Development of an AlCl₃-Urea Ionic Liquid for the Electroless Deposition of Aluminum on Carbon Nanotubes

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ABSTRACT: Unlike the easy electroless deposition of other metals, the deposition of aluminum can be challenging. This is because the standard reduction potential of aluminum lies outside the electrochemical window (EW) of water. Ionic liquids such as AlCl₃-1-ethyl-3-methylimidazolium chloride (EMIC) have been used because of their wide EW. Here, we introduce a novel ionic liquid for electroless deposition of aluminum by reacting AlCl₃ and urea, with lithium aluminum hydride (LAH) as a reducing agent. Additionally, we report the first successful effort in coating carbon nanotubes (CNTs), as an example of nanostructures with high surface area to volume ratio, with aluminum using electroless deposition. The produced aluminum coating was found to be nanostructured, uniformly covering the CNTs and in close contact with their surfaces.

INTRODUCTION

The deposition of aluminum has been the subject of intense investigations in the past decade. Aluminum is a light metal of outstanding electric and thermal conductivities, which lead to many promising applications including electronic circuits, semiconductor devices, memory devices, compact disks, composite materials for structural applications, and many more.1−5 To metallize nonconductive substrates, electroless plating has become a frequently adopted technique due to its simplicity, reproducibility, and low cost. Metals such as nickel and copper were found to be easily deposited using electroless plating in aqueous solutions.6−11 On the other hand, the electroless deposition of aluminum was found to be unfeasible in aqueous solutions due to the narrow electrochemical window of water and the nature of aluminum as a less noble metal.12−14 However, using room-temperature ionic liquids (RTILs), scientists were able to successfully electrodeposit aluminum on different substrates.15−21 A commonly used method for the electroless deposition of aluminum is based on AlCl₃-1-ethyl-3-methylimidazolium chloride (AlCl₃-EMIC) ionic liquid with either diisobutylaluminum hydride (DIBAH) in toluene as a liquid reducing agent, or lithium hydride (LiH) as a solid reducing agent.12−14,22 The AlCl₃-EMIC ionic liquid provides Al₂Cl₇⁻ ions, which are the main species for aluminum deposition when reduced by the electrons associated with the reducing agent. Attempting to use AlCl₃-EMIC RTIL to apply aluminum coats on nanostructures of very high surface area to volume ratios can be costly. Therefore, for such cases, alternatives are highly desired.

The use of carbon nanotubes (CNTs) as a reinforcement phase in aluminum matrix composites suffers from several challenges, namely, the poor wettability and the nonuniform dispersion of CNTs in the aluminum matrix.2,5,23−26 Electroless deposition of intermediate layers such as nickel, copper, and silver on CNTs was found to improve their dispersion and wettability in molten aluminum.2,5,9,10,27−31 Although coating CNTs with aluminum prior to their introduction in the aluminum matrix would avoid undesirable alloying effects that can occur when other metals are used, only minor efforts were conducted in this regard. Trials to coat CNTs with aluminum using normal electroplating were done. However, it was concluded that this is only viable when CNTs are used in the form of a thin film.23 On the other hand, coating loose powders of CNTs comprised of aggregates of individual CNTs would only be possible by electroless deposition. Nonetheless, there are no reported efforts in the literature addressing this. In the current letter, we report the use of aluminum chloride (AlCl₃)−urea ionic liquid as an alternative RTIL for electroless deposition of aluminum wherein lithium aluminum hydride...
(LAH) is used as a reducing agent. The reaction mechanisms involving the presence of $\text{Al}_2\text{Cl}_7^{-}$ ions are discussed. We also report the first effort in covering multiwalled carbon nanotubes (MWCNTs) with aluminum through an electroless deposition. Additionally, we conducted a simple time-saving one-step catalyzation process on CNTs instead of the two-step method usually followed for electroless plating. The aluminum-coated CNTs were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectroscopy.

**EXPERIMENTAL SECTION**

Figure 1 shows the general scheme of electroless deposition of aluminum on CNTs. The electroless deposition cannot take place on noncatalytic surfaces and hence catalytic activation of CNTs was first conducted using colloidal Pd–Sn nanoparticles. Because the nanoparticles are typically deposited with a thin layer of stannous hydroxide $\text{Sn(OH)}_2$ on their surfaces, an acceleration step followed to remove excess stannous hydroxide and increase the surface activity. Finally, the electroless plating of aluminum was performed, as will be explained in the next paragraphs.

For the present study, multiwalled carbon nanotubes (MWCNTs) supplied by Thomas Swan Corporation (average diameter of 10–12 nm and lengths of tens of micrometers) were used. The CNT surfaces were activated using a one-step approach inspired by the plating of plastics (POP) industry. To prepare the activation solution, 62.5 mL of a commercial colloidal Pd–Sn concentrate (supplied by MacDermid Enthone Corporation) was stirred in chlorinated DI water prepared by mixing 137.5 mL of DI water and 50 mL of concentrated hydrochloric acid (37%). CNTs (0.1 g) were immersed in the prepared Pd–Sn activation solution; the mixture was sonicated for 3 min and then stir-agitated for an extra 7 min. The activated CNTs were then filtered out by means of poly(tetrafluoroethylene) (PTFE) filter membrane.
The reaction between AlCl3 and urea is exothermic, so caution was exercised because excess heat could result in the decomposition of the entire electrolyte. Accordingly, the ionic liquid was prepared in four parts of 50 mL each. In addition, the reaction flask was cooled on a sealed rubber ice bucket to preserve the dry environment during the reaction and thus avoid the decomposition of the electrolyte. By following the previous steps, a transparent pale yellow ionic liquid was obtained. As a final step, lithium aluminum hydride (LAH) (97%, Alfa Aesar) was dissolved in diethyl ether and mixed with the prepared AlCl3–urea ionic liquid such that the final concentration of LAH in the plating electrolyte was 2.5 g/L. The previously activated CNTs were then immersed in the plating electrolyte under sonication for 5 min and magnetic stir agitation for 10 extra min. In the current work, 200 mL of the ionic liquid was used for each 0.1 g of CNTs. To reduce the viscosity of the mixture for ease of filtration, more diethyl ether was added, followed by filtration. After filtration, the CNTs were washed thoroughly with diethyl ether on the same filter membrane, dried overnight in a vacuum at 100 °C, and kept in a sealed glass container under dry argon.

The procedure of electroless plating of aluminum described above is summarized in Figure 2. The morphology of the obtained aluminum coating was investigated using SEM imaging (LEO SUPRA 55 FESEM equipped with Oxford EDS detector) and TEM imaging (JEM-2100 LaB6, JEOL, operating at 200 kV and equipped with Gatan SC200B CCD camera). The chemical composition of the Al-coated CNTs was determined by means of energy-dispersive X-ray spectroscopy (EDX) analysis. Powder X-ray diffraction (XRD) (Cu Kα, Panalytical Xpert Pro diffractometer) and selected area electron diffraction (SAED, conducted in JEM-2100) were used to analyze the crystal structure of the aluminum coat. Raman analysis (ProRaman-L, ENWAVE OPRONICOS) was used to compare the intensities of the D-band and G-band (I_D/I_G) of CNTs before and after electroless plating of aluminum to confirm their structural integrity.

RESULTS AND DISCUSSION

EDX analysis confirmed that 84.67% of aluminum and 1.67% of carbon are present in the prepared sample. In addition, the results showed that some parts of the sample are oxidized, with oxygen present in 13.67%.

SEM imaging (Figure 3a) and high-resolution TEM imaging (Figure 3b) confirmed that there is a considerable increase in the diameter of CNTs as a result of the aluminum coat. Aluminum-coated CNTs with diameters of about 100–150 nm were obtained. The aluminum coating on CNTs was found to be nanostructured, as shown in Figure 3c. It is believed that due to the refined structure of the catalytic Pd–Sn nanoparticles used in the activation step, the aluminum coating was deposited in a nanostructured manner. Further analysis to confirm the average crystallite size of the deposited aluminum was conducted using the XRD patterns collected from the sample, as explained later.

The difference in the thickness between the coated and uncoated parts of a CNT can be clearly seen in Figure 3d. The aluminum coat is noticeably much thicker than the CNT itself, which is desirable when used in a composite material. In this case, the provided aluminum coat would contribute to the overall fraction of the aluminum matrix in the final composite.

Figure 4a shows the XRD pattern of the obtained Al-coated CNTs, which confirms the existence of the aluminum coat in a crystalline form. The pattern shows the characteristic peaks for Al corresponding to the (111), (200), (220), (311), and (222) planes in the face-centered cubic (FCC) crystal structure. Interestingly, the 0002 peak of CNTs at 26° was not detected in spite of the high concentration of CNTs in the sample. This can be attributed to the CNTs being embedded inside the aluminum coat. The full width at half-maximum (FWHM) height for each of the characteristic peaks was measured from the collected pattern and average crystallite size of 31.7 nm was calculated using the Scherrer equation, thus confirming the nanosized structure of the Al coat.

Additionally, using SAED indexing shown in Figure 4b, information about CNTs, palladium, and aluminum was revealed where the aluminum pattern was superimposed on the patterns of both palladium and CNTs, indicating the presence of palladium as well as CNTs underneath the aluminum coat. Palladium was previously used to render the surface of CNTs catalytic prior to plating.
Raman analysis results, shown in Figure 5, confirmed that the difference in the ID/IG ratios between the Al-coated CNTs and the as-received CNTs is not significant. This can imply that the CNTs did not undergo any change in their structure during electroless plating. However, a slight shift toward high wavenumbers was noticed in the position of the G-band for the Al-coated CNTs compared to the as-received ones, which can be attributed to the interaction between CNTs, Pd−Sn nanoparticles, and aluminum after the coat is applied.

The AlCl₃−urea ionic liquid, utilized in the current study, was adapted from a battery electrolyte formed by reacting AlCl₃ and urea at molar ratios above 1:1. It was discovered that during the operation of the battery, aluminum was deposited on the anode by the reduction of $[\text{AlCl}_2\cdot(\text{urea})_n]^+$ shown in eq 1 and $\text{Al}_2\text{Cl}_7^-$ ions shown in eq 2.

$$2[\text{AlCl}_2\cdot(\text{urea})_n]^+ + 3e^- \rightarrow \text{AlCl}_4^- + 4(\text{urea}) + \text{Al}$$ (1)

$$4\text{Al}_2\text{Cl}_7^- + 3e^- \rightarrow 7\text{AlCl}_4^- + \text{Al}$$ (2)

The addition of extra AlCl₃ was found to enrich the ionic liquid with more $\text{Al}_2\text{Cl}_7^-$ ions, thus promoting the conversion of $\text{AlCl}_4^-$ into more $\text{Al}_2\text{Cl}_7^-$ ions as shown in eq 3.

$$\text{AlCl}_4^- + \text{AlCl}_3 \rightarrow \text{Al}_2\text{Cl}_7^-$$ (3)

In the current study, the ionic liquid was tailored for the current application by increasing the molar ratio between AlCl₃ and urea to 2:1 to promote the generation of more $\text{Al}_2\text{Cl}_7^-$ ions and adding lithium aluminum hydride as a reducing agent to promote the autocatalytic reduction process of $\text{Al}_2\text{Cl}_7^-$ ions and $[\text{AlCl}_2\cdot(\text{urea})_n]^+$ without using an external power source.

Based on the previous chemical reactions, aluminum was plated on the CNTs from three different sources represented by the reduction reaction of $\text{Al}_2\text{Cl}_7^-$ ions, the reduction reaction of $[\text{AlCl}_2\cdot(\text{urea})_n]^+$, and the decomposition of LAH.

**CONCLUSIONS**

The motivation of the current study was to explore alternative electrolytes for the electroless deposition of aluminum that are cheap and can be prepared in large quantities for coating high surface area to volume structures such as CNTs. The results confirm that the AlCl₃−urea electrolyte is effective in covering the CNTs uniformly with aluminum. In addition, the presented approach could cut at least two undesirable processing steps, which were previously thought to be essential in obtaining aluminum-coated CNTs. The first is the acid functionalization of CNTs, which was found to be unnecessary. The second is the use of a one-step colloidal Pd−Sn catalyzation approach instead of the two-step stannous chloride and palladium chloride solutions approach for surface activation. Accordingly, the processing time was reduced significantly.

The aluminum coat was found to be conformal according to the SEM and TEM analysis. In addition, the aluminum was found to be nanostructured, confirming that the colloidal palladium nanoparticles used in the activation step were effective in the nucleation and film growth of a nanostructured aluminum coat on the CNTs.

The process of electroless plating of aluminum on CNTs presented here could facilitate the use of Al-coated CNTs as a filler in aluminum matrix composites. The high energy ball milling process, which is widely used for dispersing CNTs in aluminum matrices prior to processing by other techniques but is also reported to damage the CNTs and to strain-harden the aluminum matrix, can thus be eliminated. With the present approach, the CNTs were preserved in their original form without damage in a way that makes them more effective in CNT-reinforced aluminum composites. The investigation of the mechanical behavior of Al composites reinforced with Al-coated CNTs is currently underway. Those high-performance Al-CNT composites can be potentially used in structural applications.
applications for aerospace and the automotive industries. Other potential applications for the developed electroless plating of aluminum include aluminum thin film deposition on conductive and nonconductive substrates and microdevices, especially temperature-sensitive ones as well as corrosion-resistant protective coats on steel parts. Finally, it is believed that the process can be a good alternative for aluminum physical vapor deposition (PVD) and chemical vapor deposition (CVD) thin film deposition.

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**Notes**

The authors declare no competing financial interest.

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