

Regular Article

Strategies for controlled synthesis of nanoparticles derived from a group of uniform materials based on organic salts



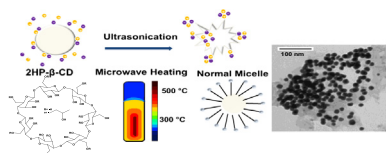
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GRAPHICAL ABSTRACT



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ABSTRACT

Over the past several years, nanomaterials derived from a group of uniform materials based on organic salts (GUMBOS) have been introduced into the scientific literature involving many analytical, biological, and technological applications. In this regard, these nanoGUMBOS have been shown to display a number of unique properties including fluorescence, magnetism, tumor targeting, and optoelectronic. To date, however, little focus has been placed on developing and refining approaches for generation of size-controlled nanoGUMBOS from GUMBOS building blocks. Herein, we describe a systematic effort to define various strategies for the production of well-defined nanoGUMBOS. Specifically, we describe methods based on (i) sonochemical, (ii) microwave-assisted, (iii) cyclodextrin-assisted, and (iv) surfactant-assisted syntheses of nanoGUMBOS, evaluating the efficiency of each technique in controlling the size, sphericity, and uniformity of nanoGUMBOS produced. The effect of systematic variation in experimental parameters such as concentration, cation-to-anion ratio, as well as presence and type of template introduced for formation of nanoGUMBOS is also investigated.

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1. Introduction

Materials at the nanoscale level frequently manifest new and interesting functionalities not shown in the corresponding bulk state. The dimensions and uniformity of such particles are often important to tailoring these functionalities, and in turn, allow expansion of the possible scope of applications. Thus, much of the current interest in nanoparticles stems from interest in the

improved physical, chemical, and electronic properties of these colloidal systems [1,2]. In this regard, non-conventional superconductive and magnetic properties that are not present in the corresponding bulk state in combination with quantum size effects have garnered considerable attention [2,3]. Such properties are highly dependent on the dimensions and stacking arrangements (e.g., assemblies of molecular aggregates) of these materials, which result in variable electronic states confined within the nanoparticles [2,4]. The significance of this size and stacking dependence is embedded in the ability to improve physical properties such as the strength and rigidity of solids and to control the electrical/optical properties of nanoparticles [2,4]. In particular, synthesis of nanoparticles with a desired size, narrow size distribution, and

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minimal aggregation is necessary for reliable performance in many applications [5,6].

Over the past several years, organic-based nanoparticles have been the subject of much research as a result of the inherent physiological compatibility of these nanomaterials. In addition, the poor water solubility of these compounds favors the conversion of bulk into nanoscale materials within aqueous media [3,7]. Many organic nanoparticles have also been shown to display size-dependent changes in electronic transitions that are often attributed to the appearance of inter- and intra-molecular overlapping structures at the nanoscale level [8]. Changes in spectroscopic properties resulting from size dependence of organic nanoparticles have been described as “structural confinement” effects [8]. Therefore, tuning the size of organic nanoparticles is of great interest to researchers because size-control of such materials can widen potential applications for photonic crystals and various light-emitting materials [8,9].

In the recent realm of organic-based nanomaterials, nanoGUMBOS which are derived from a group of uniform materials based on organic salts (GUMBOS), emerge as solid-phase materials that possess many of the ionic liquids properties. By definition, GUMBOS are organic salts with a defined melting point range of 25–250 °C and, as is true for ionic liquids, have a broad tunability via manipulation of the cation or anion [10,11]. NanoGUMBOS thus combine the versatility of GUMBOS with the enhanced properties often obtained at the nanoscale, offering the flexible design of organic nanomaterials. Within the last few years, nanoGUMBOS which possess fluorescent [12–14], magnetic [15], luminescent [16], pH-sensitive [17], optoelectronic [18], and anticancer [19] properties have been described. Previous studies from our laboratory have demonstrated the wide tunability in the spectral and physical properties, as well as the morphologies of nanoGUMBOS through variation in the associated counter ion [14,18,20]. Therefore, nanoGUMBOS have found application in various fields including analytical chemistry, biomedicine, and electronics. So far, little work has been done to formulate reliable approaches for generation of nanoGUMBOS of controlled size, uniformity, and sphericity. However, improved synthetic control of nanoGUMBOS is essential for tailoring these materials for target applications. In 2008, the Warner research group published the first report on the synthesis of ionic liquid-derived nanoparticles using a melt–emulsion–quench method [21]. Nevertheless, the size-control of melt–emulsion–quench-derived nanoparticles was still considered a major challenge. In some of our more recent studies, a reprecipitation approach commonly employed in the synthesis of organic nanoparticles [22,23] was extended to the preparation of nanoGUMBOS in an aqueous medium [12,14,18,19]. Although this method can be used to produce nanoparticles with average sizes in the nanometer regime, it is difficult to deliver nanoparticles smaller than 20 nm without using additives such as surfactants or polymers [24]. Furthermore, there are often limitations associated with the selection of poor and good solvents suitable for organic compounds used for reprecipitation [25]. Historically, nanoGUMBOS synthesis with size uniformity of 10% standard deviation alongside size-control is not easily accomplished. Templated approaches, such as reverse microemulsion [15] and hydrogel-assisted synthesis [13], have been successfully applied for the synthesis of nanoGUMBOS; however, both techniques present some limitations. Reverse microemulsions are suitable to achieve smaller nanoGUMBOS sizes, but frequently introduce unwanted agglomeration. In contrast, hydrogel-assisted synthesis routes can achieve low dispersity of nanoGUMBOS, yet cannot easily produce reduced-size nanoGUMBOS.

Here, we present our studies aimed at developing strategies for producing nanoGUMBOS with controlled sizes and narrow size distributions. The GUMBOS used in this study are derived from

imidazolium ionic liquids, which have been widely used as task-specific ionic liquids (TSILs) for metal extractions [26], for producing antimicrobial activity [27], and as electrolytes for electrochemistry, gas separations, and lignocellulose processing [28]. This study focuses on efforts to produce refined nanoGUMBOS using (i) sonochemical, (ii) microwave-assisted, (iii) cyclodextrin-assisted, and (iv) surfactant-assisted procedures. Sonochemical synthesis in this study employs a non-templating approach in the presence of ultrasonication acoustic waves (20 and 55 kHz), as well as a templating approach which involves use of a soft template (i.e., 2-hydroxypropyl- β -cyclodextrin (2HP- β -CD)). A microwave approach was employed with bath sonication in the absence of a template. In addition, we consider a surfactant-assisted approach that includes the use of Triton X-100 (TX-100) to form a normal micellar template. Overall, this study contrasts non-templated and templated techniques for the formation of uniform particles derived from GUMBOS, at the nanoscale level. Our goal of producing nanoGUMBOS with relatively low polydispersity was primarily achieved through the use of soft templating methods which yielded spherical and quasi-spherical nanoGUMBOS between 12 and 99 nm in mean size with relatively low polydispersity of 2–13 nm.

2. Experimental section

2.1. Materials

1-Hexyl-3-methylimidazolium chloride [Hmim][Cl] (97%), 2-hydroxypropyl- β -cyclodextrin (MS = 0.6 and 0.8), TX-100 were purchased from Sigma Aldrich (St. Louis, MO) and used as received. Sodium tetraphenylborate [Na][TPB] (99.5%) was purchased from TCI America (Portland, OR) and used as received. Ultrapure water (18.2 M Ω cm) was obtained from an Elga model PURELAB ultra water filtration system.

2.2. Melting point and thermogravimetric measurements

Melting point and thermogravimetric measurements were both performed on bulk [Hmim][TPB]. For acquisition of melting point data, a DigiMelt MPA 160 from SRS (Sunnyvale, CA) was used and a Hi Res Modulated TGA 2950 Thermogravimetric Analyzer from TA instruments (New Castle, DE) was employed for measurement of thermal decomposition temperatures. In our experimental procedure, equal volumes of equimolar aqueous solutions of [Hmim][Cl] and [Na][TPB] reactants were mixed. This mixture was magnetically stirred for a few hours and then centrifuged at a speed of 3800 rpm (3180 rcf) for 30 min. The white precipitate [Hmim][TPB] was washed twice with water to remove the sodium chloride by-product and then lyophilized to eliminate water.

2.3. Transmission electron microscopy

Transmission electron microscopy (TEM) micrographs were obtained using a JEOL JEM-1011 TEM (München, Germany). A volume of 4–8 μ L nanoGUMBOS sample was drop-casted onto ultra-thin carbon-coated 400-mesh Ted Pella, Inc TEM grids (Redding, CA). Grids were washed with water to avoid any unwanted adsorption of by-products resulting from the anion-exchange reaction.

2.4. Light scattering and zeta potential measurements

Dynamic light scattering (DLS) and zeta potential measurements were performed on a Malvern Zetasizer Nano ZS from Malvern Instruments Ltd (Worcestershire, England). DLS samples were prepared in a disposable sizing cuvette while zeta potential

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