Poly(methyl methacrylate) as an Environmentally Responsive Capping Material for Aluminum Nanoparticles

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ABSTRACT: We present an investigation of the photochemistry of aluminum nanoparticles (Al NPs) capped with poly(methyl methacrylate) (PMMA). Powder X-ray diffraction and Fourier transform infrared spectroscopy with total attenuated reflection confirm the presence of crystalline aluminum cores and the PMMA cap and allow us to confirm the latter’s photodegradation upon exposure to UV light. The PMMA-Al NPs were also characterized by differential scanning calorimetry coupled with thermogravimetric analysis to study the thermal profiles for polymer combustion and metal oxidation exotherms. Transmission electron microscopy confirms that the Al NPs, around 36 nm in diameter, are embedded in the PMMA matrix. Following UV irradiation, the PMMA-Al NPs react considerably faster with alkaline solutions, compared with unphotolyzed samples. Photoactivation of the nanocomposite induces partial decomposition of the PMMA capping layer, exposing the underlying reactive metal cores to the surrounding environment and accelerating its redox reactivity. Photolysis times of 1, 6, 24, and 52 h were investigated to establish a minimum UV exposure time for the activation of the PMMA-Al NPs toward hydrolytic hydrogen gas generation.

1. INTRODUCTION

There is continuing interest in the development of aluminum nanoparticles (Al NPs) owing to their high energy.1,2 Nanostructured aluminum is also a potential steady and manageable source of hydrogen gas by virtue of its reaction with aqueous solutions.1 Hydrogen, as an alternative energy source to fossil fuels, has a higher energy content but lower environmental impact.

Because of the reactive nature of Al NPs, it is necessary to passivate and stabilize them upon synthesis. There are many approaches that can be used to reach this objective based on monolayer assembly or macromolecular capping methodologies. Examples of the former include use of acrylics,8 perfluorocarboxylic acids,9–11 or oleic acid in a sonochemically assisted synthesis.12 Network elemental encapsulation by boron or carbon also provides protective shielding of the underlying Al NP cores.3,4,5

There are two general approaches to polymer capping of Al NPs: preassembled polymers directly envelope the nascent NPs or the NPs can themselves serve as scaffolds to polymerize appropriate monomers. There are a number of reports of the latter, which vary depending on whether oxide-passivated or oxide-free Al NPs are used. These include Ziegler–Natta polymerization of ethylene and propylene as well as di-tert-butyl peroxide-initiated free-radical polymerization of vinylidene fluoride.16–18 UV light has also been shown to be an effective polymerization initiator toward the production of stabilized Al NPs.19 In this instance, the photopolymerization of methacrylic acid (MAA) was carried out on the Al NP surface in the presence of a diazonium salt. Instead of utilizing oxide-passivated Al NPs, the Al NPs were first synthesized under an inert atmosphere prior to the attachment of the diazonium salt to the NP surface and subsequent photoinitiation of MAA polymerization. Liu and Ye demonstrated the ability to graft a layer of poly(trimethylolpropane triacrylate) onto the surface of commercially produced Al NPs using AIBN as a free-radical initiator.20 In a similar fashion, Crouse et al. prepared fluorinated acrylic Al nanocomposites by AIBN-initiated polymerization of 1H,1H,2H,2H-perfluorodecyl methacrylate at the Al NP surface.21

As mentioned above, stabilization of Al NPs is not solely limited to the formation of polymers/oligomers at the NP surface; NPs may also be entrapped within preformed polymer matrices. Li et al. demonstrated that the nanosized cavities within a Nafion-117 ionomer membrane could be utilized for NP growth.22 Ghanta et al. reported on the formation of Al NPs within either poly(vinylpyrrolidone) or poly(methyl methacrylate) (PMMA) matrices.23,24

In our laboratory, alkyl-substituted epoxides have been proven to be effective toward the preparation of air-stable Al NPs.24,25 Hammerstroem et al. demonstrated that the epoxide monomers could be polymerized onto the surface of the metal core, yielding a monolayer of polyether loops at the surface of incipient Al NPs in the absence of a polymerization initiator.26 Varying degrees of stability ranging from hours to weeks were reported, with more stable materials resulting from the use of capping monomers with increasing hydrophobicity. Thomas et al. later showed that alkene-terminated epoxides were also
effective toward NP capping; the additional reactive functional group was shown to be useful for the grafting of additional monomers, such as tetradecadiene, leading to the production of Al NPs that exhibited exceptional air stability (6 months) or the ability to be dispersed in numerous organic solvents.27,28 This epoxide polymerization methodology has been extended to the capping and passivation of aluminum, magnesium, zinc, and certain other d-block metal NPs produced by electrical explosion of wires (EEW).29−31 This work established that a minimum metal reducing ability (as quantified by electrode potentials) was necessary to successfully ring-open and polymerize epoxide monomers.

When our nanocomposite materials react with a dilute base, they release hydrogen gas, making them potential hydrogen generating materials for fuel cell applications. Although Al degradation can be effectively mitigated in this way, the prophylactic and often hydrophobic capping polymers used can actually hinder the access to the energy-rich metal core when required. Thus, our attention has turned to developing environmentally responsive passivating and capping components that can be readily degraded upon exposure to a simple physical stimulus such as light or temperature change.

PMMA has been widely used in engineering materials because of its good mechanical and optical properties.32,33 Because of these unique properties, PMMA is a potential coating agent to prevent metal corrosion.34,35 Nevertheless, PMMA can be degraded with exposure to UV light, with main chain scission leading to decreased elasticity and strength.36 In a preliminary communication, we carried out experiments which show that PMMA-capped Al NPs (PMMA-Al NPs) can be activated toward reaction with an aqueous base following exposure to UV radiation for 52 h.37 This length of time is not ideal, so we decided to investigate the minimum photoysis time required to effectively degrade the PMMA cap. We now provide a comprehensive report on the characterization of PMMA-Al NPs and demonstrate a proof-of-concept study, which confirms that it is possible to activate organically passivated reactive metal NPs by exposure to a light stimulus, and thus provide unfettered access to their full energetic content upon demand.

2. RESULTS AND DISCUSSION

The Al NP metallic cores may themselves be produced by one of several different top-down methods, including ball milling,38−40 laser ablation,41−43 plasma-enhanced chemical vapor deposition,44 and EEW.31,45,46 We have typically used the bottom-up approach of molecular alane decomposition, initiated by a Ti-based catalyst,37 which in this work is followed by direct addition of a PMMA solution in toluene to passivate and cap the Al NPs. The presence of crystalline Al NP cores in the product was determined by powder X-ray diffraction (PXRD) analysis (Figure 1). A comparison of the recorded patterns in the International Center for Diffraction Database (ICDD) crystallographic database shows five peaks at 2θ = 38.6, 44.8, 65.2, 78.3, and 82.6° corresponding to the lattice planes (111), (200), (220), (311), and (222) of face-centered cubic aluminum, respectively. After 50 days of air exposure, the five peaks are still clearly present, though with somewhat diminished intensity.

The peak intensity is not itself a reliable quantitative guide to air stability, but using the Scherrer equation, we can determine crystalline dimensions in both fresh and air-exposed samples. On the basis of the two most intense peaks (38.6 and 44.8°), which are expected to have the most accurate peak width determinations, the average crystallite diameter decreases by about 4 nm from 19 to 15 nm. Compared with previously reported organic capping agents such as epoxyhexane and epoxydodecane,25,26 PMMA-capped Al NPs demonstrated significant air stability up to and extending beyond 50 days.

Transmission electron microscopy (TEM) was also used to provide some visual information about the PMMA-Al NPs (Figure 2). Figure 2a reveals that the Al cores are embedded in a PMMA matrix. The darker Al cores can be readily distinguished from the lighter capping PMMA matrix. Figure 2b suggests formation of spheroidal Al NPs with an average size of 36 nm and a size distribution estimated to range from about 23 to 45 nm, somewhat larger than that predicted by the Scherrer equation. This can be attributed to the inclusion of the PMMA capping thickness in the overall TEM evaluation. Scherrer calculations do not take account of this amorphous layer around the Al NP crystallite cores. Furthermore, TEM allows the observation of some degree of NP agglomeration to the extent that multiple nanoaluminum crystalline cores may be embedded in a larger PMMA matrix.

The PMMA-Al NPs were characterized by differential scanning calorimetry coupled with thermogravimetric analysis (DSC/TGA), and the results are shown in Figure 3. DSC/TGA can further confirm the presence of active aluminum.26,48 The TGA plot reveals ca. 35% decrease in mass by 410 °C. This decrease corresponds to the first broad exothermic peak from 25 to 410 °C in the DSC trace; together they indicate the degradation of the PMMA polymer cap primarily through depolymerization.12 The broadness of the DSC exotherm and the wide temperature range over which mass loss occurs are consistent with our previous observations with copolymerized epoxide−alkene aluminum nano-composites.27 These observations suggest that up to 60% of the NP mass is composed of Al metal. The sharp exotherm around 660 °C in the DSC trace represents the oxidation onset of the aluminum metal cores, which supports the TGA results, indicating a rapid mass gain, attributable to the formation of both Al2O3 and AlN (vide infra).12,23,49−51 This, the Al ignition exotherm can clearly be observed, which we have found to not always be the case with other Al NP systems.

To have a deeper understanding of this phenomenon, the samples produced by DSC/TGA analysis were studied using PXRD analysis (Figure 4). It indicates that the final product comprises both oxygen-depleted aluminum oxide (PDF# 01-078-5519) and aluminum nitride (PDF# 01-080-6097).
Thus, the peaks at 33.3, 36.3, 38.1, 50.0, 59.4, 66.7, and 71.5° correspond with diffraction from the lattice planes (100), (002), (101), (102), (110), (103), and (112) of aluminum nitride, respectively. Meanwhile, the same lattice planes can be assigned to those of oxygen-depleted alumina with the exception of that at 71.5°, which corresponds to diffraction from the (200) plane. The formation of aluminum nitride is not surprising given that the DSC/TGA protocol flows nitrogen over the sample during heating. The formation of alumina can be accounted for by recalling that PMMA contains 13 mol % oxygen, and this presumably is the oxygen source. Given the limited oxygen content, formation of oxygen-depleted alumina during combustion is not altogether surprising either. The mass ratio of aluminum nitride to aluminum oxide was 56:44 using either the reference intensity ratio method or the whole power pattern fitting method.

The PMMA-Al NP composite was next examined for hydrolytic reactivity as a function of the UV exposure time. Suspensions of the material in toluene were stirred under an argon flow while irradiated by UV light from a 450 W mercury lamp for 1, 6, 24, and 52 h. Our preliminary results suggested that 52 h is sufficient photolysis time to sufficiently degrade the PMMA-Al NPs but this is a long time to subject our reactive metal nanocomposite material to UV irradiation, and we wondered if we could reduce that time to some optimal level that activates the Al NPs toward hydrolysis sufficiently yet does not degrade the active Al content significantly.

Figure 2. TEM images of the PMMA-Al NP nanocomposite material showing (a) Al NPs embedded in the PMMA matrix and (b) the spheroidal nature of the Al NPs.

Figure 3. DSC/TGA traces for PMMA-Al NPs under nitrogen flow.

Figure 4. PXRD of the PMMA-Al NP composite following DSC/TGA under nitrogen flow.
FTIR-ATR analysis suggests that 6 h is more than sufficient photolysis time to degrade the PMMA cap and activate the Al NPs toward hydrolysis, although even shorter photolysis times would be considerably more attractive for optimizing the utility of such Al nanomaterials for energy applications.

To further investigate the degradation of PMMA and reactivity upon UV irradiation, we carried out a hydrogen emission study to evaluate the active aluminum content and gauge the rate of hydrolysis as a function of photolysis time. To allow for batch-to-batch variation, we divided the product of a single synthesis into two accurately weighed 40 mg samples and photolyzed one, while leaving the other in the dark, prior to hydrolysis and measured the H₂ emission volume as a function of time. We plotted the normalized volume versus time, and the results are shown in Figure 6.

![Figure 5. FTIR-ATR spectra of photolyzed and unphotolyzed PMMA-Al NPs (left intensity scale) and neat PMMA (right intensity scale).](image)

Figure 6. Normalized H₂ emission plots for unphotolyzed samples and following UV irradiation of samples for 1, 6, 24, and 52 h. The measured volumes were averaged over three trial runs for each sample. Kinetic data are shown in Table 1.

From these plots, we determined the initial rate of hydrogen production, d[H₂]/dt, and the time taken (t₁/₂) for 50% of the hydrogen volume to be evolved for each set of samples. The active aluminum (Al⁰) content was determined from the gross hydrogen emission volume based on a H₂/Al mole ratio of 3:2 according to the following reaction and expressed as a percentage of the total aluminum (oxidized and elemental) content.

\[
2\text{Al}(s) + 6\text{H}_2\text{O}(l) \rightarrow 2\text{Al(OH)}_3(s) + 3\text{H}_2(g)
\]

The total aluminum content was determined by the complexometric Zn²⁺-ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) back-titration of the hydrolyzed sample and expressed as mass percent of the nanocomposite material. Results are given in Table 1.

![Table 1. Kinetic Data from H₂ Emission Trials and Total and Active Al Contents of Al-PMMA Samples](table)

Unphotolyzed samples were clearly slowest to hydrolyze with an initial rate of hydrogen production of 0.3 min⁻¹ and a t₁/₂ of over 2 min. Our original work examined only a long photolysis time of 52 h based on the idea that PMMA is somewhat slow to photochemically degrade under normal ambient UV exposure. Thus, we were somewhat surprised to see that the photolysis time as little as 1 h was sufficient to degrade the organic PMMA capping agent, with samples reacting at twice the rate (0.6 min⁻¹) and a t₁/₂ of just under a minute. The highest rate and lowest t₁/₂ time (3.3 min⁻¹ and 10 s) were essentially reached after a photolysis time of 6 h, with longer photolysis times (24 h and our original 52 h) showing no appreciable statistical differences.

Speciation analysis of unphotolyzed PMMA-Al NPs reveals that ca. 50% of the aluminum is present as active Al⁰, which is still respectable for an organically capped reactive metal nanocomposite system but appreciably lower compared to that synthesized in our laboratory using 1,2-epoxydecene (75–90%), for example. However, this is not entirely unsurprising given that PMMA is significantly more oxygen-rich with ester functionalities that are likely to be more reactive with electron-rich metal NPs than ether groups.

It would appear that photolysis times up to 6 h have little impact on the active Al⁰ content, suggesting that photodegradation of the polymer is taking place without any significant attrition of the Al NP cores. After 24 h photolysis, it is likely that the compromised PMMA shell is allowing access to oxidative and solvolytic species, such as trace O₂ and MeOH, a byproduct of PMMA UV degradation, and thus lowering the active Al⁰ content below 40%.

The overall mass percent of Al (active plus oxidized) in the nanocomposite material appears to be little affected until the longest photolysis time of 52 h. The slight upturn in this value may be attributed to some degradative mass loss of the PMMA polymer through photoevolution of volatile and gaseous components (CO, CO₂, MeOH).

3. CONCLUSIONS

In a mission to develop environmentally-sensitive reactive metal nanocomposite materials, we have shown that air-stable Al NPs passivated and capped with PMMA may be photodegraded and activated by UV irradiation toward base
hydrolysis. An optimal photolysis time of ca. 6 h led to a maximal hydrolysis rate that was an order of magnitude faster than that for unphotolyzed samples (as determined by H2 emission experiments) and without significantly compromising active Al content.

4. EXPERIMENTAL SECTION

4.1. Reagents and Materials. Alane N,N-dimethylethylamine complex solution (AlH3-NMe2Et, 0.5 M in toluene), titanium(IV) isopropoxide (Ti(Oi-Pr)4, 99.99% trace metal basis), toluene (anhydrous, 99.8%), PMMA (Mw = 120 000, pellets), zinc sulfate heptahydrate (99.99% trace metal basis), EDTA (≈99%), sodium hydroxide, sodium acetate trihydrate, xylenol orange sodium salt, and nitric acid were all purchased from Sigma-Aldrich. Toluene was distilled over sodium metal under an argon atmosphere to remove trace amounts of water and oxygen. PMMA (5 × 10−3 M) solution in toluene was subjected to freeze–pump–thaw cycles several times to remove any dissolved oxygen.

4.2. Synthesis. The synthesis protocol is based on a modification of the decomposition of AlH3-NMe2Et first reported by Haber and Buhro.6 Because of purging air sensitivity, all reactions were carried out using Schlenk line techniques under an argon atmosphere. After purging three times with argon, 10 mL of freshly distilled toluene and 6.5 mL of AlH3-NMe2Et were added to a clean, dry reaction flask equipped with a magnetic stir bar. The resulting clear solution was heated to 85 °C. Titanium isopropoxide (0.8 mL, 3.3 × 10−2 M in toluene) was added, followed by immediate addition of 5 mL of the PMMA solution (10:1, Al/PMMA molar ratio). The reaction solution changed from clear to black-brown. The reaction was heated at 85 °C for 2 h and then allowed to cool to room temperature. All solvent was removed, and the resulting gray powder was heated in vacuo at 85 °C overnight.

4.3. PXRD. PXRD measurements were performed on a Rigaku MiniFlex 600 diffractometer equipped with a Cu Kα source and a scintillation counter detector. Assignments were confirmed by comparison with the appropriate pattern from the ICDD Crystallographic Database, and instrument software was used to carry out Scherrer analysis to determine crystallite dimensions.

4.4. Thermal Analysis. The thermal profiles reported in this work were gathered using a TA Instruments SDT Q600 simultaneous DSC/TGA instrument. The samples were analyzed using a platinum cup (25−800 °C) under a constant flow rate of 50 mL/min of N2 and a 10 °C/min temperature ramp.

4.5. Electron Microscopy. TEM was used to gain information on gross NP dimensions and morphology. The images presented in this work were collected using a JEOL 1200EX TEM operated at 80 kV and under 20 000× magnification.

4.6. FTIR-ATR Spectroscopy. The infrared spectra were measured on a Shimadzu model FTIR-8400S spectrometer equipped with an ATR attachment.

4.7. Ultraviolet Photolysis. Photochemical UV equipment was purchased from Ace Glass Inc., consisting of a power supply, reactor, water cooling condenser, and medium-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, whereas 40−43% is in the visible region with a peak wavelength, λmax = 254 nm. The UV apparatus was heated under vacuum for 5 min and purged three times with argon to ensure an oxygen-free environment.

To allow for batch-to-batch compositional variation, we divided the product of a single synthesis into two accurately weighed 30−40 mg samples and photolyzed one, while leaving the other in the dark. For the sample to be photolyzed, the PMMA-Al NPs were dispersed in toluene and stirred while being photolyzed for 1, 6, 24, or 52 h. To increase the reproducibility and maintain an oxygen-free environment, argon was flowed continuously during photolysis to sweep away small organic molecules produced by PMMA degradation. Both photolyzed and unphotolyzed samples were then hydrolyzed in aqueous 10 M NaOH, and the hydrogen volume evolved was determined using equipment employed for the active aluminum analysis and plotted as a function of time.

4.8. Active and Total Al Content Determination. The active and total aluminum contents were determined by previous reported methods.26,27 The active aluminum content was determined by the measurement of the hydrogen volume generated from the reaction of Al NP samples with NaOH (aq). The total Al, oxidized and unoxidized, content was determined via a complexometric Zn2+−EDTA back-titration.56

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Notes

The authors declare no competing financial interest.

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