Journal of Colloid and Interface Science 505 (2017) 847–857

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

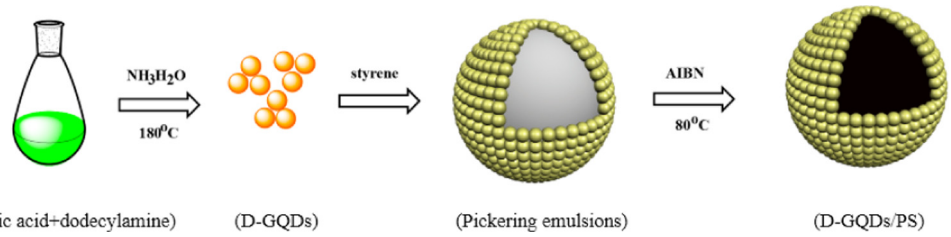
Synthesis of dodecylamine-functionalized graphene quantum dots and their application as stabilizers in an emulsion polymerization of styrene

Wang Xuan [a], Li Ruiyi [a], Li Zaijun [a,b,*], Liu Junkang [a]

[a] Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, China
[b] School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China

GRAPHICAL ABSTRACT

The paper reported synthesis of dodecylamine-functionalized graphene quantum dots via thermal pyrolysis of citric acid and dodecylamine in an ammonium hydroxide solution. The graphene quantum dots exhibit high surface activity. It has been successfully applied as a stabilizer in Pickering emulsions polymerization of styrene.



ARTICLE INFO

Article history:
Received 23 April 2017
Revised 22 June 2017
Accepted 26 June 2017
Available online 27 June 2017

Keywords:
Synthesis
Amphiphilicity
Solid particle surfactant
Emulsion polymerization
Polystyrene spheres

ABSTRACT

Pickering emulsions have attracted considerable interest due to their potential applications in many fields, such as the food, pharmaceutical, petroleum and cosmetics industries. The study reports the synthesis of dodecylamine-functionalized graphene quantum dots (D-GQDs) and their implementation as stabilizers in an emulsion polymerization of styrene. First, D-GQDs are prepared by thermal pyrolysis of citric acid and dodecylamine in 0.1 M ammonium hydroxide. The resulting D-GQDs consist of small graphene sheets with abundant amino, carboxyl, acylamino, hydroxyl and alkyl chains on the edge. The amphiphilic structure gives the D-GQDs high surface activity. The addition of D-GQDs can reduce the surface tension of water to 30.8 mN m^{-1} and the interfacial tension of paraffin oil/water to 0.0182 mN m^{-1}. The surface activity is much better than that of previously reported solid particle surfactants for Pickering emulsions and is close to that of sodium dodecylbenzenesulfonate, which is, a classical organic surfactants. Then, D-GQDs are employed as solid particle surfactants for stabilizing styrene-in-water emulsions. The emulsions exhibit excellent stability at pH 7. However, stability is lost when the pH is more than 9 or less than 4. The pH-switchable behaviour can be attributed to the protonation of amino groups in a weak acid medium and dissociation of carboxyl groups in a weak base medium. Finally, 2,2′-azobis(2-methylpropionitrile) is introduced into the Pickering emulsions to trigger emulsion polymerization of styrene. The as-prepared polystyrene spheres display a uniform morphology with a narrow diameter distribution. The fluorescent D-GQDs coated their surfaces. This study presents an approach for the fabrication of amphiphilic GQDs and GQDs-based functional materials, which have a wide range of potential applications in emulsion polymerization, as well as in sensors, catalysts, and energy storage.

* Corresponding author at: School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China.
E-mail address: zaijunli@jiangnan.edu.cn (L. Zaijun).

http://dx.doi.org/10.1016/j.jcis.2017.06.091
0021-9797/

1. Introduction

Pickering emulsions are stabilized by solid particles [1,2]. The stabilization of emulsion droplets takes place through adsorption of solid particles at the surface of emulsion droplets [3]. The emulsion stability often depends on the oil phase polarity [4], pH and ionic strength [5], monomer type [6] and other factors [7]. To improve emulsion stability and introduce functional materials, many nanomaterials have been developed as solid particle surfactants, such as silica nanoparticles [8,9], titania nanoparticles [10], ZIF-8 [11], ovalbumin [12], clay nanoparticles [13,14], Fe_3O_4 nanoparticles [15] and soft s protein microgel particles [16]. Recently, Pickering emulsions have attracted high interests due to potential applications in many fields such as food [17], pharmaceutical [18], petroleum [19] and cosmetics [20]. However, current solid particle surfactants for Pickering emulsions lack ideal surface activity, which may lead to poor emulsion stability. The fabrication of amphiphilic solid particles with high surface activity fo Pickering emulsions has received significant attention.

At the present, graphene is known as the most researched material in academia [21]. The growing interests of graphene are predominantly attributed to its remarkable properties, which have been shown to reach the highest theoretical limit known for materials [22]. The facile natures in the material preparation process and high production scalability have propelled extensive research, thus leading to the expansion of its applications in supercapacitors [23], lithium ion batteries [24], sensors [25], photodetectors [26] and drug delivery [27,28]. In recent years, graphene and its derivatives have also been investigated as solid surfactants for stabilizing Pickering emulsions [29]. Graphene has extremely high hydrophobicity and weak hydrophilicity. The inappropriate amphiphilicity gives it low surface activity. Pickering emulsions stabilized by graphene often display poor emulsion stability. To improve the amphiphilicity, graphene is hybridized with water-soluble macromolecules [30]. Contrary to graphene, graphene oxide (GO) contains more hydroxyl and epoxide groups on the basal planes and carboxylic acid groups at the edges. This structural characteristic gives GO a more appropriate amphiphilicity compared to graphene [31,32]. As a solid surfactant, GO also has inherent deficiencies from the micron size of the graphene sheets. These large graphene sheets can easily aggregate on the fluid interface and form a rigid interfacial layer, thus leading to low surface activity. To resolve this problem, Huang et al. developed an approach for the preparation of GO sheets with a lateral dimension smaller than 100 nm via chemical exfoliation of graphite nanofibers [33]. The investigation proved that GO sheets are surfactants with size-dependent amphiphilicity. Smaller GO sheets should be more hydrophilic due to their higher density of charges originating from the ionized carboxyl groups on their edges. Thus, the nano-GO can act as a better dispersing agent for insoluble materials in water compared to regular GO, creating a more stable colloidal dispersion. Nano-GO has been used as the stabilizer in mini-emulsion polymerization for the construction of a graphene-based composite [34]. Compared with nano-GO, graphene quantum dots (GQDs) consist of smaller graphene sheets with more hydrophilic groups [35–37]. The nano-size allows the graphene sheets to be neatly arranged on an oil-water interface and to exhibit high surface activity. The number of hydrophilic groups means that GQDs have better water-solubility compared with GO. More importantly, the unique structure of GQDs leaves us a vast design space to adjust the amphiphilicity. Cho et al. functionalized GQDs with hexylamine and investigated how the polymerization reaction was affected by the amount of amine grafted onto the GQD surfaces [38]. Zeng et al. modified GQDs with octadecylamine and studied how the GQDs concentration and the relative proportions of oil and water in the emulsions influenced the type of emulsion stabilized by the GQDs [39]. These studies showed that the introduction of alkyl chain on the edge of graphene sheets is an effective approach to improve the surface activity of GQDs.

In the study, we report a facile synthesis of dodecylamine-functionalized graphene quantum dots (d-GQDs) via the thermal pyrolysis of citric acid and dodecylamine. The as-prepared d-GQDs offer excellent surface activity due to the appropriate amphiphilic structure. It is then successfully applied as a stabilizer in the emulsion polymerization of styrene.

2. Experimental

2.1. Materials

Citric acid, 2,2′-azobis(2-methylpropionitrile) (AIBN), dodecylamine, ammonium hydroxide solution and styrene were purchased from Sigma-Aldrich (Mainland, China). Britton-Robinson buffer solution (BR buffer, H_3PO_4-HAc-H_3BO_3, 0.04 M) was prepared and its pH was adjusted using 0.2 M sodium hydroxide (NaOH) aqueous solution. Other reagents were purchased from Shanghai Chemical Company (Shanghai, China). All chemicals used were of analytical grade or of the highest purity available unless otherwise stated and used as received without further purification. Ultrapure water (18.2 MΩ cm) purified from a Milli-Q purification system was used throughout the experiment.

2.2. Synthesis of d-GQDs

d-GQDs were synthesized by one-step thermal pyrolysis of citric acid and dodecylamine in an ammonium hydroxide solution [40]. In a typical synthesis, citric acid (0.96 g), dodecylamine (0.056 g) and ammonium hydroxide (0.04 ml) were dissolved in ultra pure water (10 ml). The mixed solution was transferred into a 20 ml autoclave pressure vessel, followed by heating at 180 °C for 3 h and cooling to room temperature. The resulting d-GQDs were dissolved in ultra-pure water to form a transparent d-GQDs solution (60 mg ml^{-1}). The acidity of the solution was adjusted to pH 7.0 by adding NaOH. The solution was filtered with 0.22 μm filter membrane to remove larger product and by-products and then dialysed in a dialysis bag with a molecular weight cut-off 3 kDa. Water was changed every 6 h before precipitation occurred in the bag. The collected solution in the bag was dried by freeze-drying to obtain a solid sample of d-GQDs. Two control samples, butylamine-functionalized graphene quantum dots (B-GQDs) and octylamine-functionalized graphene quantum dots (O-GQDs), were also prepared by using the same procedure by using butylamine and octylamine instead of dodecylamine.

2.3. Material characterization

Scanning electron microscopy (SEM) and energy dispersive X-ray spectrum (EDX) analysis were performed using a HITACHI S4800 field emission scanning electron microscope. The SEM sample was prepared by dropping diluted ethanol dispersion of the products on a copper sheet attached to an aluminium sample holder, and the solvent was completely evaporated at room temperature. Transmission electron microscope (TEM) analysis was carried out on a JEOL 2010 (HR) transmission electron microscope at 200 keV. The sample was prepared by dispersing a small amount of powder-like product into absolute ethanol. Then, one drop of the above suspension was dropped on the surface of 300 mesh copper and was dried under an infra-red lamp to volatilize the ethanol. X-ray diffraction (XRD) pattern was obtained on a X-ray D8 Advance instrument operated at 40 kV and 20 mA using Cu Kα radiation source with λ = 0.15406 nm. Infrared spectrum (IR) was recorded