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Solid-state synthesis of embedded single-crystal metal oxide and phosphate nanoparticles and *in situ* crystallization

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ABSTRACT

A new solid state organometallic route to embedded nanoparticle-containing inorganic materials is shown, through pyrolysis of metal-containing derivatives of cyclotriphosphazenes. Pyrolysis in air and at 800 °C of new molecular precursors gives individual single-crystal nanoparticles of SiP_2O_7, TiO_2, P_4O_7, WP_2O_7 and SiO_2, depending on the precursor used. High resolution transmission electron microscopy investigations reveal, in most cases, perfect single crystals of metal oxides and the first nanostructures of negative thermal expansion metal phosphates with diameters in the range 2–6 nm for all products. While all nanoparticles are new by this method, WP_2O_7 and SiP_2O_7 nanoparticles are reported for the first time. *In situ* recrystallization formation of nanocrystals of SiP_2O_7 was also observed due to electron beam induced reactions during measurements of the nanoparticulate pyrolytic products SiO_2 and P_4O_7. The possible mechanism for the formation of the nanoparticles at much lower temperatures than their bulk counterparts in both cases is discussed. Degrees of stabilization from the formation of P_4O_7 affects the nanocrystalline products: nanoparticles are observed for WP_2O_7, with coalescing crystallization occurring for the amorphous host in which SiP_2O_7 crystals form as a solid within a solid. The approach allows the simple formation of multimetallic, monometallic, metal-oxide and metal phosphate nanocrystals embedded in an amorphous dielectric. The method and can be extended to nearly any metal capable of successful coordination as an organometallic to allow embedded nanoparticle layers and features to be deposited or written on surfaces for application as high mobility pyrophosphate lithium–ion cathode materials, catalysis and nanocrystal embedded dielectric layers.

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1. Introduction

Chemical reactions at nanoscale level are of increasing interest from many standpoints [1–4]. Organometallic approaches have been shown to be generalized to several metal oxides from semiconducting to magnetic materials as well as from monometallic to mixed-metal-oxide nanomaterials. Control over size, shape, size distribution and surface state is very important and the rational preparation of nanoparticles has wide implications from a fundamental point of view and also for applications. The high surface areas exhibited by nanoparticles produce intrinsically high surface reactivities allowing surface reactions to approach stoichiometric conversions [5]. Metal oxides exhibit fascinating electronic and magnetic properties including metallic, insulating or semiconducting and ferro-, ferri-, or antiferromagnetic behavior [6]. Some oxides possess ferroelectric or piezoelectric properties, some others are superconducting, or exhibit colossal magnetoresistance. Many examples of metal-oxide nanostructure application include catalysis, sensing, magnetic recording media, and energy storage/conversion have been recently discussed [7].

Chemical techniques are widely used to produce nanostructured materials due to their straightforward nature and the potential for producing large quantities of the final product. Methods such as chemical and physical vapor deposition, oxidation or condensation have been used [8]. A crucial aspect is the stabilization of the nanoparticles and the ability to rationally form either metallic, oxidic, semiconducting, and compound phases of the metal. There are very few reports of solid-state methods for preparing nanoparticles; the majority involve solution-based approaches, or colloidal chemistry [9]. Aside from the standard approach to many nanoscale materials, more novel approaches have recently shown that Co_9O_8 and Ni_2P hollow nanocrystals can be prepared using the nanoscale Kirkendall effect [10,11]. Organometallic complexes have also been used for metal-oxide nanostructure formation, by

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employing their sensitivity to moisture and the resulting exothermic decomposition [12].

Many of the routes that result in controllable and phase-pure metallic and metal-oxide nanoparticles are limited to metals and oxides due to the nature of the organometallic complex and its coordinative properties. Detailed observations of nanocrystallization during decomposition of solution-based organometallics are also relatively scarce. Obtaining single-crystal nanoparticles of any valve or transition metal as their corresponding metallic and oxidic nanoparticles is a minimum next-step requirement; obtaining phosphate and, in addition, any other nanoscale compound by similar routes is a considerable advantage given the usefulness of nanoscale oxides and phosphates in lithium–ion batteries for example. The method outlined here allows a simple and effective route to positive and negative thermal expansion materials as individual nanostructures or as a deposited film. Pyrophophates $A^{IV}M_2^VO_7$, where the A^{IV} cation includes Zr, Ti, Mo, Re, W, Th, U, Pu, Ce, Hf, Pb, Sn, Ge, and Si; M^V = P, V, or As, are known for their unusual high temperature behavior [13]. Thermal expansion is a necessary consideration in a number of applications where increases and decreases in temperatures can affect physical dimensions, stability, integrity, and mechanical properties of materials. To the best of our knowledge, there are no dedicated reports of controlled metal-phosphate nanomaterial synthesis through organometallic syntheses and subsequent procedures.

Chemical reactions of nanoparticles can also occur under exposure to the electron beam of a transmission electron microscope. Many of the previous reports on this phenomenon are linked to uncontrolled crystallization even though the information leads to a better understanding of the crystallization mechanism. Various mechanisms such as quasi-melting, particle diffusion and phase transition–resolidification have been reported for some time [14,15]. Examples of nanocrystallization of anatase or rutile TiO_2 by laser treatment have been also reported [15] and the transformation from core/shell Se@C to yolk/shell M/Se@C (M = Au, Ag) can be achieved through electron beam irradiation from the microscope [15]. Controlling such reactions, allowed through electron beam induced heating interactions, is best achieved via organometallic routes, as is commonly observed in many applications such as focused ion beam metal deposition.

The molecular precursor route to nanostructured materials both in solution [16–18] or in the solid-state [19,20] is an unconventional, yet suitable, way to obtain metallic, metal-oxidic and semiconducting nanoparticles and nanostructures. Organometallic derivatives, both cyclic and polymeric phosphazenes, are emerging as useful precursors of metallic nanostructured materials [21–23]. Precursors containing two different organometallic fragments coordinated to the phosphorus ring of a cyclotriphosphazene have not yet been successfully realized as nanomaterial precursors [24]. This method is so versatile it allows us to form many transition metals to form as oxide, phosphate and also pyrophosphates which offer high lithium–ion mobilities for fast charging lithium–ion phosphate-based cathode materials [25].

Here, we report the synthesis of new organometallic derivatives of cyclotriphosphazenes that result in individual single-crystal nanoparticles of metal oxides and phosphates embedded in an amorphous matrix after pyrolysis in air. Coordination of precursors (1) and (2) shown in Scheme 1 by Cp_2TiCl and $W(CO)_5$ fragments is done to create new bi-organometallic derivatives (1a)–(2b) reported here. To our knowledge, these precursors are the first dinuclear heterobimetallic derivatives of cyclotriphosphazenes containing both silicon and a transition metal attached to the phosphazene ring [26]. Pyrolysis at 800 °C in air result in nanostructured materials: using precursors (1a) and (2a) we produce both Ti and Si-containing single-crystal nanoparticles (TiO_2 and SiO_2) respectively, with the first report of Si and W-oxide and phosphate single-crystal nanoparticles from precursors (1b) and (2b). High resolution electron microscopy and various spectroscopic analyses were used to identify the elusive W and Si pyrophosphates (WP_2O_7 and SiP_2O_7) as either perfect single-crystal or heavily twinned nanoparticle form using a solid-state method of direct deposition on a surface. We also detail the observation of single crystal nanoparticles of SiP_2O_7 formed *in situ* by electron beam-induced reaction of between the SiO_2 and remnant phosphazenes (post pyrolysis), and show the solid-state stabilizing effect of P_4O_7 formed from pyrolysis of their respective organometallic derivatives. This paper also details a mechanism for writing these nanoparticles into the host material using this pyrolytic approach at lower crystallization temperatures than bulk materials. One potential limitation with organometallic routes to nanomaterials is that they are almost all conducted in solution based form. This solid state method can replicate what is formed in solution based approaches, extends the technique to new nanomaterials through design of new phosphazene based polymeric precursors, but also allows for deposition on surfaces that do not wet, or are sensitive to, solution-based deposits.

2. Experimental

2.1. General

All reactions were carried out under nitrogen using standard Schlenk techniques. Infra-red (IR) spectra were recorded on an FT-IR Perkin–Elmer 2000 spectrophotometer. Solvents were dried and purified using standard procedures. $N_3P_3Cl_6$, $W(CO)_6$, $H_2N(CH_2)_3Si(OEt)_3$, $HN(CH_3)(CH_2)_3CN$, $HOC_6H_4CH_2CN$, Cp_2TiCl_2, and NH_4PF_6 (Sigma–Aldrich) were used as received.

2.2. Characterization methods

Nuclear magnetic resonance (NMR) spectra were conducted using a Bruker AC-300 instrument with $CDCl_3$ as the solvent unless otherwise stated. ^1H and $^{13}C\{^1H\}$ NMR are given in δ relative to TMS. $^{31}P\{^1H\}$ are given in δ relative to external 85% aqueous H_3PO_4. Coupling constants are in Hz.

X-ray diffraction (XRD) was carried out at room temperature on a Siemens D-5000 diffractometer with θ–2θ geometry. The XRD data was collected using Cu Kα radiation (40 kV and 30 mA). Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were acquired with a JEOL 5410 SEM with a NORAN Instrument micro-probe transmission microscope and with a Hitachi SU-70 FESEM operating at 10 kV equipped with an Oxford Instruments X-max 50 mm^2 solid-state EDX detector.

Transmission electron microscopy (TEM) was carried out on a JEOL JEM-2011 using a LaB_6 filament operating at 200 kV. The finely powdered samples were dispersed in *n*-hexane and iso-propyl alcohol (IPA), dropped on a conventional holey carbon copper grid and dried under a lamp. TEM image measurements and Fast Fourier Transform (FFT) analyses were made using DigitalMicrograph™ software with a Gatan Multiscan 794 CCD camera.

The pyrolysis experiments were carried out by pouring a weighed portion (0.05–0.15 g) of the organometallic trimer into aluminum oxide boats placed in a tubular furnace (Lindberg/Blue Oven model STF55346C-1) under a flow of air, heated from 25 to 300 °C and then to 800 °C, and annealed for 2 h. The heating rate was 10 °C min^{-1} under an air flow of 200 mL min^{-1}.

2.3. Synthesis of precursors

(1a) Synthesis of $N_3P_3[NH(CH_2)_3Si(OEt)_3]_3[NCH_3(CH_2)_3CN\cdot Cp_2TiCl]_3[PF_6]_3$.

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