

Research Article

The Synthesis of Amphiphilic Luminescent Graphene Quantum Dot and Its Application in Miniemulsion Polymerization

Minxiang Zeng,¹ Xuezheng Wang,^{1,2} Yi-Hsien Yu,³ Lecheng Zhang,^{1,2} Wakaas Shafi,¹ Xiayun Huang,¹ and Zhengdong Cheng^{1,2,3}

¹Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843-3122, USA

²Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843-3122, USA

³Department of Material Science and Engineering, Texas A&M University, College Station, TX 77843-3003, USA

Correspondence should be addressed to Zhengdong Cheng; zcheng@tamu.edu

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Although emulsion applications of microscale graphene sheets have attracted much attention recently, nanoscale graphene platelets, namely, graphene quantum dots (GQDs), have been rarely explored in interface science. In this work, we study the interfacial behaviors and emulsion phase diagrams of hydrophobic-functionalized graphene quantum dots (C_{18} -GQDs). Distinctive from pristine graphene quantum dots (p-GQDs), C_{18} -GQDs show several interesting surface-active properties including high emulsification efficiency in stabilizing dodecane-in-water emulsions. We then utilize the C_{18} -GQDs as surfactants in miniemulsion polymerization of styrene, achieving uniform and relatively small polystyrene nanospheres. The high emulsification efficiency, low production cost, uniform morphology, intriguing photoluminescence, and extraordinary stability render C_{18} -GQDs an attractive alternative in surfactant applications.

1. Introduction

In Pickering emulsions, the solid particles play a key role at the interface of two immiscible phases to prevent the coalescence by generating a mechanically robust monolayer [1]. This field received widespread scientific interests for developing stable Pickering emulsions/foam [2–4], double emulsions [5–8], liquid marbles, and superhydrophobic barriers [9, 10]. As nanomanufacturing processes are getting mature and well-controlled, more and more nanomaterials are adopted as the stabilizers for Pickering emulsions, such as functionalized silica, titania nanoparticles, zirconium phosphate, protein microgel, clay, and polymer particles [11–21]. However, most procedures are still relatively complicated and require costly reagents for synthesizing the amphiphilic nanoparticles with desired properties, resulting in limited applications.

Carbon-based nanoparticles have attracted much attention in the past decades owing to their low cytotoxicity, chemical inertness, cost-effectiveness, and biocompatibility [22–28]. Because it is also difficult to obtain the desired surface

properties, there were only few works reporting graphene-based materials as surfactants [11, 29]. Recently, Yin et al. demonstrated that graphene oxide (GO) nanosheets were utilized in Pickering emulsion polymerization to form GO coated polystyrene (PS) microspheres with a narrow range of size distribution [30]. Although pristine GO nanosheets could not stabilize the styrene droplets in aqueous phase due to high hydrophilicity of GO, the hydrophobic modification by adsorbing PS oligomers on GO surface led to the nascent nuclei formation and continuous Pickering emulsion polymerization successfully. In 2014, Kim et al. reported a top-down method for synthesizing graphene quantum dots (GQDs) as surfactants [11]. Pristine GQDs (p-GQDs) were first studied and showed poor emulsification performance. By thermally reducing the oxygen-containing groups on p-GQDs, the hydrophobicity was improved and further enabled the reduced GQDs (r-GQDs) to serve as the interface stabilizer in toluene-in-water emulsions. However, due to the limited hydrophobicity introduced by thermal reduction, the

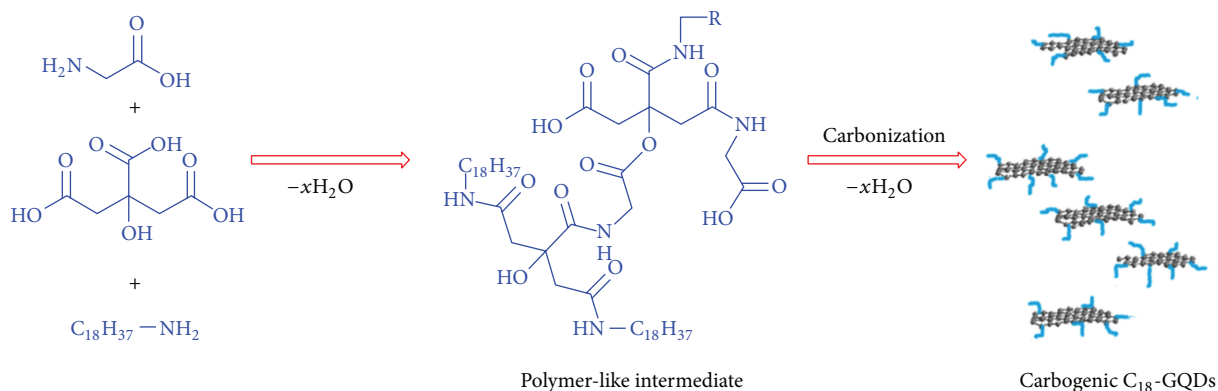


FIGURE 1: The schematic illustration of the formation of C_{18} -GQDs.

average size of Pickering emulsions stabilized by r-GQDs was relatively large, and the size distribution of PS colloidal particles was much broader than that of PS colloidal particles stabilized by organic/polymer surfactant [31]. Therefore, it is desirable to develop a highly efficient particle surfactant by controlling the wettability of the amphiphilic GQDs.

An alternative method to improve hydrophobicity of nanoparticles can be achieved by introducing hydrophobic functional groups, such as alkane chain. In this study, we developed a facile bottom-up approach to synthesize octadecyl grafted luminescent graphene quantum dots (C_{18} -GQDs) surfactant with controllable wettability. The oleophilicity and hydrophilicity of C_{18} -GQDs were balanced by controlling the chemical condensation of hydrophobic alkane chain. As a novel class of efficient particle stabilizers for Pickering emulsions, C_{18} -GQDs demonstrated the ability to stabilize dodecane-in-water emulsions and were employed to produce PS/GQDs microspheres via miniemulsion polymerization of styrene. The pristine graphene quantum dots (p-GQDs) were also synthesized without octadecyl group grafting for comparison.

2. Materials and Methods

2.1. Materials. All chemicals and solvents were used as received without further purification unless otherwise stated. Citric acid monohydrate (Sigma-Aldrich, USA), azobisisobutyronitrile (AIBN, Sigma-Aldrich, USA), glycine (Fluka, USA), octadecylamine (Acros, USA), styrene (Acros, USA), and dodecane (Acros, USA) were used.

2.2. Synthesis of C_{18} -GQDs. Figure 1 shows the schematic illustration of C_{18} -GQDs synthesis. First, 1.0 g of citric acid monohydrate (4.8 mmol) was dissolved in 25 mL of ethanol, followed by adding an ethanol solution containing 0.75 g of octadecylamine (2.8 mmol). The mixture was stirred for 1 hour, and the formed precipitate was filtered and washed with ethanol several times. After drying in an oven at 65°C for 24 hours, the white solid product was mixed with 0.3 g of glycine (4.0 mmol) and then transferred into a 20 mL glass vial and calcinated in air at 200°C for 3 h. The dark solid residue was further purified by column chromatography to remove unreacted starting materials for obtaining C_{18} -GQDs. For

comparison, hydrophilic p-GQDs were prepared by a previous work [23]. Specifically, the citric acid was heated in a 20 mL glass vial in air at 200°C without the addition of octadecylamine for comparison.

2.3. Contact Angle Measurement. Homogeneous C_{18} -GQDs films were prepared by coating a few drops of C_{18} -GQDs dispersion (0.18 wt%) onto precleaned glass plates, followed by drying at 70°C for 4 h. After cooling down to room temperature, one drop of deionized water was placed onto the surface and allowed to equilibrate for 20 s before making any measurement. Homogeneous p-GQDs films were prepared by the same procedure. A digital camera was used to record the images and their contact angles were calculated by *PolyPro* software package.

2.4. Preparation of C_{18} -GQDs Pickering Emulsions. To prepare aqueous dispersion, the purified graphene quantum dots were dissolved in 1 mL acetone followed by 20 mL deionized water. Then, the acetone was removed at 65°C under a reduced pressure. Finally, the C_{18} -GQDs dispersion was centrifuged for 20 minutes at 4000 rpm to remove possible aggregates. Part of the final dispersion was taken out to determine concentration by drying at 75°C in an oven for 2 days. For Pickering emulsion formation, C_{18} -GQDs and p-GQDs dispersions with the designed weight percentages were brought into a glass vial, and then dodecane was slowly added to the dispersion under sonication for 2 minutes.

2.5. Preparation of C_{18} -GQDs/PS Composites. First, prepare 0.9 mL C_{18} -GQDs aqueous solution (0.18 wt%) in a 5 mL glass vial, and 0.1 mL styrene and 2 mg azobisisobutyronitrile (AIBN) were then introduced. This mixture was manually shaken for 30 seconds. Finally, the entire suspension of C_{18} -GQDs/PS precursor was transferred into a 70°C oven for 4 hours, allowing for the full polymerization of styrene. The products were washed with warm DI water (50°C) twice and then dried using a freeze drier.

2.6. Characterization. The morphologies of C_{18} -GQDs and C_{18} -GQDs/PS composites were characterized by transmission electron microscopy (TEM, JEM-2010, JEOL) operated at an accelerating voltage of 200 kV and field emission

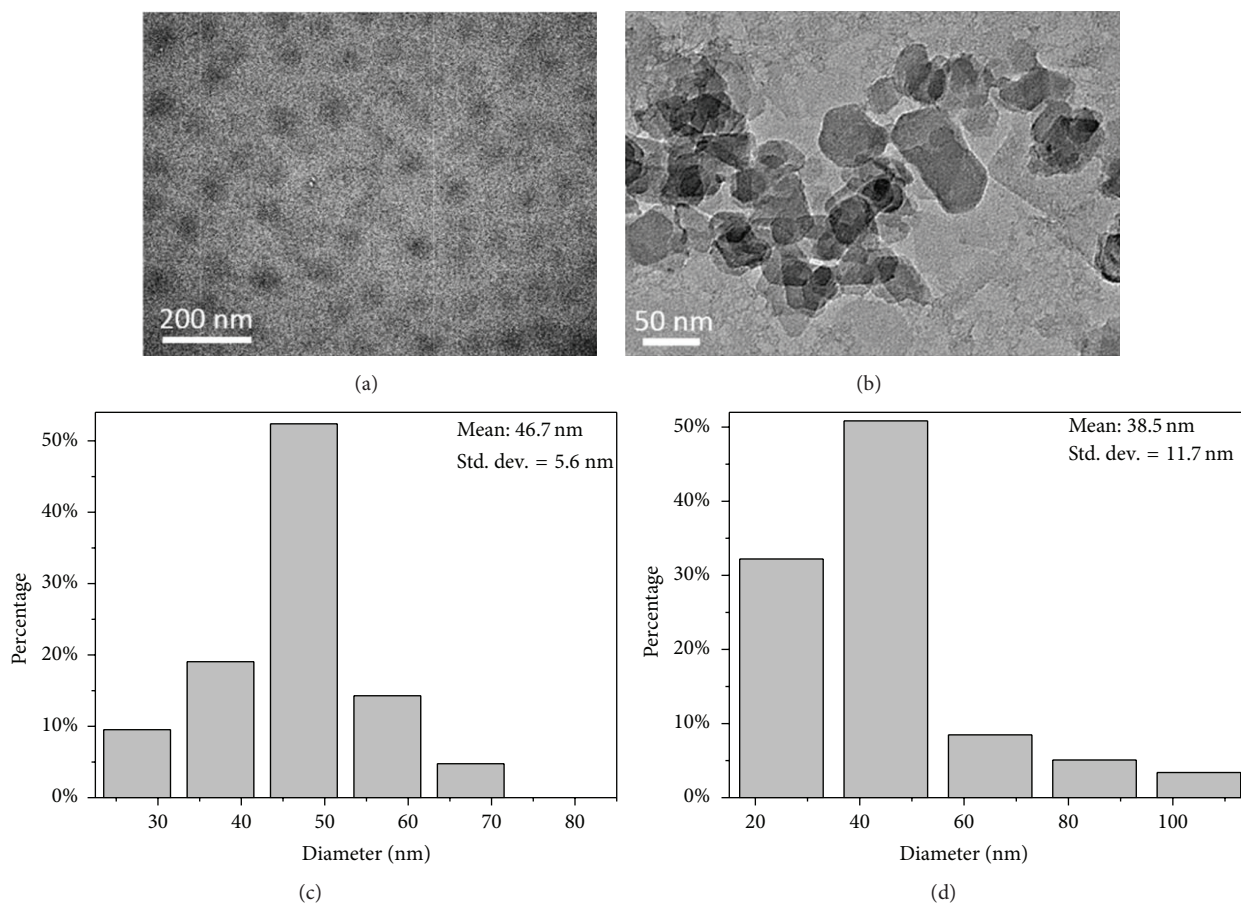


FIGURE 2: TEM images of (a) C₁₈-GQDs and (b) p-GQDs and the size distribution histograms of (c) C₁₈-GQDs and (d) p-GQDs.

scanning electron microscopy (FE-SEM, Quanta 600, FEI). The particle-size distribution of C₁₈-GQDs Pickering emulsion droplets was determined by dynamic light scattering (DLS, Zetasizer Nano ZS90, Malvern Instruments).

3. Results and Discussions

3.1. Characterization of C₁₈-GQDs. Graphene quantum dots are commonly considered as mono- or few layered graphene sheets or polyaromatic species with lateral dimensions in the range of 1–100 nm [32]. TEM images of C₁₈-GQDs were taken to verify their morphologies. In Figure 2(a), C₁₈-GQDs showed an average size of 46.7 ± 5.6 nm, which resembled the results reported previously [27, 33, 34]. Comparing with p-GQDs, the low resolution/contrast of TEM image of C₁₈-GQDs might be due to the functionalization of edge of graphene sheets, which were also observed in other polymer functionalized GQDs [27, 35].

Size distributions of GQDs were performed by analysis of TEM images, counting at least 100 particles. As shown in Figure 2(c), the size distribution of as-prepared C₁₈-GQDs was relatively narrow, suggesting a uniform arrangement. The morphologies of p-GQDs were also studied by TEM, as shown in Figure 2(b). The average size of p-GQDs was 38.5 nm with standard deviation of 11.7 nm, indicating that

the average sizes of C₁₈-GQDs and p-GQDs were similar. The C₁₈-GQDs were found to be well dispersed in organic solvents such as acetone and toluene but had only limited solubility in water, which indicated successful grafting of organophilic groups on graphene nanoplatelets [35]. In contrast, p-GQDs behaved more like graphene oxide and were well dispersed in the water due to the existence of hydrophilic carboxylic group (-COOH) [23].

The surface chemistry of C₁₈-GQDs was further confirmed by Fourier transform infrared spectroscopy (FTIR). In Figure 3, the characteristic vibrational bands at 1090, 1370, 1710, 2920, and 3380 cm⁻¹ were found, which can be assigned to the stretching vibrations of C-N/C-O, vibrational band of carboxylate ion (-COO⁻), the overlapped vibrational absorption bands of C=C and HN-(C=O)-R, the C-H stretching vibration, and the stretching vibrations of C-OH and N-H. These results indicated that the hydrophobic groups (i.e., alkyl groups) were functionalized by amide bonds [36–38].

In order to further prove the successful synthesis of graphene quantum dots, the optical properties of C₁₈-GQDs were examined by the ultraviolet-visible spectrophotometry (UV-Vis) and photoluminescence (PL) spectra at variable excitation wavelengths, as shown in Figure 4. The UV-Vis absorption spectrum of C₁₈-GQDs was generally broad in the range from 350 nm to 600 nm. In the inset in Figure 4,

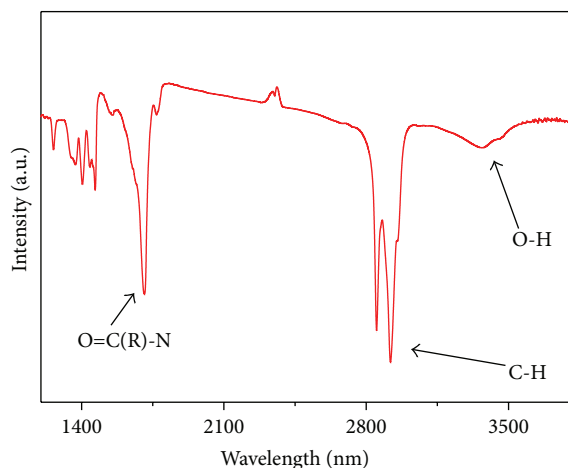


FIGURE 3: FTIR spectrum of C_{18} -GQDs.

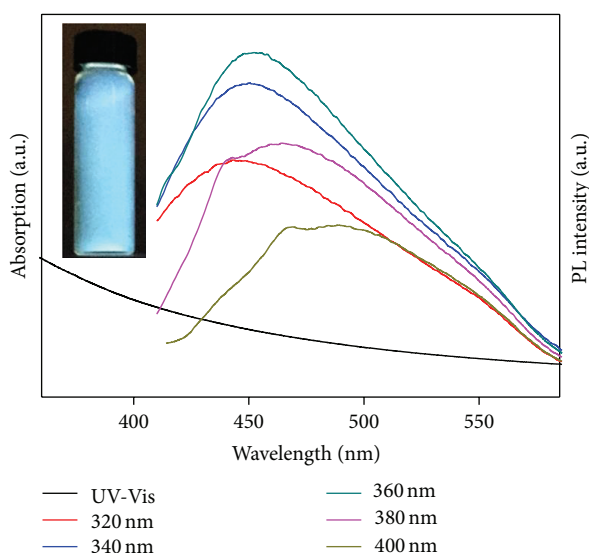


FIGURE 4: UV-Vis and PL spectra of functionalized C_{18} -GQDs. Inset: digital photograph of the C_{18} -GQDs under 365 nm UV light.

a bright blue luminescence light was observed at a low concentration (0.5 mg/mL) under the illumination of UV ($\lambda = 365$ nm). The PL spectra of C_{18} -GQDs were also broad and apparently dependent on the excitation wavelength. The PL peaks shifted to longer wavelengths as excitation wavelength increased from 320 to 400 nm. In particular, C_{18} -GQDs showed strong blue photoluminescence and had optimal excitation and emission wavelengths at 360 nm and 450 nm, respectively. Although the mechanisms underlying the PL properties of graphene quantum dots have not been completely understood yet, some theoretical modelling and calculations gave good insights into understanding PL mechanism of GQDs. For instance, by employing density-functional theory (DFT) and time-dependent DFT calculations, Sk et al. recently demonstrated that PL of a GQD could be essentially originated from the quantum confinement of conjugated π -electrons in sp^2 carbon grid and can be tuned by its size,

shape, edge configuration, attached chemical functionalities, and heteroatom doping and defects [39].

The wettability of C_{18} -GQDs was determined by measuring contact angles at water-air interface. As shown in Figure 5, the contact angle for p-GQDs is 14.6° , indicating the high hydrophilicity due to the existence of hydrophilic carboxylic group [23]. By contrast, the contact angle of 105.8° for C_{18} -GQDs is significantly larger than p-GQDs as well as 21.8° on glass substrates, proving that functionalization of graphene quantum dots with octadecyl group introduces substantial hydrophobicity. The effective improvement of surface amphiphilicity suggested that C_{18} -GQDs is expected to be an attractive candidate for stabilizing Pickering emulsions in comparison with highly hydrophilic p-GQDs.

3.2. Properties of the Emulsions. To examine the potential of the hydrophobic octadecyl grafted GQDs as the surfactant during emulsification, both p-GQDs and C_{18} -GQDs were used to prepare Pickering emulsions. At the relatively low concentration (0.1 wt%), p-GQDs were observed to have rarely emulsified the dodecane-in-water droplets (Figure 6(c)), while the dodecane/water mixture in the presence of C_{18} -GQDs formed a uniform emulsion (Figure 6(b)) that was similar to emulsions produced by amphiphilic polymer-based surfactants [31]. The poor emulsification efficiency of p-GQD indicated its overwhelming hydrophilicity, because the as-prepared p-GQDs contained a huge amount of oxygen-containing groups, including C-OH groups and -COOH groups [23, 27]. Thus, p-GQDs preferentially stayed in the aqueous medium. The introduction of octadecyl group on GQDs, however, induced a significant increase in the hydrophobicity and oleophilicity of the graphene quantum dots. The hydrophobic octadecyl group allowed GQDs to be strongly absorbed at the interface of water/dodecane, leading to a remarkable improvement in the emulsification efficiency. Moreover, as an effective means for estimating the emulsion stability and the emulsification effect [40], the droplet size distribution of the Pickering emulsions stabilized by C_{18} -GQDs was studied by DLS, as shown in Figure 6(a). The average droplet size for dodecane-in-water emulsions was 263 nm, with standard deviation of 51 nm. Microscopic study of Pickering emulsion droplets was also performed, suggesting uniform Pickering emulsion droplets. However, well-focused microscopic images were difficult to obtain because the Pickering emulsion size falls into the range of visible light wavelength, as shown in Figure 6(d).

Figure 6(e) shows the observations of oil-in-water emulsions preferentially formed when C_{18} -GQDs were introduced into the system at a relatively high concentration (2.0 wt%) [15, 41]. The emulsion types (oil-in-water and water-in-oil) were examined qualitatively by checking their miscibility in the water or oil phase [15]. That is, a drop of each emulsion was added to pure dodecane or to deionized water. In water, the oil-in-water emulsions dispersed but remained as drops in dodecane, and vice versa. As shown in Figure 6(e), the dodecane phase showed a dark brownish color due to the good solubility of C_{18} -GQDs in dodecane. Besides, oil-in-water emulsions (Winsor I type) were preferred to be formed when dodecane volume fraction was higher than 20%.

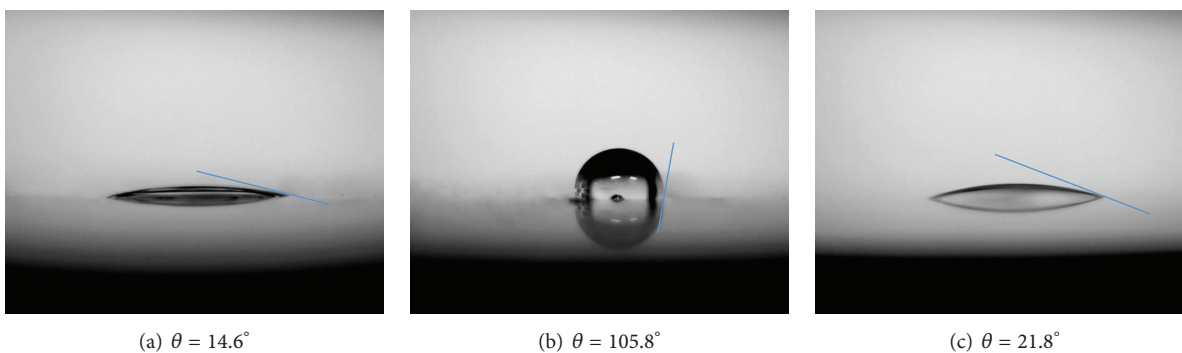


FIGURE 5: Contact angle measurements of (a) p-GQDs, (b) C_{18} -GQDs, and (c) bare glass substrate.

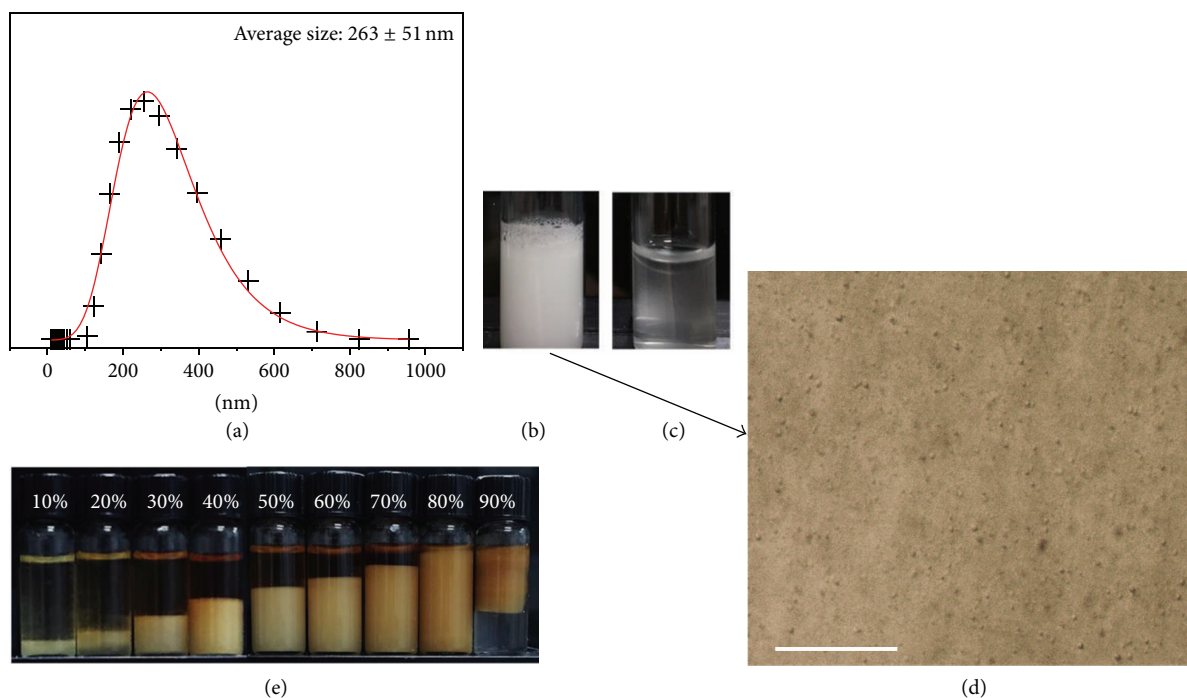


FIGURE 6: (a) The DLS spectra of Pickering emulsions stabilized by C_{18} -GQDs. Photographic images of dodecane/water mixtures containing (b) C_{18} -GQDs (0.1 wt%) and (c) p-GQDs (0.1 wt%). (d) Microscopic images of oil-in-water emulsions stabilized by C_{18} -GQDs (0.1 wt%) with scale bar of $50 \mu\text{m}$. (e) The emulsion phase diagram of C_{18} -GQDs (2.0 wt%) stabilized dodecane/water mixture with various volume fraction of aqueous phase from 10% to 90% at 20°C .

However, phase inversion occurred if oil volume fraction was low according to phase diagram [15, 41].

To further demonstrate the potential of C_{18} -GQDs as a surfactant, C_{18} -GQDs were employed to produce polymeric nanocapsules through miniemulsion polymerization method. To date, predominantly, the formation of polymeric capsules with a size of $1 \mu\text{m}$ and larger is demonstrated by Pickering polymerization. However, for many practical uses, especially in medicine and high-resolution electronic inks, smaller capsules with size between 50 and 300 nm are of high interest [42]. To achieve successful miniemulsion polymerization, the emulsion surface is required to be stabilized by adsorption of surfactants. By using C_{18} -GQDs as a surfactant and AIBN as an initiator, styrene was successfully emulsified

and polymerized to fabricate the uniform C_{18} -GQDs/PS microspheres, as shown in Figure 7. It was shown that the size of small microspheres was comparable to that of “thermodynamically” stable Pickering emulsions prepared by mechanical stirring of 3-methacryloxypropyltrimethoxysilane/ H_2O mixture with magnetite nanoparticles [14]. An average size of the PS nanoparticles was determined to be $152 \pm 8 \text{ nm}$, which was smaller than that of previously reported PS colloidal particles stabilized by graphene-based materials [11, 29, 30, 43–48]. In addition, the morphologies of C_{18} -GQDs/PS composites are similar to that of PS nanoparticles produced by commercial surfactants [31]. These results show that C_{18} -GQD is a promising candidate for a highly efficient surfactant forming oil-in-water Pickering emulsions. Further research is

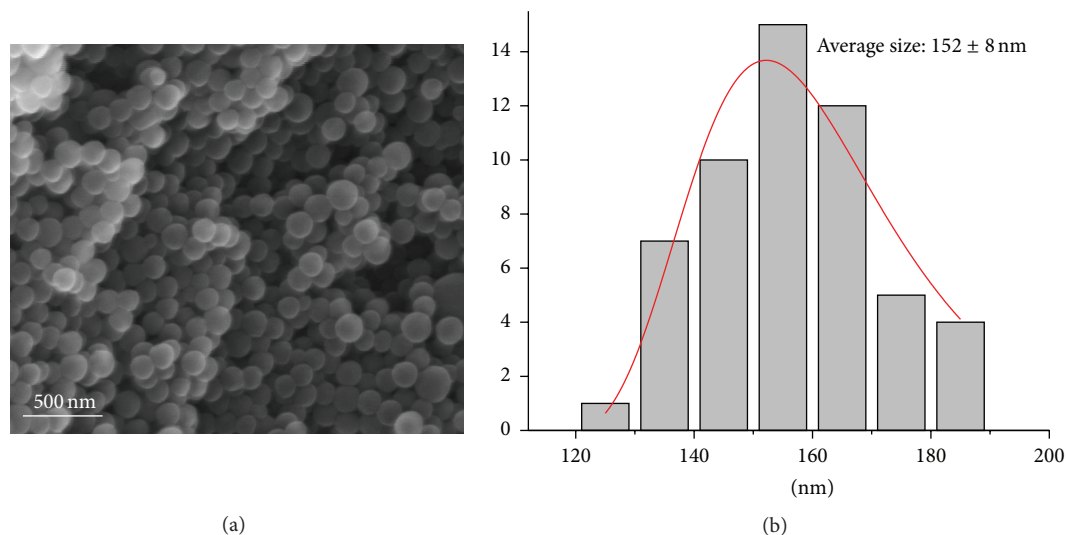


FIGURE 7: (a) SEM image of uniform PS particles stabilized by C_{18} -GQDs and (b) the corresponding histogram of PS colloidal particles stabilized by C_{18} -GQDs (0.18 wt%).

still needed, however, to address issues such as how to utilize photoluminescent properties and how to optimize the surface chemistry of functionalized graphene quantum dots.

4. Conclusions

In summary, we demonstrated that octadecyl grafted graphene quantum dots (C_{18} -GQDs) surfactants could be used as effective emulsifiers for stabilizing Pickering emulsions as well as for miniemulsion polymerization. Both the photoluminescent and excitation-dependent properties were characterized. Furthermore, by using functionalized graphene quantum dots, uniform Pickering emulsions of dodecane and water were formed with an average size of 263 ± 51 nm; in contrast, no stable Pickering emulsions were produced with the sole addition of nonfunctionalized p-GQDs. Phase diagram of C_{18} -GQDs further confirmed the well-balanced amphiphilic property and suggested that water-in-oil emulsions could be created by C_{18} -GQDs. Moreover, C_{18} -GQDs exhibited high efficiency as surfactants to synthesize uniform C_{18} -GQDs/PS nanocapsules via the miniemulsion polymerization. In the presence of C_{18} -GQDs, polymeric nanocapsules with an average size of 152 ± 8 nm were achieved. This facile one-pot bottom-up synthesis of amphiphilic GQDs combined with their luminescent property provides a possible direction for multifunctional carbon-based quantum dots.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

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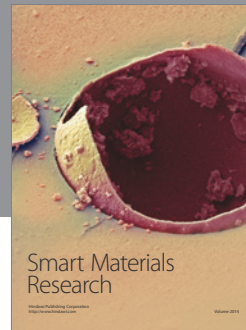
and Technology Development Project “Study on Asymmetric Modification Methods for Nanoplatelet Particles” (405550). The authors acknowledge the Microscope and Imaging Center (MIC) at Texas A&M University for access to the FE-SEM and TEM. The FE-SEM instrument was supported by the National Science Foundation under Grant DBI-0116835. The authors also thank Dr. Mustafa Akbulut for using his dynamic light scattering instrument.

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