



Reactive aluminum metal nanoparticles within a photodegradable poly(methyl methacrylate) matrix



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ABSTRACT

We report here on new photoreactive core-matrix reactive metal nanoparticles. Poly(methyl methacrylate)-capped aluminum nanoparticles (PMMA-Al NPs) were synthesized and demonstrated air stability on the order of 2 months. Upon exposure of the PMMA-Al NPs to UV radiation the composite reacts more rapidly to release H₂ gas from alkaline solution. FTIR spectroscopy indicates that the PMMA cap degrades under UV irradiation, exposing the reactive metal core.

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1. Introduction

Many interesting photoinduced reactions are reported for elemental metallic nanoparticles [1]. Such photoinduced reactions include electron transfer [2–9], aggregate formation and disassembly [10,11], crystal growth and shape transformation [12,13], and conductance modulation [14]. Many of these processes involve photoinduced transformations of the nanoparticle shell with a corresponding morphology change in the nanostructure, such as photodimerization of neighboring shells to induce aggregation of the nanoparticles [15].

Aluminum nanoparticles (Al NPs) are important for many energetics applications due to their high reactivity and energy storage capacity [16,17]; however, they provide challenges in terms of storage and handling because of high reactivity with atmospheric constituents [18–22]. We have found methods to vary the reactivity and stability of small (<20 nm) Al NPs using substituted epoxides, alkenes, and alkynes as monomers for NP surface polymerization reactions [23–26]. Some of the monomers produce nanoparticle caps that prevent water penetration and oxidation of the core for many months under standard atmospheric conditions. These particles are also stable under water for short periods of time (days).

In this Letter, we report on the synthesis of Al NPs coated with poly(methyl methacrylate) (PMMA). The metal-polymer nanocomposite is air stable for more than 2 months. The nanocomposite can be photoactivated by irradiation with UV light. Upon photoactivation the reactivity is substantially increased. The PMMA cap photodegrades under irradiation, leaving the underlying Al NP core accessible to reactive atmospheric components.

2. Experimental section

2.1. Reagents and materials

N,N-Dimethylethylamine alane (H₃Al-NEtMe₂, 0.5 M in toluene), titanium (IV) isopropoxide (99.999% trace metals basis, 0.0338 M in toluene), poly(methyl methacrylate) (PMMA, *M_w* = 1.2 × 10⁵ Da, 5.0 × 10⁻⁵ M in toluene) and sodium hydroxide (≥98.0%, pellets) were all supplied by Sigma-Aldrich. Alane and titanium (IV) isopropoxide were stored under Ar atmosphere to prevent oxygen/moisture exposure. Toluene was distilled over sodium metal under Ar atmosphere to remove water. Several freeze-pump-thaw cycles were performed for the PMMA solution to remove trace amounts of O₂.

2.2. Synthesis

All reactions were carried out using a Schlenk line under Ar atmosphere. *N,N*-Dimethylethylamine alane solution (6.5 mL) and freshly distilled toluene (15 mL) were added to a clean, dry round-bottom flask and purged 3 times with argon. The resulting clear solution was heated to 85 °C with stirring. At this temperature, 0.8 mL titanium (IV) isopropoxide solution was added followed by the immediate addition of 5 mL of PMMA solution as a capping agent, which afforded a color change from clear to brown. The resulting mixture was refluxed at 85 °C for 1 h and then cooled to 25 °C. All solvent was then removed and the resulting gray powder was heated *in vacuo* at 85 °C overnight.

2.3. Ultraviolet photolysis

The UV irradiation study was carried out using photochemical UV equipment that was purchased from Ace Glass Inc, consisting of a power supply, reactor, water cooling condenser, and medium

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pressure mercury lamp. Of the total power radiated by the mercury lamp (450 W), about 40–48% is in the ultraviolet region of the spectrum, while 40–43% is in the visible region with a peak wavelength, $\lambda_{\text{max}} = 254$ nm.

2.4. Characterization

All powder X-ray diffraction (PXRD) experiments were performed on a Rigaku Ultima IV diffractometer equipped with a Cu $K\alpha$ source operated at 40 kV, 44 mA, and 1.76 kW, and a scintillation counter detector. The presence of face-centered cubic (fcc) Al was confirmed by comparison with the appropriate pattern from the International Center for Diffraction Database (ICDD) crystallographic database. The oxidation of elemental Al was observed using a TA Instruments model Q2000 differential scanning calorimeter (DSC) and a TA Instruments Q500 thermogravimetric analyzer (TGA). Samples were analyzed from 25 to 725 °C using a 10 °C/min temperature profile under constant N_2 /air flow. All Fourier transform infrared (FTIR) spectroscopic measurements were made on a Shimadzu model FTIR-8400S spectrometer equipped with an attenuated total reflectance (ATR) attachment.

PXRD analysis was used to qualitatively determine gross sample air stability following 60 days storage of the powder in its sample holder in air (humidity $\approx 25\%$), undisturbed in the dark.

For the H_2 evolution study, ca. 50 mg of freshly synthesized PMMA-Al NPs were accurately weighed out and treated with 10 M NaOH solution in a glass retort attached to a glass burette filled with satd NaCl(aq) solution. By monitoring the NaCl(aq) level within the burette, the amount of evolved H_2 (g) was determined.

3. Results and discussion

3.1. Synthesis and characterization

The Al NPs were synthesized using the alane (AlH_3) decomposition method [27]. Addition of titanium (IV) isopropoxide (catalyst) was immediately followed by the addition of PMMA. A grey powder was obtained after heating overnight under vacuum at 85 °C. PXRD was used to identify crystalline Al NP cores by comparison of the observed pattern with that in the ICDD crystallographic database. In addition, PXRD analysis was used as a qualitative guide for air-stability of the PMMA-Al NPs composite. Figure 1

shows the PXRD pattern of the PMMA-Al NPs with 0 day of air exposure and 60 days of air exposure to determine if Al oxide (Al_2O_3) formation had occurred. The five peaks at $2\theta = 38.5^\circ$, 44.8° , 65.2° , 78.3° , and 82.4° correspond to the lattice planes 111, 200, 220, 311, 222, respectively, of fcc Al. After 60 days of air exposure these five peaks were still clearly present. The average core size of Al was estimated from the PXRD patterns using the Scherrer equation. Strictly speaking, this represents an average crystallite size and cores may in theory be made up of up of multiple crystallites. However, our previous reports of polymer-enveloped Al NPs synthesized by the same basic alane decomposition method appear to produce single crystallite cores as supported by electron microscopy. At 0 days exposure, the Al core size was 12 nm and only decreased by 1 nm (to 11 nm) after 60 days air exposure. Thus the PMMA cap has effectively mitigated oxidation of the underlying metallic Al core. Our previous work with alkylepoxy-capped systems produced Al NPs that completely degraded upon air exposure within 48 h [24,26], although Al NPs passivated with epoxide-diene admixtures were shown to be reasonably stable in air for several weeks [25].

We also characterized the product using thermal analysis techniques with Figure 2 showing the DSC/TGA results for the PMMA-Al NPs. A small initial mass loss (10%) in the TGA up to 190 °C accompanied by an endotherm in the DSC suggests the loss of a small amount of volatile material, most likely residual entrapped toluene from the synthetic procedure. This is followed by a broad exothermic peak from 190 to 430 °C in DSC measurement resulting from the depolymerization and oxidation of the involatile polymer cap. This behavior corresponds to a mass loss of about 35% from 190 to 430 °C in the TGA and suggests that at least 35% of the composite mass is polymer with the remaining 55% being Al. The delineation between these two mass loss regimes is more clearly seen in a first derivative plot of the TGA data (Figure S1, Supplementary data).

DSC and TGA measurements show no Al oxidation onset around 560 °C and only a modest discernible mass gain corresponding to the formation of Al_2O_3 . Similar behavior was observed in the TGA of a PMMA-Al NPs composite by Ghanta and Muralidharan [28]. The differential thermal analysis (DTA) of their PMMA-Al composite also showed no oxidation peak for Al. This behavior for Al NPs coated with PMMA in our DSC and TGA measurements can be understood as follows. In the temperature range 190–430 °C during the DSC scan the PMMA undergoes thermal oxidative degradation. This is a well-studied phenomenon for neat PMMA samples

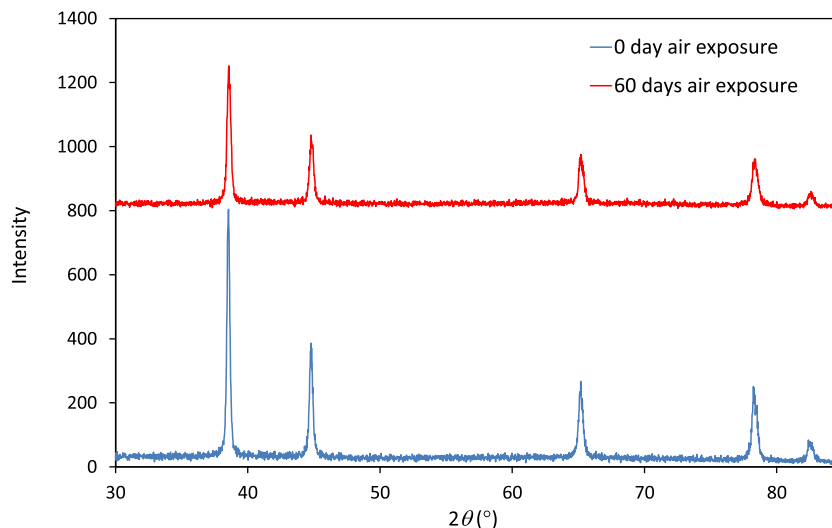


Figure 1. PXRD of the PMMA-Al NPs composite following 0 and 60 days air exposure.

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