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Fabrication and characterization of aluminum nanoparticles entrapped in hollow polymer capsules

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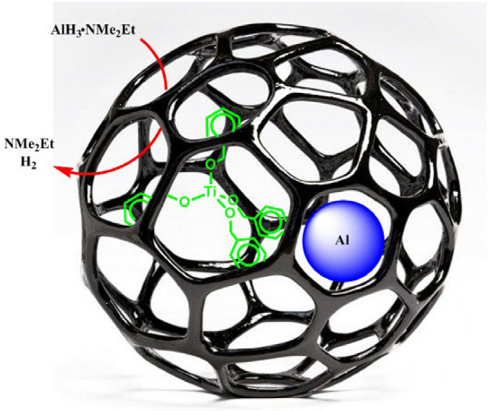
HIGHLIGHTS

- Hollow polymer nanocapsules synthesized by assembly within surfactant vesicles.
- Nanoreactor with titanium (IV) benzyloxide catalyst entrapped in hollow capsules.
- Al nanoparticles formed in nanocapsules with high active metal content.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we report on the *in situ* synthesis of aluminum nanoparticles within the cavity of hollow polymer nanocapsules. A novel titanium (IV) benzyloxide initiator was synthesized within and trapped inside the nanocapsule. The initiator and nanocapsule complex formed a nano-reactor environment in which alane was decomposed to form the nanoparticles, producing reactive metal–polymer nanorattles. The synthetic protocol resulted in air-stable nanoparticles with crystalline active core sizes of 18–23 nm. Thermal analysis showed combustion and metal ignition exotherms associated with the presence of aluminum confirming successful fabrication of Al NPs. The ratio of active aluminum (Al^0) to total aluminum present in any oxidation state was determined to be 85 %.

1. Introduction

Nanoscience and nanotechnology are being promoted by the remarkable merging of diverse fields including chemistry, material science, applied physics, optics, computational analysis and modeling. Metal nanoparticles (NPs) have attracted tremendous interest due to their applications in different areas such as catalysis, sensing, energetics, and imaging, resulting from their unique electronic [1], catalytic [2] and photonic [3] properties. Carbon nanotubes, for example, have been reported to offer signal enhancement in biosensors for cancer antigens through integrated microfluidic channels due to better sensitivity [4]. Astafyeva et al. recently reported on the theoretical platform for characterization and thermo-optical properties of various spherical metallic NPs for photonic and photothermal applications [5]. Gold nanoparticles have also been reported for use in plasmonic applications [6]. The unique physical and chemical properties of the nanoparticles, distinct from the bulk materials, have led to studies on the utilization of nanoscale materials for ultrasonic assisted adsorption

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of dyes [7]. Other ultrasonic assisted adsorption studies have also been reported for activated carbon loaded with copper sulfide nanoparticles (CuS-NP) [8], Fe_3O_4 magnetite nanoparticles [9] and Mn@CuS/ZnS nanocomposites [10] have been studied for possible enhanced removal of toxic dyes from wastewaters. Ardahaie et al. explored the effects of adding nanoparticles to blood to study fluid flow of non-Newtonian fluids [11]. The high thermal conductivities of nanoparticles have also been used to study heat transfer and thermal radiation in non-Newtonian nanofluids [12–15]. The possibilities of using monodispersed metal nanoparticles as electrodes for solar cells have been reported too [16].

Aluminum nanoparticles (Al NPs) are important in energy and fuel related applications because of Al's high energy density and reactivity with water and oxygen. The oxidation process of Al results in the production of large amounts of heat and, in reaction with protic systems, hydrogen gas [17]. The susceptibility of Al NPs to oxidation is, however, a major challenge during and after the synthesis; thus, careful passivation of the surface is required [18,19]. There are many methods that can be utilized to achieve this objective using organic molecules such as alkenes, alkyl-substituted epoxides, and acrylics among others [20–27]. Additionally, we have developed reactive metal/Al NPs that may be capped with an environmentally responsive organic polymer; such nanomaterials may be activated toward metal core reactivity (such as hydrolysis) by exposure to a specific physical stimulus e.g. light [28]. Inorganic agents and transition metals such as nickel, boron, and carbon have also been reported to provide shielding to the active Al NP cores [29–32]. Without passivation, an amorphous oxide layer, 2–6 nm thick, rapidly forms on the surface of the Al NPs upon exposure to air or water vapor [33,34]. Oxidized Al NPs have low volumetric energy density and a much higher ignition temperature to access the active metallic cores [35]. Furthermore, bare metal NPs have neither a kinetic nor a thermodynamic barrier to agglomeration [36]. The study on main group nanoparticles has indicated that the product distribution is driven by the thermodynamic stability of the nanoparticles [37]. Passivation limits agglomeration of the NPs by obstructing their growth in the initial stages. Hence, the particles are unable to come in contact and grow into larger sizes.

Nanocapsules (NCs) are spherical hollow polymeric structures. The control over their morphology can be achieved using self-assembly and templating techniques [38]. NCs with variable morphologies have been produced by a variety of methods [39,40]. The pores on the surface of NCs allow for diffusion into and out of their structure. Nanoencapsulation techniques also produce nanomatrices and core–shell nanocapsule structures, opening further avenues of exploration in nanotechnology [41]. Pinkhassik and coworkers have produced metal NPs with unreactive metals that were entrapped in NCs to produce structures they term "nanorattles" [42]. The metal NPs remained trapped in the interior of the nanorattle because the interior of the hollow capsules was functionalized to encapsulate and retain the guest materials that were bigger than the capsule pores. Nanorattles have also been demonstrated to be useful for sensing and catalysis applications of non-reactive metal NPs like gold [43,44].

In this work, we report on the first synthesis of nanorattles composed of reactive metal nanoparticles, specifically Al NPs, that are entrapped in polymeric nanocapsules. These new nanocomposite structures have been demonstrated to show significant air stability, with the Al NPs maintaining their energy density for extended periods of time upon exposure to ambient atmospheric conditions.

2. Experimental

2.1. Reagents and materials

Cetyltrimethylammonium tosylate (CTAT), sodium dodecylbenzenesulfonate (SDBS), *tert*-butyl methacrylate (*t*-BMA), butyl methacrylate (BMA) and ethylene glycol dimethacrylate (EGDMA) were purchased from Sigma-Aldrich and were passed through an aluminum oxide column to remove the inhibitor before sample preparation. The photo-initiator 2,2-dimethoxy-2-phenyl-acetophenone (DPA), alane *N,N*-dimethylethylamine alane ($AlH_3{\cdot}NMe_2Et$, 0.5 M) solution, titanium (IV) chloride, benzyl alcohol, ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA, $\sim$ 99%), and zinc sulfate heptahydrate (99.999%) were purchased from Sigma-Aldrich and were used without any additional purification. Toluene solvent was distilled over sodium metal under a dry argon atmosphere to remove any trace water and oxygen. Other solvents and chemicals used in this study were HPLC or ACS reagent grade, respectively, and were used as received.

2.2. Synthesis

2.2.1. Polymer nanocapsules

Hollow polymer nanocapsules were prepared by an existing protocol using controlled polymerization of hydrophobic monomers in the interior of bilayers of self-assembled surfactant vesicles [45]. When mixed with hydrophobic acrylate monomers, *tert*-butyl methacrylate (*t*-BMA), butyl methacrylate (BMA), ethylene glycol dimethacrylate (EGDMA) as a cross-linker and a photo initiator (2,2-dimethoxy-2-phenyl-acetophenone, DPA), aqueous solutions of cetyltrimethylammonium tosylate (CTAT, 20 mg) and sodium dodecylbenzenesulfonate (SDBS, 80 mg) form vesicles containing monomers in the hydrophobic interior of bilayers, which have been confirmed by DLS, SANS, and SAXS as previously described by Kim et al. [45].

2.2.2. Nanoreactor system

The nanoreactors were created by entrapping an organometallic catalyst in hollow NCs (0.400 g) with semipermeable nanometer-thin shells. We synthesized the catalyst from the reaction of titanium (IV) chloride and benzyl alcohol in 1:4 molar ratio. The reaction was performed in a glove box with purified toluene as solvent at room temperature. The NCs were first dried in an oven at 125.0 °C to remove any traces of water from the washes. Solid state FTIR analysis was performed to ensure that no water molecules were present before the catalyst was synthesized. The NCs were then transferred into the glovebox in a vial and toluene was added. The mixture was stirred for 30 min before sequentially adding titanium (IV) chloride and benzyl alcohol in the vial. The vial content was stirred for 5 min, after addition of the reagents, then left to stand for 15 min. The resulting product was centrifuged and washed repeatedly with toluene to remove any unreacted benzyl alcohol. IR analysis was performed for each wash to ensure the absence of benzyl alcohol (Fig. S1, Supplementary Information).

2.2.3. Metal nanoparticle@nanocapsule composite

The Al NPs were produced via catalytic decomposition of alane [36]. In previous work, our group has used titanium (IV) isopropoxide as the decomposition catalyst [20,23,27]. This work utilized a larger and more complex titanium derivative, entrapped in the NCs as the catalyst. The nanoreactor catalyst@NC complex was resuspended in toluene and kept in an inert environment. A Luer-lock syringe was used to inject both alane complex (4.00 mL, 0.20 mmol) and toluene (10.0 mL) in a round-bottom Schlenk flask. The mixture was heated to 85.0 °C, at which point the catalyst@NC suspension was transferred into the reaction mixture. Following a 45 min reflux period, all the solvent was removed and the resulting gray solid composite was heated *in vacuo* at 85.0 °C to remove any remaining volatile components.