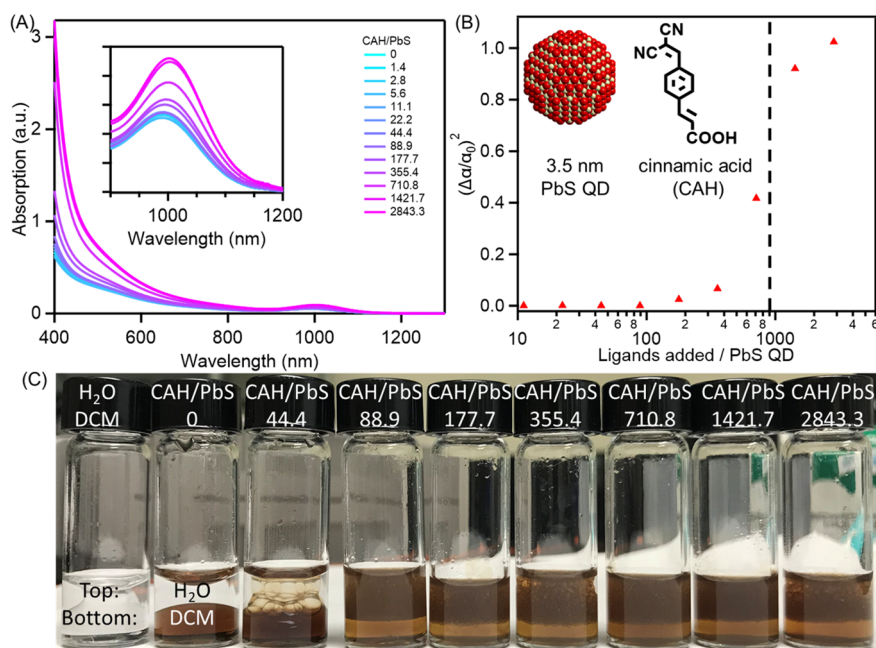


Figure 2. (A) Absorption spectra of PbS QDs with different surface loadings of CAH. The inset is absorption of the first excitonic peaks of PbS QDs. (B) Adsorption isotherm of a ligand-exchange reaction. $(\Delta\alpha/\alpha_0)^2$ is proportional to the number of bound CAH ligands, where α_0 is the integrated area of the absorption curve from 500 to 1200 nm when CAH/PbS = 0, and $\Delta\alpha$ is the subtraction of α_0 from the integrated area for each ligand-exchange condition. The dashed line labels the condition where the CAH surface coverage is 50%. (C) Photographs of ligand-exchanged solutions after the addition of equivolumes of water and sonication for 1 min. Labels are the mole ratios of CAH over PbS QDs in ligand exchange. The first sample is dichloromethane with an equivolume of water as the control.

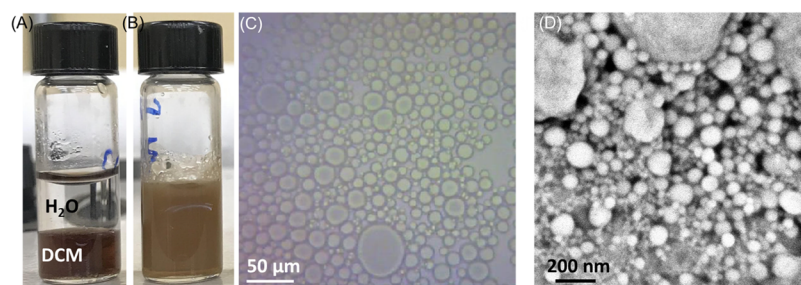


Figure 3. (A) Photograph showing separation of the water (top) and dichloromethane (bottom, PbS/OA) phases after homogenization. (B) Photograph showing the formation of water–dichloromethane emulsions with Janus-ligand PbS QDs after homogenization. (C and D) Optical microscopy and SEM images, respectively, of the Pickering emulsion in part B.

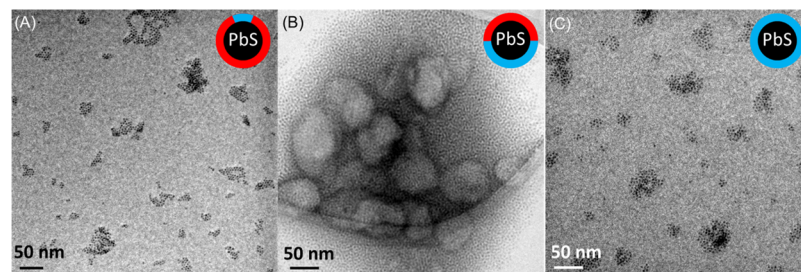


Figure 4. TEM images of emulsion samples prepared with ligand-exchanged PbS QDs with CAH loadings of 10% (A), 50% (B), and 100% (C). The bottom dichloromethane layer was taken to prepare the sample in part A after homogenization and the top water layer for samples in parts B and C.

ligand shells. The sharp increase is indicative of a beneficial ligand–ligand cooperative exchange that results in ligand segregation and the formation of Janus-ligand shells. The isotherm plateaus after the CAH/PbS ratio equals 3000 and the CAH loading is close to saturation.

We demonstrate the lipophilic-to-hydrophilic transition of PbS QDs as the CAH loading increases by the addition of an equivolume of water to the ligand-exchange solutions and then sonication for 1 min (Figure 2C). PbS QDs transfer from the dichloromethane phase when the CAH/PbS ratio equals 0 and to the water phase when the CAH/PbS ratio (in ligand exchange) is greater than 88.9, indicating the formation of emulsions of the oil-in-water type. This is due to the hydrophilic dicyano group as discussed above. We conclude that the amphiphilicity of PbS QDs can be tuned by the CAH ligand exchange. With a CAH/PbS ratio (in ligand exchange) of 900, the surface coverage of CAH corresponds to 50% based on the titration isotherm, and the Janus-ligand shells are expected to form, which is confirmed by 2D nuclear Overhauser effect spectroscopy (Figure S3). With this condition, QDs are amphiphilic in both dichloromethane and water and are used to construct the Pickering emulsions shown below.

Pickering emulsions are formed with PbS QDs having Janus-ligand shells. The ligand-exchange reaction was initially performed in dichloromethane. Homogenization of the ligand-exchange solution after the addition of equivolumes of water generates emulsions (Figure 3B). No apparent changes regarding the QD size are observed during this process (Figure S8). As a comparison, no emulsions are observed for PbS QDs capped with OA (Figure 3A) but rather there is an immediate phase segregation into immiscible water and dichloromethane phases. Figure 3C shows an optical microscopy image of the homogenized sample in Figure 3B. The spherical emulsions exhibit lighter cores and darker edges due to the self-assembly

of PbS QDs at the water–dichloromethane interface. After dilution of the sample with water, emulsions float on top, suggesting an oil-in-water type of emulsion. This is consistent with the theory of Pickering emulsion formation: more hydrophilic particles yield oil-in-water emulsions.^{3,17} Additionally, Pickering emulsions are observed as spherical nano-assemblies (Figure 3D) under scanning electron microscopy (SEM), with a mean diameter of 48.3 nm (Figure S9). Analysis of these emulsions with SEM and energy-dispersive X-ray spectroscopy (EDS; Figure S5) confirms that these spherical structures are assemblies of PbS QDs. From the optical microscopy images, the diameter of the emulsions is on the order of tens of micrometers. However, only small emulsions with diameters of tens to hundreds of nanometers are observed in the SEM images. This could be due to the instability of larger emulsions in the preparation of SEM samples. To avoid the effect of free CAH ligand in the formation of emulsions, a control experiment with washed PbS QDs after ligand exchange was conducted, and emulsions were observed (Figure S4), with lighter edges compared with the results in Figure 4B, indicating thicker QD layers at the oil–water interface. The size distribution of Pickering emulsions in SEM and transmission electron microscopy (TEM) images is relatively wide, which could be improved by optimizing the ligand exchange and homogenization conditions.

The stability of Pickering emulsions depends on the three-phase contact angle of solid particles at the oil–water interface, which is determined by the wettability of the nanoparticles to the oil-in-water phase. In this work, the wettability of PbS QDs to the dichloromethane and water phases is tuned by the CAH surface coverage (Figure 2C). For emulsions formed with PbS QDs with low Janus ratios, i.e., the CAH surface coverage is 10%, PbS QDs are more soluble in dichloromethane with a large contact angle. In this case, QD aggregates are observed after homogenization (Figure 4A). This is similar to the

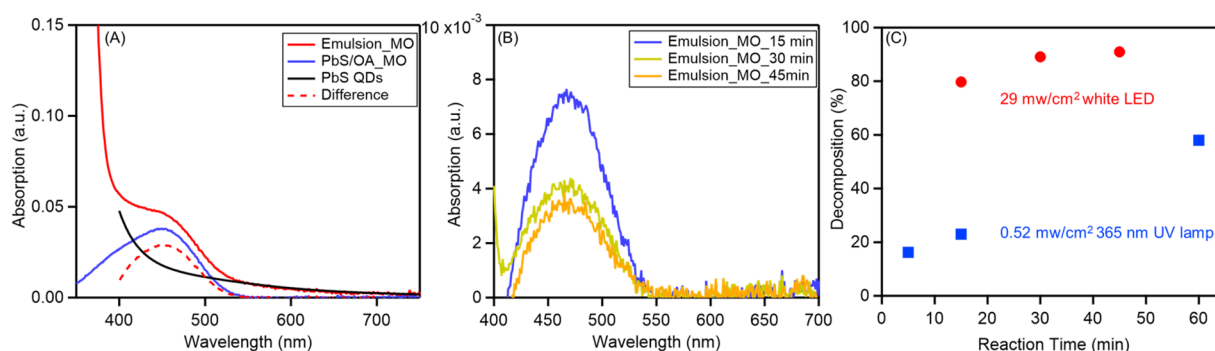


Figure 5. Photocatalytic degradation of MO. (A) Absorption spectra of an MO aqueous solution after photocatalytic degradation by Pickering emulsions (solid red curve) and PbS/OA in dichloromethane (blue curve) under the illumination of a 365 nm UV lamp. The black curve is the absorption spectrum of PbS QDs with Janus-ligand shells, which is scaled to match the red curve from 550 to 750 nm. The dashed red curve is the difference spectrum of the solid red and black curves. (B) Difference spectra of an MO aqueous solution (contributions from PbS QDs are removed) after photocatalytic degradation by Pickering emulsions with different reaction times under illumination of a white LED. (C) Percentages of MO decomposition photocatalyzed by Pickering emulsions with different reaction times and light sources. The calculation is based on the decrease of the absorption maximum of MO.

emulsions prepared with 100% CAH covered PbS QDs (Figure 4C) because of the strongly hydrophilic QDs and the corresponding small contact angle. As a comparison, stable Pickering emulsions are obtained with 50% CAH coverage (Figure 4B), i.e., the ideal conditions for the formation of Janus-ligand shells. With equal surface coverages of OA and CAH on PbS QDs, the three-phase contact angle would be close to 90°. This is consistent with the results from the literature,^{18,19} showing that the contact angle close to 90° yields the most stable Pickering emulsions. Further stability tests of the formed Pickering emulsions against different temperatures were not conducted because of the low boiling point of dichloromethane.

The photocatalytic properties of Pickering emulsions were evaluated by the photodegradation of MO dye molecules. The photodegradation of MO catalyzed by PbS QDs follows a direct pathway through the redox reaction between MO and photogenerated electrons and holes in the QDs and an indirect pathway in which MO reacts with reactive oxygen species such as hydroxyl radicals and superoxide electrons from the photoredox of water and oxygen.^{20,21} By a comparison of the redox potentials of 3.5 nm PbS QDs²² and MO,²³ it is less likely that direct charge transfer occurs between these two species, and therefore an indirect pathway dominates the photodegradation of MO in this case. Here, we first performed a heterogeneous reaction consisting of MO in the aqueous phase and PbS/OA QDs in the dichloromethane phase. The two phases were mixed by strong agitation, which is typically used in such heterogeneous reactions to increase the contact of substrates that are in two dissimilar phases with the catalyst. A 365 nm UV lamp with relatively low power density (0.52 mW/cm²) was used as the light source. The MO absorption maximum in the absorption spectrum of the aqueous phase was used as an indicator of the photodegradation products. For this heterogeneous reaction, no photodegradation of MO was observed (Figure S6A), which is likely due to the low excitation power and lack of contact between the QDs and MO. As a comparison, Pickering emulsions were prepared with an aqueous solution containing MO dye molecules. With Pickering emulsions as photocatalysts, the MO absorption maximum dropped under the same reaction conditions (Figure 5A). It is worth noting that, because of the amphiphilic properties of Pickering emulsions, the absorption spectra of the

aqueous layer contain features indicative of PbS QDs (Figure 5A, solid red). Subtraction of a scaled absorption spectrum (Figure 5A, black) of PbS QDs yields a different spectrum that reflects only that of MO molecules (Figure 5A, dashed red). Changes to the MO absorption maximum intensity are used to calculate the percentage of photodegradation reaction. Under the same conditions as those discussed above, we found that MO was degraded by 23% in the presence of Pickering emulsions. Increasing the intensity of light and/or increasing the reaction time increases the MO photodegradation reaction. Figure 5B exhibits the difference spectra of an MO aqueous solution after photodegradation with Pickering emulsions for different reaction times (see Figure S7 for details). The yield of the photodegradation reaction increases with the reaction time and is over 80% for all three conditions, much higher in comparison with the 23% yield for the reaction with a weaker excitation (Figure 5C). As a control experiment, no MO degradation was observed when PbS/OA was used under light-emitting-diode (LED) illumination (Figure S6B). Additionally, a CAH molecule by itself does not photocatalyze the MO degradation reaction (Figure S6B), which confirms the photocatalytic effect of Pickering emulsions.

In summary, we demonstrated the formation of Pickering emulsions with electrooptic-active semiconductor QDs. The amphiphilicity of PbS QDs was realized by the construction of Janus-ligand shells comprising lipophilic OA and hydrophilic CAH. The homogenization of PbS QDs with Janus-ligand shells together with water and dichloromethane forms spherical-shaped Pickering emulsions observed under both optical and electron microscopes. With MO photodegradation as a model reaction, we demonstrated that Pickering emulsions can be used to enhance the reaction yield of heterogeneous reactions photocatalyzed by PbS QDs. We believe this study will be helpful for extending applications of QD Pickering emulsions to a wider range of photocatalytic organic transformations, such as C–C coupling, dehalogenation, etc.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnm.2c00341>.

Synthesis of PbS QDs and CAH, experimental details about the preparation of Pickering emulsions, photo-

catalytic reactions, a 2D NMR spectrum, and TEM and SEM-EDS analysis (PDF)

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Notes

The authors declare no competing financial interest.

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