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A General Process for the Fabrication of Air-Stable Metallic Particles (Cd, Zn and Al) by the Decomposition of Alkyl–Metal Compounds

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The thermolysis of alkyl–metal compounds under autogenic pressure, with the three metals Cd, Zn, and Al as examples, suggest that this might become a general method for preparing a composite where the metal is the core and carbon the shell. The air-stability of these composites is also demonstrated.

Introduction

Metallic nano- and micromaterials have been intensively studied in recent years with respect to their novel properties and their potential commercially valuable applications. However, these particles tend to oxidize easily under ambient conditions, especially those containing metals with a negative reduction potential, therefore methods that can produce air-stable metallic nano- and microparticles are of great importance. The most common solution for stabilizing such particles is to form a coating layer on their surface, which prevents oxidation. If this layer still enables solutions to reach the metallic core, we will benefit from the large variety of applications of these nano- and microparticles. The applications of encapsulated metallic nano- and micromaterials range from catalysis, purification of water wells, food additives,[1–3] fuel amplifiers,[4] electronic devices, as well as the field of energy storage and conversion.

Various methods have been reported in the literature for the formation of core/shell nanocrystals (CSNCs), for example sonochemistry,[5,6] electrochemistry,[7] sol–gel methods,[8] ammonia catalysis,[9] and laser-induced fusion,[10] amongst others. Herein we report a simple, efficient, and economic synthesis technique for the fabrication of NCCs nanostructures where the metallic nano- or microparticles form the core. This method is general and can be applied to less reactive metals such as Cd as well as to a very reactive metal such as aluminum. The spherical core/shell structure is obtained in a one-step, solvent-free, single precursor reaction without using a catalyst, at 500, 700, and 800 °C. These reactions are referred to as RAPET (Reaction under Autogenic Pressure at Elevated Temperature), and reports on the formation of core/shell nanostructures of a variety of transition metals and transition metal oxides have already been published.[11,12] For example, the RAPET of nickel acetate has led to Ni–C (graphitic) core/shell nanostructures at a relatively low temperature,[13] and that of molybdenum alkoxide to an MoO_2/C core/shell structure. However, oxygen-containing compounds were dissociated in all previous cases and these led to the formation of metal oxides when this process was applied to highly active metallic precursors.

To synthesize active nano- and microparticles with Cd (standard reduction potential –0.4 V), Zn (–0.76 V) and even Al (–1.7 V), the corresponding alkyl–metal compounds were tested in the RAPET reaction and $Zn(C_2H_5)_2$, $Cd(CH_3)_2$, and $Al(C_2H_5)_3$ were found to yield Zn/C, Cd/C, and Al/C core/shell structures, respectively. This method could therefore become a general method for the fabrication of air-stable metallic nano- and microparticles. We also examined the efficiency of the Zn/C particles in the elimination of aliphatic chloro compounds from contaminated water sources. The results were compared with those obtained with ZVI (zero-valent iron) and point to the ability of water to penetrate the protective carbon layer and reach the zinc core. These results will not be discussed further herein. It is worth mentioning that the nano dimension in our products appears mostly in the carbon shell and that the cores are always between 1 and 10 micrometers in diameter.

Results and Discussion

XRD

The composite products obtained from the RAPET reactions were characterized by XRD measurements. These measurements for Zn/C, Cd/C, and Al/C were performed one week after their synthesis after the materials had been

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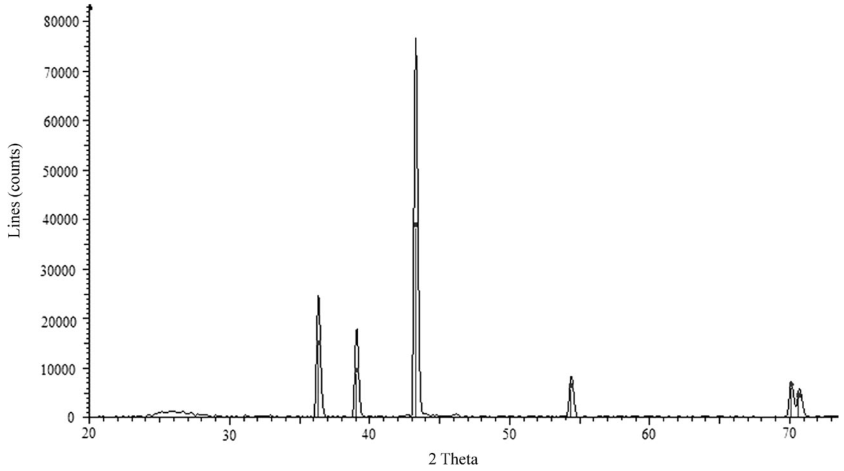

Figure 1. XRD pattern of Zn nanoparticles measured after annealing at 800 °C for 3 h. The vertical lines represent the positions of the XRD peaks as reported by the International Center for Diffraction Data (ICDD).

left to age under ambient conditions. The reactions were performed at 500, 700, and 800 °C. Figure 1 shows the XRD pattern of the as-prepared powder obtained after heating diethylzinc to 800 °C for 3 h. All the diffraction peaks can be assigned to metallic zinc and no diffraction peaks due to impurities can be detected. The peak positions match the PDF file for Zn (PDF: 5973-065-03) very well. A small, broad peak is observed at $2\theta = 26°$ in the diffractograms measured for the products of the reactions at 700 and 800 °C. This diffraction peak can be assigned to the graphitic carbon that serves as the protective layer around the central metallic particle. This diffraction peak is not observed for the product of the reaction at 500 °C – only Zn diffraction peaks are obtained at this temperature. Raman spectroscopy further substantiated this interpretation.

Dimethylcadmium was pyrolyzed under the same conditions as diethylzinc and subsequent XRD analysis revealed that air-stable Cd particles had formed. Figure 2 shows the XRD pattern of these Cd particles [Powder Diffraction File (PDF): 1183-065-03].

To demonstrate that RAPET is a general method applicable to any metal, even for a very reactive metal such as aluminum, we also investigated the RAPET of triethylaluminium. The XRD pattern of triethylaluminum after treatment at 500 °C for 3 h is shown in Figure 3. The main peaks can be assigned to metallic Al (PDF: 0787-004-00), al-

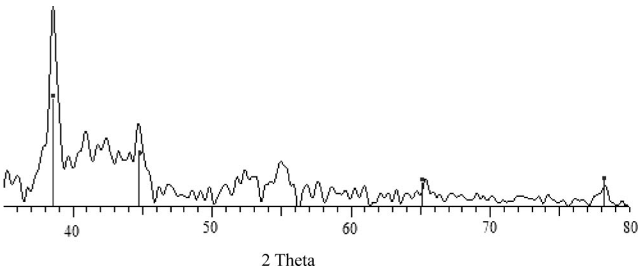

Figure 3. XRD pattern of Al nanoparticles measured after annealing at 500 °C for 3 h. The vertical lines represent the positions of the XRD peaks as reported by the International Center for Diffraction Data (ICDD).

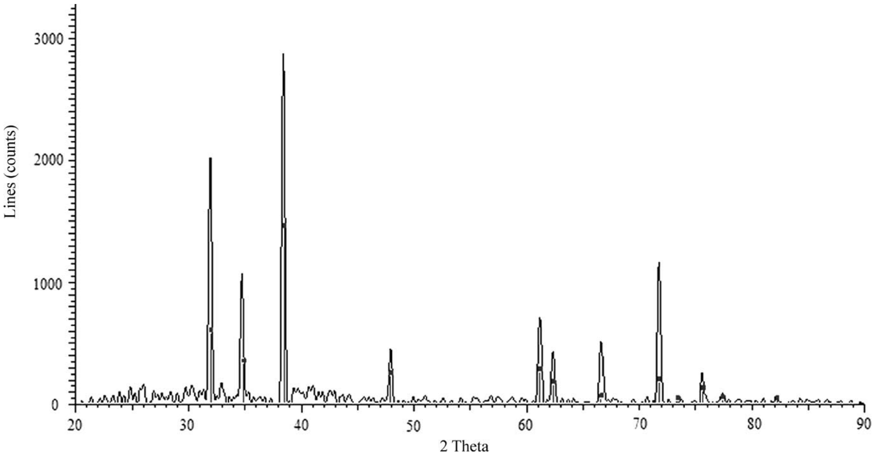

Figure 2. XRD pattern of Cd nanoparticles measured after annealing at 700 °C for 3 h. The vertical lines represent the positions of the XRD peaks as reported by the International Center for Diffraction Data (ICDD).

though impurity peaks due to aluminum carbide can also be detected.

The reaction yields of the three alkyl–metal compounds at 500, 700, and 800 °C varied between 26.2% and 78.8%. These yields are influenced by two factors, namely the volatility of the starting materials, which leads to a weight loss of the precursor in the glove-box before capping of the reaction vessel, and a second weight loss due to over-pressure in the cell, which leads to the release of gases at pressures above about 100 atm.

Morphology

Figure S1 (Supporting Information) shows an SEM micrograph of the Zn powder obtained after heating for 3 h at 500 °C. The image is that of an egg shell with a rough surface. In contrast, a smooth egg-shell surface is observed when dialkylzinc is heated for 3 h at 800 °C (Figure S2 in the Supporting Information). The diameters of the egg shells formed at 700 and 800 °C vary between 500 nm and 5.5 µm, which means that RAPET does not yield a narrow size distribution. Unlike the well-separated particles obtained at 700 and 800 °C, a highly agglomerated product is obtained after heating the precursor at 500 °C for 3 h. Heat treatment also has a significant effect on the particle's surface. Thus, while rough surfaces are obtained at low temperatures, the reaction product obtained after RAPET at 800 °C reveals a smooth surface. We attribute these morphological changes to sintering of the product at higher temperature and pressure. Similar morphological changes to those observed for RAPET of the Zn precursor were also found for the decomposition of dimethylcadmium. Thus, larger particles and rough surfaces were obtained at 500 °C, while smooth surfaces were obtained at 800 °C.

The spheres obtained at 800 °C were analyzed by HRTEM and SAED, which revealed a core/shell structure with Zn constituting the core and carbon the shell. Figure 4 shows the two locations at which the SAED spectra were measured. The ED spectrum of the shell shows 69.29 and 30.71 wt.-% for carbon and the copper, respectively (see Figure S4 in the Supporting Information). The copper originates from the grid. No zinc was detected in the 130-nm shell (Figure 4, a). The composition of the core measured at the location marked in Figure 4, b is 5.16, 48.51, and 46.32 wt.-% for carbon, copper, and zinc, respectively (see Figure S5 in the Supporting Information).

The SEM images of the Cd/C composite are similar to those obtained for Zn/C, although they indicate a wider size distribution and spheres of up to 10 micrometers in size. The HRSEM image in Figure 5 clearly shows the core/shell structure, in agreement with the HRTEM results of the Zn/C composite, thereby indicating that perhaps this is the general dissociation scheme for alkyl–metal compounds leading to a metal–carbon core/shell structure. Our first assumption was that the large spheres might be of pristine carbon, however an investigation of the composition of the large and small spheres found Cd in both of them.

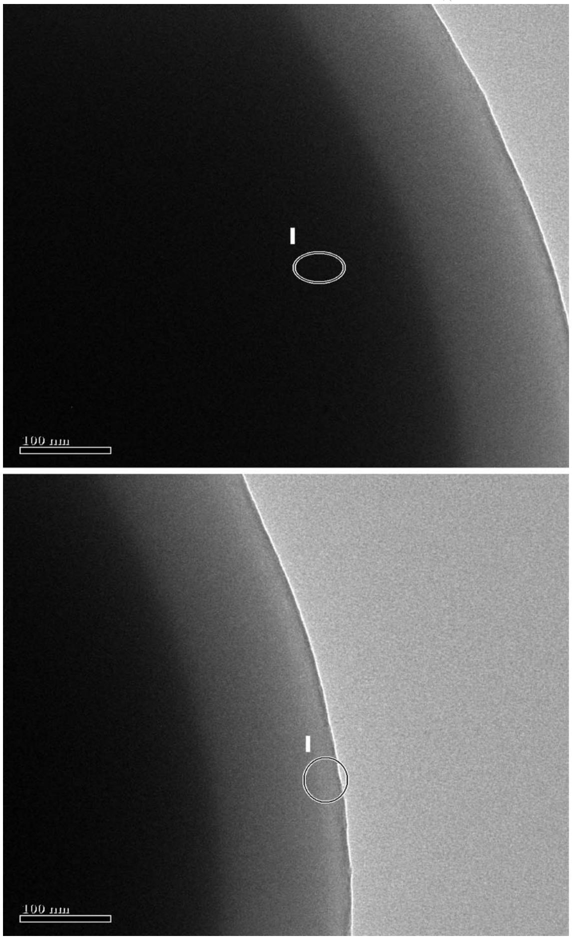

Figure 4. HRTEM images of a) the core of the egg-shell Zn/C composite and b) the carbon shell of the Zn/C composite. The areas where SAED was performed are marked with a circle.

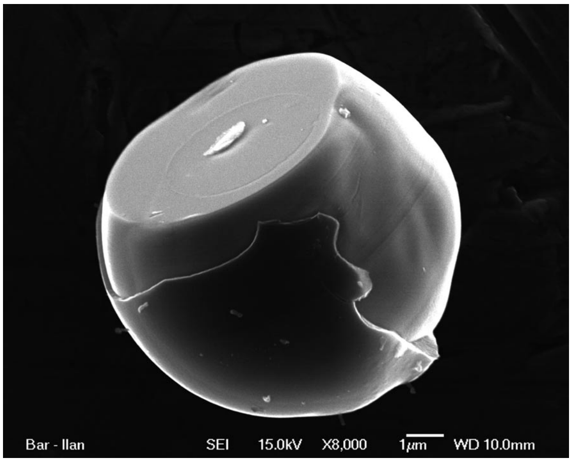

Figure 5. HRSEM image of a Cd/C core/shell structure.

Although the reaction conditions applied to triethylaluminum were the same as those for dimethylcadmium and diethylzinc, different morphologies were obtained for the product of this reaction. Figure S3 in the Supporting Information shows the formation of Al wires coated with carbon as the main reaction product when the reaction is conducted at 500 °C. The XRD pattern also reveals the presence of small amounts of aluminium carbide. The first layer coated on the surface of Al is most probably aluminum carbide, which serves as an intermediate layer between Al and C. It is worth mentioning that the reactions of triethylaluminum at 700 and 800 °C yielded aluminum carbide and not metallic aluminum as their main product.

The differences in shape between the Cd- and Zn-containing products, which are spherical, and the Al-containing products, which are rod-shaped, are related to the nature of the metallic seed. The length of the wires in the Al/C particles varies between 500 nm and 5 µm, and the width varies between 50 and 100 nm. In all cases the metal is precipitated first and it is then surrounded by a protecting carbon layer. The crystallization of the metal determines the shape of the final product. The morphologies of the products were also analyzed by transmission electron microscopy (TEM). The TEM image of the Cd/C composite formed at 800 °C shows a smooth surface, and small aggregates of nanoparticles with a nearly spherical morphology are seen in the TEM images of Zn/C and Cd/C.

Raman Spectroscopy

Raman spectroscopy was used to define the nature of the carbon that forms part of the metal/carbon composite for all three metals. When the long-range order of the graphite lattice is disrupted, a second line appears at about 1360 cm^{-1} in addition to the normal graphitic Raman peak at 1590 cm^{-1}. The intensities of these two lines, denoted respectively as G and D lines (graphite and defect carbon) in the literature, can vary enormously. The Raman spectra of many carbon materials, including some films and graphitized fibers, exhibit extensive broadening and overlap between the two bands, although the Raman spectra of the Zn/C nanoparticles synthesized at 700 and 800 °C show two peaks at 1580 and 1360 cm^{-1}. For the Zn/C nanoparticles obtained at 800 °C, however, more than 50% of the carbonaceous material is present as graphitic carbon, as derived from the peak intensities (see above).

Conclusions

The dissociation pattern of metal alkoxides and the formation of core/shell structures have been discussed previously,[11] and three categories that differ in the nature of the core and shell have been observed. For alkyl–metal compounds, for example compounds of the three metals (Cd, Zn, and Al; the same is true for Sn) studied here, the metal forms the core and carbon the shell. It is assumed that dissociation of the precursor leads to the formation of metal and carbon particles, as well as gaseous H_2 and hydrocarbons. In the study of the RAPET of metal alkoxides,[11] we have demonstrated that the kinetics of the reaction rather than the thermodynamics determines the morphology of the product. The same holds true for alkyl–metal compounds. It is obvious that if thermodynamics were to control the structure then carbon would solidify first and would become the core as carbon has a higher boiling point. Since the opposite is observed in our studies, where the metal solidifies first and creates the core while carbon constitutes the shell, it can be concluded that this RAPET reaction is kinetically controlled.

In all three cases a core/shell morphology was observed, although the size distributions of both the core and shell are very broad. Unlike the RAPET of mesitylene,[14] which yields a very narrow size distribution of carbon spheres, we have detected very different sizes for the spheres obtained for Cd/C and Zn/C. This could be due to a temperature fluctuation due to heat evolved during aggregation of the metal and carbon atoms upon crystallization.

This manuscript has demonstrated the formation of air-stable core/shell nano- and microstructures of three active metals. The lack of oxygen in the starting materials is essential to obtain these air-stable metals, which distinguished the work reported here from that reported previously by us.[11] This proposed method might apply to other metals as well, thereby making it a general technique for creating and protecting reactive metallic nano- and microparticles. Indeed, preliminary results show that similar results are obtained for the dissociation of tetraalkyltin.

Experimental Section

The metal/carbon core/shell structures were prepared by thermolysis of the corresponding alkyl–metal compounds. The precursors for the reactions were diethylzinc [$Zn(C_2H_5)_2$], dimethylcadmium [$Cd(CH_3)_2$] (97%), and triethylaluminum [$Al(C_2H_5)_3$] (93%), which were purchased from Aldrich and STREM and used without further purification. The preparation of the core/shell structures was carried out in a 5-mL closed cell. The cell was assembled from stainless steel LET-LOCK union parts (HAM-LET, Ziporit, Israel). A half-inch union part was attached on both sides by standard caps. A standard union is shown in ref.[11]

For these syntheses, 1 mL of one of the above precursors was introduced into the cell at room temperature under nitrogen (the cell was filled in a glove box). The filled cell was then closed tightly with the other plug and placed inside an iron pipe in the middle of the furnace. The temperature was raised at a rate of 10 °C per minute and the closed cell was heated at 500, 700, or 800 °C for 3 h. The reaction proceeds under the autogenic pressure of the precursor. The LET-LOCK was gradually cooled (over about 5 h) to room temperature and the resulting dark black powder was collected. Gases were released upon opening the cell. The total yield of product/carbonaceous material was about 42.0% for Zn/C, 78.8% for Cd/C at 800 °C, and 26.2% for Al/C at 500 °C. All yields are relative to the weight of the starting materials. All the products were characterized by structural and morphological techniques.

XRD patterns were collected with a Bruker AXS D8 advance powder X-ray diffractometer (Cu-K_α radiation; wavelength: 1.5406 Å). The morphologies and nanostructures of the as-synthesized products were further characterized by TEM (model: JEM-1200EX) and FESEM (model: JEOL JSM-7000F) at an accelerating voltage of 1 and 30 kV, respectively, and a JSM-840 scanning electron microscope (SEM). The SAED (selected-area energy-dispersive X-ray analysis) of one individual Zn/C particle was conducted with a JEOL-2010 HRTEM model. Samples for TEM and HRTEM were prepared by ultrasonically dispersing the products into absolute ethanol, placing a drop of this suspension onto a copper grid coated with an amorphous carbon film, and then drying under air. The particle-size distributions of Zn/C and Cd/C were determined with a SEM micrograph at a zoom of 20 μm. The diameters of 70 particles were measured with Scion image software and integrated into a histogram of percentages vs. particle size. An Olympus BX41 (Jobin Yvon Horiba) Raman spectrometer was employed, using the 514.5-nm line of an Ar laser as the excitation source, to analyze the nature of the carbon present in the Zn/C product only.

Supporting Information (see footnote on the first page of this article): Experimental details and images of Zn/C and Al/C micro- and nanoparticles (PDF).

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