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Formation of organometallic polymer nanorods using a nanoporous alumina template and the conversion to magnetic ceramic nanorods

Madlen Ginzburg-Margau, Sébastien Fournier-Bidoz, Neil Coombs, Geoffrey A. Ozin* and Ian Manners*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6.
E-mail: imanners@chem.utoronto.ca or gozin@chem.utoronto.ca

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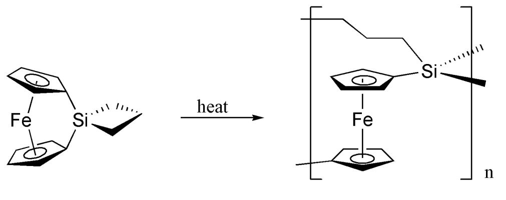
Polyferrocenylsilane nanorods were prepared using a porous anodic aluminium oxide template followed by chemical etching; pyrolysis was used to obtain magnetic iron oxide-containing ceramic nanorods.

There has been tremendous interest in template-based synthesis of nanomaterials for numerous nanotechnology applications.[1] For example, porous anodic alumina[2] (**PAA**) has been employed as a templating material to fabricate nanowires because of its high pore density, uniform pore distribution, and tunable pore diameters of *ca.* 5–300 nm.[3] A range of materials have been infiltrated into **PAA** including metals,[4] semiconductors,[5] carbon nanotubes,[6] conducting polymers[7] and ceramics.[8] Magnetic nanorods containing elements such as Fe, Co and Ni are potentially interesting for magnetic recording media applications.[4] Barcode nanorods have also recently been prepared by sequential electrochemical deposition of different metals into **PAA** templates.[9]

Recently, we reported the synthesis of shaped magnetically tunable ceramics in high yield from a highly crosslinked, polyferrocenylsilane (**PFS**).[10,11] **PFS** was prepared *via* the thermal ring-opening polymerization (ROP) of a strained spirocyclic [1]silaferrocenophane (**SSF**).[12] Organometallic polymers possess interesting physical properties; for example, **PFS** is semiconductive when doped and electrochemically active.[13] We have demonstrated that **PFS** and its ceramic pyrolysis products could be fabricated into various architectures including nanostructures,[14] spheres,[15] patterned films,[10] and inverted opals.[16] In this communication we report the synthesis of **PFS**-nanorods using **PAA** templating and its subsequent conversion to iron oxide-containing ceramic (**CER**)-nanorods. These organometallic and metal-containing nanorods may possess interesting charge transport and magnetic properties, respectively.

Fig. 1 shows a schematic representation of the templating procedure that was employed to prepare the nanorods. The **PAA** template used was prepared using one anodization step as previously described.[17,18] Due to the insolubility of the highly crosslinked **PFS**, the **SSF** monomer was infiltrated into the **PAA** template, which was pre-treated at 300 °C to remove any adsorbed water. The dry **PAA** template was combined with an excess amount of **SSF** in a Pyrex tube. The tube was then placed under vacuum (*ca.* 10^{-4} Torr) to promote sublimation of the **SSF** monomer into the **PAA** pores and then sealed. To speed up the **SSF** infiltration the **SSF/PAA** sample was placed in an oven at 50 °C and the temperature was raised in steps over one week up to 180 °C, and was then held at that temperature for 12 h to ensure complete ROP to form the desired **PFS/PAA** composite. The pyrolysis of the **PFS/PAA** composite under a N_2 atmosphere yielded an iron oxide-containing **CER/PAA** replica as shown on the right side of Fig. 1. The route on the left side of Fig. 1 involved the chemical etching of the **PAA** template using a 1% NaOH solution to yield **PFS**-nanorods. Due to the vacuum infiltration method employed and the insolubility of the crosslinked **PFS** there was a film of excess **PFS** on the top and bottom of the nanorods. Subsequent pyrolysis under N_2 of the **PFS**-nanorods, after the **PAA** template removal, yielded **CER**-nanorods that replicated the structure of the **PFS**-nanorods.



SSF **PFS**

The nanorods were imaged using electron microscopy as shown in Fig. 2. Fig. 2A shows a scanning electron microscopy (SEM) image of the **PFS**-nanorods running from top to bottom of the image. The nanorods remain aligned due to the excess **PFS** that holds them together at both ends. The connection seems to have been broken at the edge of the image, which could be a result of sample cleavage during sample preparation. Fig. 2B shows a transmission electron microscopy (TEM) image of a cross section of the **CER/PAA** composite prepared by pyrolysis at 900 °C for 6 h. The iron oxide particles are clearly visible inside the ordered **PAA** nanopores. Fig. 2C shows a SEM image of the **CER**-nanorods obtained form **PFS**-nanorods after pyrolysis at 900 °C for 6 h. The excess ceramic is clearly seen on the top and bottom of the nanorods. Fig. 2D shows a magnified view of the ends of the well aligned **CER**-nanorods. Energy dispersive X-ray (EDX) analysis indicated the absence of any Al in the **CER**-nanorods, as would be expected after the complete removal of the **PAA** template.

The crystalline species present in the ceramic were identified using powder X-ray diffraction (PXRD) studies. To obtain a highly crystalline **CER/PAA** composite, **PFS/PAA** was pyr-

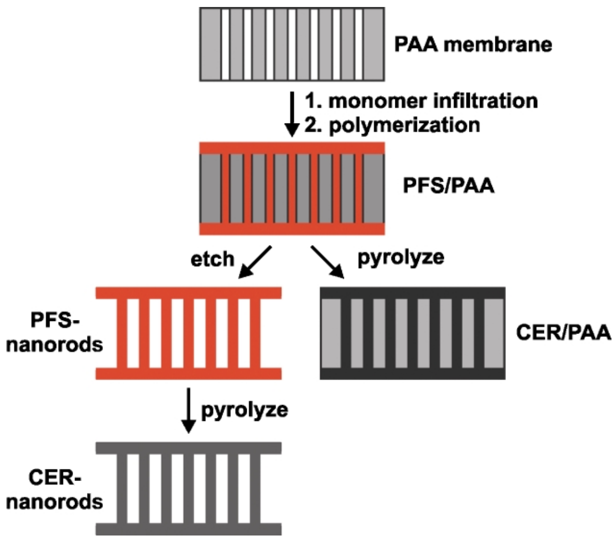


Fig. 1 Schematic representation of the templating procedure used to make the **PFS/PAA** composite material followed either by: etching to form **PFS**-nanorods and subsequent pyrolysis to give the **CER**-nanorods (left), or pyrolysis to give the **CER/PAA** composite (right).

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olyzed at 1000 °C for 6 h. Fig. 3 shows the PXRD pattern obtained for the **CER/PAA** composite. The crystalline species present were maghemite (γ-Fe_2O_3), graphite and Al_2O_3 from the crystallization of the **PAA** template. Interestingly, two polymorphs of Al_2O_3 were identified including γ-Al_2O_3 as previously observed with annealing[3] and ι-Al_2O_3.

Using the Scherrer equation,[19] γ-Fe_2O_3 magnetic nanoparticles of size *ca.* 62 nm were calculated from the PXRD pattern for the **CER/PAA** composite prepared at 1000 °C. Previously we reported α-Fe pyrolysis products from bulk forms of **PFS**.[10] In contrast to the bulk **PFS** pyrolysis, the **PAA** template in the **PFS/PAA** composite serves as an oxygen source, therefore an iron oxide ceramic was expected. We have previously observed γ-Fe_2O_3 as a pyrolysis product from a **PFS** inverted opal prepared using silica colloidal crystal templating,[16] as well as, Fe_3O_4 coated iron particles from the pyrolysis of **PFS** infiltrated into mesoporous silica.[14] Additionally, the pyrolysis of bulk hyperbranched poly[ferrocenyl(methyl)silane] resulted in hematite (α-Fe_2O_3) particles.[20]

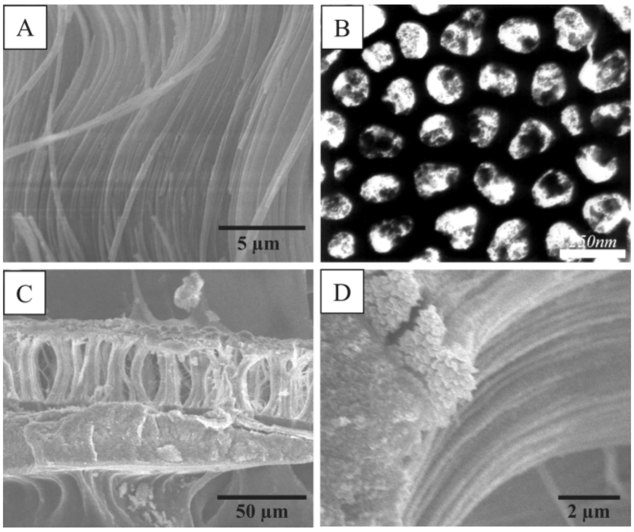

Fig. 2 (A) shows an SEM image of the **PFS**-nanorods. (B) shows a TEM image of a cross section of the **CER/PAA** composite looking down the **PAA** channels. (C) and (D) show SEM images of the **CER**-nanorods. In (C) the excess ceramic is seen on either end of the **CER**-nanorods and (D) shows one end of the **CER**-nanorods.

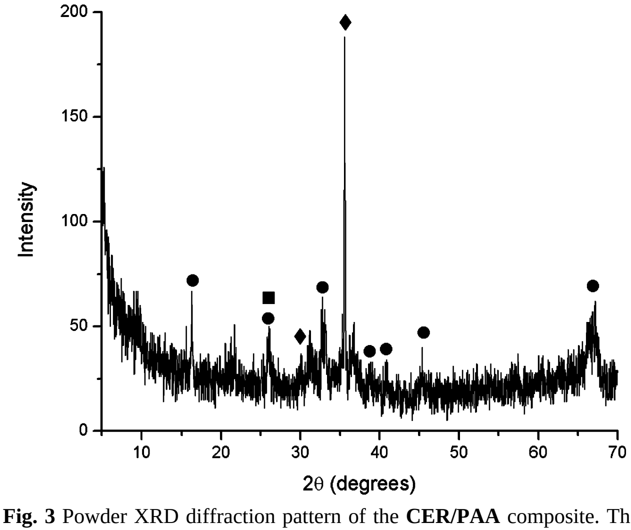

Fig. 3 Powder XRD diffraction pattern of the **CER/PAA** composite. The crystalline species observed were Fe_2O_3 (◆), Al_2O_3 (●) and graphite (■).

In summary, we report the preparation of organometallic polymer nanorods using a nanoporous alumina template. Additionally, we show the conversion of the polymer nanorods to γ-Fe_2O_3-containing ceramic nanorods. Preliminary microscopy studies indicate that by using low monomer loadings hollow tubular structures can also be prepared. Further investigations on the hollow tubes and the magnetic properties of the ceramic nanorods are in progress.

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