



Factors influencing the preparation of hollow polymer-graphene oxide microcapsules via Pickering miniemulsion polymerization



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ABSTRACT

The synthesis of hollow, cross-linked polymer particles ('capsules') via Pickering miniemulsion polymerization using graphene oxide (GO) nanosheets as sole surfactant is reported. The influence of monomer, cross-linker and initiator type was studied, in addition to hydrophobe loading and initiator concentration. The desired hollow capsule morphology was shown to be strongly dependent on the choice of cross-linker; an aromatic crosslinker (divinylbenzene) consistently yielded hollow structures as determined by transmission electron microscopy, whereas ethylene glycol dimethacrylate typically resulted in polymer particles with a solid core. The use of an aromatic monomer with high propagation rate coefficient (benzyl methacrylate) and a strongly oil-soluble initiator, lauroyl peroxide, resulted in capsule synthesis with very high conversion (>85%) after 6 h. Surface area and pore analysis of the capsules established that while the capsules possessed a hollow interior, the shell was essentially non-porous. The potential of these materials towards novel nanocarbon-based materials was demonstrated via the preservation of colloidal stability and particle morphology after chemical reduction of GO, in addition to successful encapsulation of hydrophobic nanoparticles within the capsule core.

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1. Introduction

The preparation of nanoparticles with a thin carbon-based shell and hollow core ('nanocapsules') is of intense interest in numerous fields of nanotechnology. Due to their unique particle morphology and high surface area, nanocapsules find application in an array of areas including controlled release or encapsulation [1–3], supercapacitors [4,5], refractive index modulation [6] as well as catalytic supports [7,8]. Methods of preparing nanocapsules (and microcapsules) reported over the past few decades range from sol–gel methods (typically for inorganic-based capsules) [9], sacrificial colloidal templates [5,7], layer-by-layer assembly [10–12], Ostwald ripening [13,14], as well as polymerization-based approaches [15–17]. In examples where a

'hard template' is used (e.g. silica or polymer nanoparticles) to build the capsule-like structure, a final etching or template removal step is required – typically requiring the use of hazardous materials such as HF, which is often undesirable.

One of the most convenient methods towards the preparation of nanocapsules with a polymer shell is via miniemulsion polymerization. The miniemulsion process involves the polymerization of emulsified monomer droplets, typically prepared via high energy shear methods such as ultrasonication [18,19], and has been previously used to create composite particles of a wide variety of morphologies, including hollow structures [20,21]. This is typically achieved via the emulsification of an oil phase consisting of monomer, cross-linker (i.e. a monomer with two polymerizable groups) and a relatively large amount of a very hydrophobic compound such as hexadecane, whereby the polymer formed during polymerization is insoluble within the droplet interior (the very hydrophobic compound), resulting in phase separation. Interfacial tension results in the formed polymer adsorbing at the oil/water interface, yielding a cross-linked polymer capsule with a hollow interior [22–24]. The mechanism of miniemulsion polymerization also enables materials of interest to be encapsulated within the

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particle interior, ultimately leading to the creation of unique nanocomposite materials [21,25].

A particularly interesting sub-class of miniemulsion polymerization methods to generate polymeric capsules is that of Pickering miniemulsion polymerization [26]. A Pickering emulsion is an emulsion stabilized by a solid [27], as opposed to a more 'conventional' ionic or non-ionic surfactant, whereby adsorption of the solid nanoparticles at the emulsion droplet interface greatly reduces the interfacial energy of the system [28,29]. Examples of Pickering stabilizers in the context of miniemulsion polymerization include laponite clay [30,31], ceria [32], various modified or unmodified silicas [33–37], titania [38], and graphene oxide (GO) [39–43], of which silica, titania and GO have been used in the preparation of capsules with a hybrid (polymer/nanoparticle) shell and a hollow core [36,38,41]. In these cases, the polymer shells consisted of cross-linked poly(styrene-co-divinylbenzene) of varying composition (Cao et al. prepared shells of poly(styrene-co-divinylbenzene-co-4-vinylpyridine [36])), which were shown to be structurally stable in the dry state. In the case of GO as a Pickering stabilizer, reduction of GO after the preparation of the capsules (e.g. via chemical methods such as the use of hydrazine hydrate) enables the restoration of the graphitic framework within the shell with minimal loss of colloidal stability [41], which has potentially exciting applications in the field of graphene-based hybrid materials.

The use of GO as an effective oil-in-water (o/w) emulsion stabilizer is due to its amphiphilic nature and two-dimensional structure [44–47], however this phenomenon does come with certain limitations for polymer capsule synthesis. For example, GO-stabilized emulsions are readily formed for aromatic monomers (e.g. styrene, divinylbenzene, benzyl methacrylate) or particularly hydrophobic monomers (e.g. lauryl methacrylate) [39,40], due to the significant reduction in o/w interfacial tension upon adsorption of a GO nanosheet at the interface [48]. For more polar monomers, however, no significant reduction in interfacial tension is achieved and GO sheets are unlikely to wet the interface of an emulsion droplet. Previous work in our group on the preparation of both solid and hollow particles stabilized by GO also demonstrated a significant reduction in the polymerization rate (and low final conversion) for styrene, overcome only via the addition of an exceptionally high initiator concentration (e.g. 100 mM or 250 mM AIBN). This was not observed for methacrylates, potentially suggesting unexpected termination of growing poly(styrene) chains with functional groups at the surface of GO. The use of very high initiator concentrations also reduces the average primary chain length of the growing polymer, in turn reducing the degree of cross-linking of the polymer network, which has important implications in the preparation of hollow particles.

In this work, we present a thorough investigation of the numerous factors that influence the preparation of polymer capsules by Pickering miniemulsion polymerization, using GO as a colloidal surfactant. A range of monomers and cross-linkers of varying hydrophobicity and aromaticity have been analyzed, in addition to studying the influence of both initiator type and concentration. As one of the most crucial factors in the creation of hollow nanostructures by miniemulsion polymerization is the use of a hydrophobic non-solvent for the resultant polymer (which yields a hollow core), the effect of non-solvent loading has also been studied. We thus arrive at a suite of knowledge toward the synthesis of a variety of different hollow carbon nano- and micro-structures with differing chemistry, based on the nature of the polymeric shell. The results and approach represent an attractive route towards the preparation of such hybrid hollow nanoparticles with specific morphologies via a soft templating method.

2. Experimental

2.1. Materials

Styrene (Sigma Aldrich, >99%), Benzyl methacrylate (BzMA, Sigma Aldrich, >96%), Lauryl methacrylate (LMA, Sigma Aldrich, >96%), *tert*-Butyl Acrylate (tBA, Sigma Aldrich, >98%), Methyl methacrylate (MMA, Sigma Aldrich, >99%), Ethylene glycol dimethacrylate (EGDMA, Sigma Aldrich, 98%) and divinylbenzene (DVB, Sigma Aldrich, technical grade, 80%) were purified by passing through a column of activated basic aluminum oxide (Ajax) to remove inhibitors. Azobisisobutyronitrile (AIBN, Eastman Chemical Company) was purified by recrystallization twice from methanol; lauroyl peroxide (LPO, Sigma Aldrich, 97%) was recrystallized twice from ethanol. All other materials were used as supplied: graphite nanofibres (Catalytic Materials Ltd, >98%), hexadecane (HD, Sigma Aldrich, 99%), hydrazine hydrate (Sigma Aldrich), titanium dioxide (TiO₂, Degussa, P25), HCl (Ajax, 32%), H₂SO₄ (Ajax, 98%), H₃PO₄ (Chem Supply, 85% w/w), NaCl (Ajax, 99%), stearic acid (Sigma Aldrich, >98.5%), KMnO₄ (Ajax), H₂O₂ (Ajax, 30% w/w). All water used was Milli-Q grade.

2.2. Synthesis of graphene oxide (GO)

GO was synthesized via the oxidation of graphite nanofibres and using the method described in Marcano et al. [49] Firstly, 2 g of graphite was oxidized with 12 g KMnO₄ for 24 h in 250 mL of a 9:1 v/v mixture solution of H₂SO₄ and H₃PO₄ at 45 °C. After the reaction, the mixture was poured onto 400 g ice, followed by the addition of 15 mL of 30% w/w H₂O₂ and subsequent purification via multiple centrifugation and washing cycles of 3% w/w HCl, acetone and diethyl ether. The resultant material (yield 3.01 g) was dried in a vacuum oven and stored in a dessicator until use. The C:O atomic ratio was determined to be 1.87 by XPS (high resolution C1s spectra in Fig. S1a in Supporting Information), and TGA analysis revealed 29.4% of the original sample mass remained upon heating to 800 °C (Fig. S1c, Supporting Information).

2.3. Synthesis of hollow polymer-graphene oxide capsules via Pickering miniemulsion polymerization

A typical procedure is as follows. An aqueous solution of GO was prepared by dispersing 50 mg of GO in 9 mL water via 60 min of ultrasonication on ice (Branson Model 450 Digital Sonifier with microtip, 3 × 20 min cycles, 50% amplitude, 200 W). The number mean diameter (D_n) of GO nanosheets was 77 nm by DLS. The oil phase mixture, which consisted of monomer (one of styrene, BzMA, LMA, tBA or MMA), crosslinker (DVB or EGDMA) and hydrophobe (hexadecane, HD) was prepared independently; in to which the initiator (AIBN or LPO) was dissolved at certain concentration. The total mass of oil phase was maintained at 1 g for all experiments. Prior to mixing the two phases, a small quantity of NaCl was added to the GO dispersion to keep the aqueous phase at a constant ionic strength of 20 mM. The two phases were mixed gently by hand and ultrasonicated for 10 min in an ice bath (50% amplitude) to form a miniemulsion. The miniemulsion was degassed for 10 min via nitrogen bubbling in an ice bath, followed by polymerization at 70 °C under constant stirring (typically for 6 h). Conversion of monomer to polymer was determined via gravimetry.

2.4. Chemical reduction of capsules with hydrazine hydrate

Reduction of GO-stabilized polymer capsules occurred via the addition of 20 µL of hydrazine hydrate and 20 µL of ammonia per

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