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Ruthenium / aerogel nanocomposits via Atomic Layer Deposition

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Abstract

We present a general approach to prepare metal/aerogel nanocomposites via template directed atomic layer deposition (ALD). In particular, we used a Ru ALD process consisting of alternating exposures to bis(cyclopentadienyl)ruthenium ($RuCp_2$) and air at 350 ^oC to deposit metallic Ru nanoparticles on the internal surfaces of carbon and silica aerogels. The process does not affect the morphology of the aerogel template and offers excellent control over metal loading by simply adjusting the number of ALD cycles. We also discuss the limitations of our ALD approach, and suggest ways to overcome these.

1. Introduction

Nanoporous metals exhibit a combination of unique physical and chemical properties linked to the very high surface-to-volume ratio of these materials, and as such, have significant technological potential as sensors [1,2], actuators [3,4], catalysts [5], and electrodes [6]. However, the traditional method to prepare nanoporous metals by alloy corrosion[7-9] is limited by the number of suitable alloy systems available. On the other hand, it has been demonstrated that nanoporous materials with tailored functionality can be developed using aerogels as a flexible and robust material platform [10-16]. Furthermore, metal-loading of aerogels should allow one to fine-tune material properties by exploiting the size-effect frequently observed for metal nanoparticles [17,18]. The techniques which have been developed to synthesize metal-loaded aerogels can be divided into two groups based on whether the metal is added before or after the sol-gel process. However both approaches have severe limitations: the former interferes with the sol-gel process and the latter involves time intensive and/or complicated steps such as supercritical deposition of metal nanoparticles. On the other hand, macro-cellular open-cell polymer foams can be easily loaded with metals using chemical or physical vapor deposition [19]. Unfortunately, this simple technique is difficult to scale down as shadowing effects and diffusion limitations become more and more important at the submicron length scale.

Here, we take advantage of the self-limiting nature of atomic layer deposition (ALD) to overcome the above mentioned limitations. The ALD process utilizes a suitable pair of sequential, self-limiting surface reactions and therefore offers excellent atomic level control of the deposited film thickness [20-22]. The method directly produces metallic deposits and generates only volatile co-products and therefore eliminates the necessity to perform additional reduction and cleaning steps which are usually required for wet impregnation techniques. We recently demonstrated that ALD can be used to prepare uniform, millimeter-sized samples of tungsten-coated alumina and GeO_2 aerogels [23]. However, the deposited W nanoparticles/films were not stabile and oxidized upon exposure to air. In the present work, we use a noble metal ALD process to prepare stable metal/aerogel nanocomposites. Specifically, we selected Ru as a reliable ALD process that has been established in the literature [24,25]. To study the effect of aerogel morphology and composition, we use two different aerogel templates: a high density carbon aerogel (520 mg/cc) with pores and ligaments on the micrometer length scale and a low-density silica aerogel (~10 mg/cc) with pores and ligaments on the nanometer length scale. In particular the ruthenium/carbon aerogel nanocomposite is technologically relevant as carbon-supported Ru nanoparticles are very efficient catalysts in a variety of reactions including the industrially important ammonia synthesis [26-28].

2. Experiment

The aerogels were synthesized at the Lawrence Livermore National Laboratory, and details of the synthesis can be found in Ref. [29,30]. The ALD experiments were performed at the University of Helsinki in a flow-type reactor, and the Ru ALD process was preciously described in the literature [24,25]. Nominally 8 nm thick Ru films were deposited by 200 cycles of alternating exposures to bis(cyclopentadienyl)ruthenium ($RuCp_2$) and air at 350 ^{o}C. To ensure penetration of the ALD precursors as deep into the aerogel samples as possible, long pulse times of 12 s were applied for both precursors, and also the purge times (12 s) were much longer than those used on planar surfaces. In order to facilitate the nucleation of Ru, the aerogels were first coated with a thin layer of alumina by 10 cycles of alternating exposures to trimethyl aluminum ($AlMe_3$) and water at 350 ^oC with 6 s pulse and purge times. After coating, the aerogel samples were fractured, and cross sections were analyzed by means of time-of-flight secondary ion mass spectrometry (TOF-SIMS, TRIFT III, Physical Electronics), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM, Philips CM300FEG), and x-ray photoelectron spectroscopy (XPS, Quantum 2000).

3. Results and discussion

Cross-sectional SEM micrographs reveal that Ru ALD on carbon aerogels results in formation of a dense layer of Ru nanoparticles on the surface of the ligaments rather than deposition of a continuous film (Fig. 1). This is a typical result for noble metal ALD films which are known to suffer from low nucleation density and thus yield individual metal nanoparticles rather than continuous films when a low number of cycles are applied. In our previous W ALD study we have demonstrated that the nucleation and growth mode depends on the particular surface chemistry, and that aerogels can be coated with continuous W films which show easier nucleation than noble metals. Ligaments fractured after Ru ALD can be easily identified by the absence of Ru nanoparticles on the exposed ligament cross-sections. An example is shown in Figure 1b. In this particular micrograph one can also see a thin delaminated film supporting Ru nanoparticles indicating the formation of a continuous alumina nucleation layer. SEM images collected from different areas of the sample reveal that both the density and the size of Ru particles decrease with increasing distance form the original monolith surface. However, over the length scale of the images shown in Fig. 1b,c we observe a relatively narrow size distribution. Energy dispersive x-ray (EDX) spectroscopy reveals that the metal loading of sample area shown in Fig 1b is ~20 at. % (~67 wt. %). Note that the ALD technique allows one to control both metal loading and the particle size by simply adjusting the number of ALD cycles. For example, in our previous study of W ALD on alumina and germania aerogels we achieved weight gains due to metal loading up to several hundred percent.[23] Furthermore, the deposition of Ru nanoparticles did not modify the morphology of the aerogel.

The Ru nanoparticles were further characterized by HRTEM (Figure 2) and XPS (data not shown). HRTEM reveals the formation of dome-shaped crystalline Ru nanoparticles, and XPS demonstrates that the Ru nanoparticles are metallic and stabile in air ($Ru3d_{5/2}$ XPS peak at 280 eV using the Al 2p peak of Al_2O_3 at 74.7 eV as reference). In contrast, traditional techniques for metal loading of aerogels usually require an additional reduction step to obtain metallic nanoparticles.

The Ru gradient revealed by cross-sectional SEM was further studied by TOF-SIMS (Figure 3). Images collected from fracture surfaces (fractured after Ru ALD) reveal that the Ru concentration is non-uniform and decreases with increasing distance from the aerogel surface. The Ru concentration decreases below the detection limit of our TOF-SIMIS system at a distance of approximately 300 micron from the top surface. Unlike

Ru, aluminum from the alumina nucleation layer is homogeneously distributed throughout the sample as demonstrated by the concentration profiles shown in Figure 3. This difference is attributed to the lower vapor pressure of the $RuCp_2$ precursor and indicates that the Ru ALD process remained in the diffusion-limited regime.

The Ru concentration gradient observed in the carbon aerogel sample (Fig. 3) clearly reveals the limitations of the technique. Uniform coating of macroscopic aerogel samples requires either the use of a sufficiently volatile metal precursor or very long exposure times. The first requirement is currently difficult to meet because there is only a limited number of suitable precursor pairs for metal ALD known [31,32], and among those WF_6 is the only high volatility metal precursor. The possibility to scale up the method by increasing the exposure time is also limited as the necessary exposure required to obtain uniform coatings scales with the square of the aspect ratio [33]. Further increase in exposure times would lead not only to increased process times but also increasing waste of the relatively expensive $RuCp_2$ precursor. In the reactor configuration used here, as well as in all conventional ALD reactors, the precursors are transported along the surface of the substrate and to saturate the surfaces inside the porous substrate the precursor molecules need to be transported by diffusion from the main flow into the pores. At the same time a major part of the molecules still flows over the substrate without being used. This brief discussion clearly demonstrates the need to develop new metal precursors with higher vapor pressures. An alternative solution may be found from reactor technology, however. Recently a new reactor configuration has been introduced [34] where the precursors molecules are forced to flow through the porous monolith, rather than flowing over it. This increases both the precursor utilization and the speed with which the surface inside the porous substrate can be saturated. A solid source for this reactor is still under development, however, and thus Ru coating of aerogels with this reactor will remain a topic of the next study.

To study the influence of the length-scale of aerogel templates, we performed additional ALD experiments on low-density silica aerogels with pores and ligaments on the length scale of a few nanometers. Already the visual inspection of the processed aerogel reveals the inhomogeneity of Ru coating (at least on a millimeter length scale) as judged by the presence of both transparent (original silica aerogel) and opaque (Ru rich) regions. Opaque regions were further analyzed by TOF-SIMS, SEM, and HRTEM (Fig. 4). TOF-SIMS reveals that Ru and Al are relatively evenly distributed throughout the opaque regions, at least on the length scale accessible by this technique (a few hundred micrometers). SEM micrographs do only show very faint Ru related features (spherical nanoparticles similar to those observed by TEM), although energy dispersive x-ray spectroscopy reveals the presence of ~50 at. % Ru (~80 wt. %). HRTEM confirms the formation of roughly spherical Ru nanoparticles with a diameter of ~ 5 nm (Fig. 4c). XPS reveals that these Ru particles are metallic and stable in air as in the case of the carbon aerogel. The large-scale inhomogeneity of the sample could be related to the presence of micro-cracks which facilitate rapid diffusion of the ALD precursor into certain regions of the sample.

4. Conclusions

The metal ALD/ aerogel template approach described here offers the unique opportunity to synthesize tunable metal/aerogel hybrid materials. At the current stage, the technique is limited to thin samples due to the need to transport the precursor molecules into the pores by diffusion from the main gas flow. For enhancing the precursor transportation into the pores the recently introduced flow-through reactor configuration may turn out very useful. Further enhancement may also be sought from high volatility metal precursors. Nevertheless, the technique is very promising for thin film applications such as the development of highly efficient electrodes for fuel cells.

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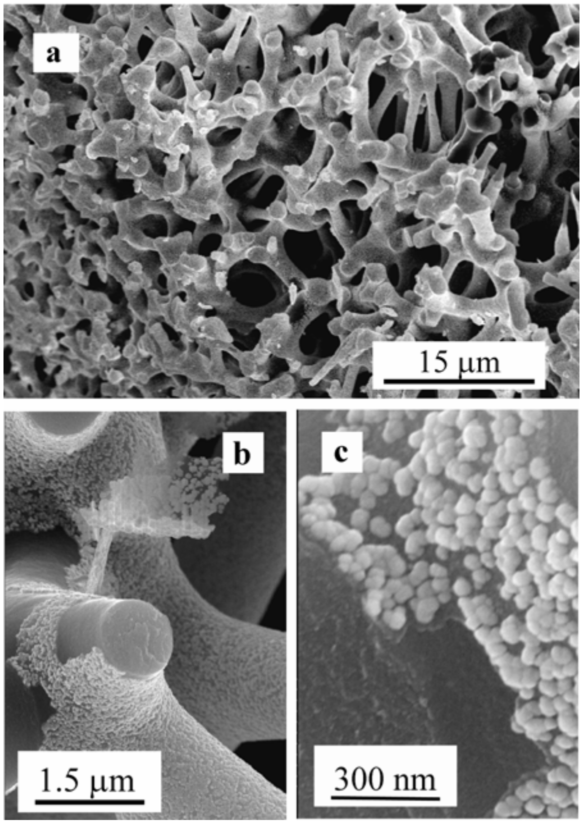
Figure Caption:

Figure 1 SEM micrographs of the fracture surface of a Ru-coated aerogel at different magnification levels (a-c). Note the uniform coating of the carbon ligaments with Ru nanoparticles. Fractured (after Ru ALD) ligaments can be identified by the absence of Ru particles on the exposed ligament cross-sections (b).

Figure 2: HRTEM image of Ru nanoparticles grown via ALD on a carbon aerogel.

Figure 3 TOF-SIMS analysis of a fracture surface of a Ru-coated carbon aerogel: optical image (top right) as well as the corresponding TOF-SIMS images (left) collected in the Ru and Al channels. Two-dimensional Ru and Al concentration profiles (collected along the white line) are shown in the lower right corner.

Figure 4: Characterization of Ru coated silica aerogels: Ru and Al channel TOF-SIMS images (a) as well as a SEM micrograph (b) collected from fractured samples. HRTEM micrograph revealing the growth of embedded Ru nanoparticles (c).



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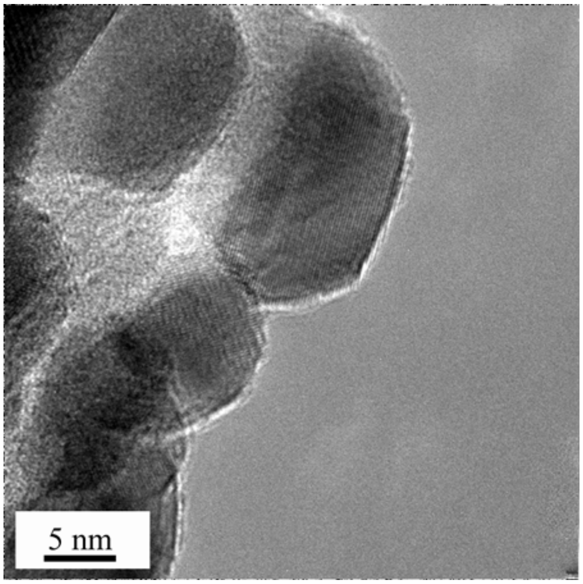

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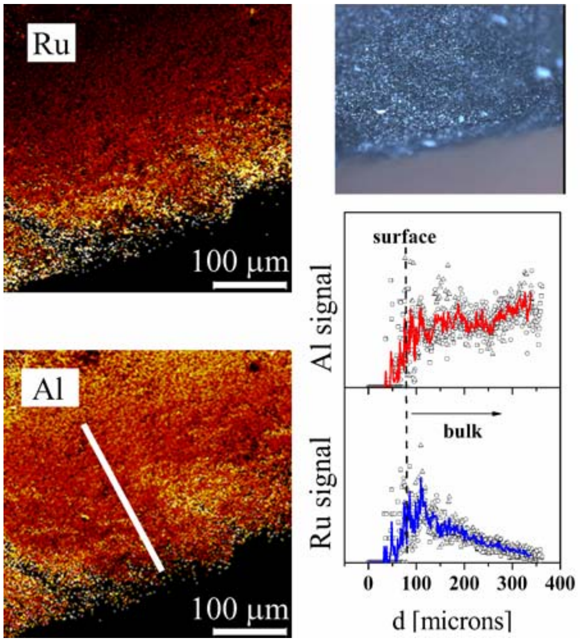

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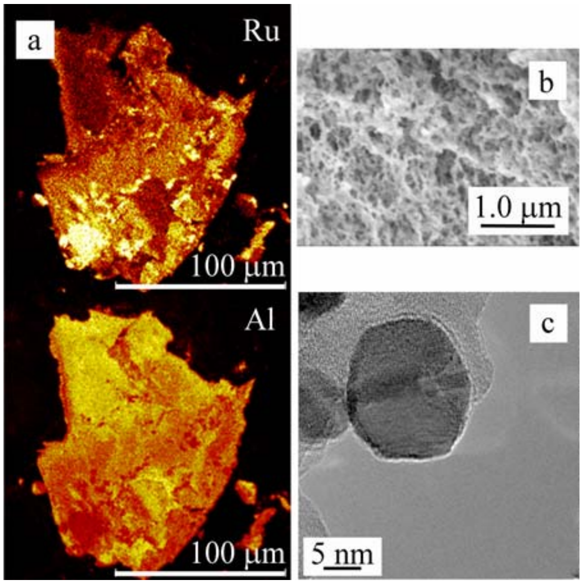

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