

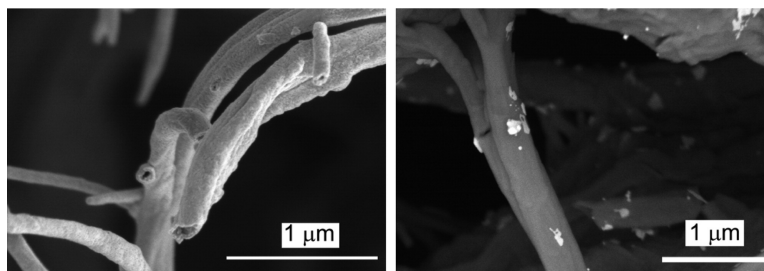
Communication

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J. Am. Chem. Soc., **2005**, 127 (41), 14178-14179 • DOI: 10.1021/ja0532887 • Publication Date (Web): 24 September 2005

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Atomic Layer Deposition in Nanometer-Level Replication of Cellulosic Substances and Preparation of Photocatalytic TiO₂/Cellulose Composites

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Conformal replication of the morphologies of natural fibrous materials at the nanometer scale offers a relatively simple, low-cost, and environmentally benign method for the formation of sophisticated nanostructures.¹ As compared, for example, to the commonly used template synthesis using porous alumina templates,² replication of natural fibers requires fewer process steps. Because of the natural starting structures, the nanostructures formed by replication are not as regular as those prepared using the alumina templates or other man-made templates. This is not necessarily a drawback, however, because many catalytic and sensor applications, for example, require only a high surface area, and a perfectly ordered structure is not necessary. On the other hand, replication of complicated biological structures may introduce some of the superb properties of biomaterials into man-made materials.³

Due to their high surface area, free-standing TiO₂ replicas of cellulose fibers have potential applications in photocatalysis, for example, but their fragility may limit their use. The fragility issue can be overcome if the cellulose is not removed: a TiO₂/cellulose composite is more robust than the replica alone. However, TiO₂ films deposited at low temperatures are usually amorphous and do not show high photocatalytic activities,⁴ while the post-anneal temperatures needed to crystallize an amorphous TiO₂ film are high enough to decompose the organic part of the composite. Therefore, for the preparation of TiO₂/cellulose composites, the as-deposited TiO₂ films should be crystalline.

Huang and Kunitake⁵ have prepared TiO₂ and ZrO₂ replicas of natural cellulosic fibers by a surface sol-gel process where the film growth occurs by two alternating reactions: adsorption of a metal alkoxide, for example Ti(OⁿBu)₄, from a solution on a hydroxyl-terminated surface, and hydrolysis of the adsorbed layer. Free-standing hollow metal oxide replicas were formed by removing the filter paper by air-anneal.⁵ The same group utilized the surface sol-gel process also in preparation of TiO₂/Au nanoparticle replicas⁶ and polypyrrole/TiO₂ composites on natural fibers.⁷

While the surface sol-gel process gave excellent results in replication,^{5,6} there still remains an issue of limited penetration into the finest details of the material being replicated. This is because surface tension may prevent wetting of the smallest pockets of the nanostructures. Gas-phase techniques obviously do not have this limitation. Cook et al.³ used chemical vapor deposition (CVD) in replicating with silica butterfly, housefly, and ultrahydrophobic plant leaves. This silica CVD process appears to be exceptionally good in uniformity and conformality, however. With other materials CVD is likely to meet problems in maintaining uniformity through the whole replica because of precursor depletion from the gas phase.

In this study, atomic layer deposition (ALD)^{8,9} was used for the preparation of TiO₂ replicas of cellulose fiber structure of filter paper and TiO₂/cellulose composites. Being a self-limiting chemical

gas-phase technique for thin-film deposition, ALD combines the benefits of surface sol-gel and CVD in replication of fibrous structures. Film growth in ALD occurs via alternating saturative surface reactions. The precursor vapors are pulsed into the reactor one at a time, and the precursor pulses are separated by inert gas purges. After each precursor pulse and the subsequent purge, the substrate surface is saturated by a monolayer of that precursor. Since the gas phase is free of the precursor, the next precursor reacts only with the adsorbed surface layer. Thus the film growth occurs (sub)monolayer by (sub)monolayer, and the film thickness can be accurately controlled by the number of the deposition cycles. Because of this self-limiting growth mechanism, ALD-grown thin films are conformal, and their thicknesses and compositions are uniform over large areas. These features make ALD a very suitable method for conformal coating of complex shaped structures. ALD has been successfully employed for a variety of materials, including metal oxides, nitrides, and noble metals.^{8,10} Moreover, the temperature ranges for ALD growth are wide for many ALD processes, and hence many of them are applicable at low temperatures for natural fibers. For atomic layer deposition of TiO₂ thin films, halides and alkoxides are commonly used Ti precursors, and H₂O is the most common oxygen precursor.^{8,9} Depending on the deposition temperature, the resulting TiO₂ films are either amorphous or crystalline.⁴

The TiO₂/cellulose composites and replicas were prepared by depositing thin (30–55 nm) TiO₂ films on an ashless filter paper (Schleicher & Schuell 589/2, measured BET surface area 1.4 m²/g) by ALD at 150 and 250 °C. Ti(OMe)₄ (Aldrich, 95%) and H₂O as the titanium and oxygen precursors, respectively, were alternately supplied on the paper in 2 s pulses.⁴ Between the precursor pulses, the reactor was purged for 4 s with nitrogen, which served as the carrier and purging gas. The process was run under a pressure of about 10 mbar.

TiO₂ replicas of the paper were prepared by first depositing an amorphous TiO₂ film on an ashless filter paper at 150 °C and removing the paper by subsequent annealing in air at 450 °C for 6 h according to Huang et al.⁵ FESEM micrographs in Figure 1a,b show details of the structure of a TiO₂ replica, and Figure 1c,d shows corresponding STEM images. A hollow replica has been formed as expected. The structure of the paper has been successfully replicated down to the smallest details; see, for example, the triangle-shaped intersection of three nanotubes (Figure 1c). The wall thickness is about 30 nm. As the TiO₂ film was deposited by using 1000 ALD cycles, the growth rate is about 0.03 nm/cycle, in a good agreement with the deposition rate on planar substrates at this deposition temperature. XRD measurements showed that the as-deposited TiO₂ was amorphous, while after annealing it was crystallized into anatase structure. The replica prepared this way was very fragile, however. This is also reflected in its high BET surface area of 70 m²/g.

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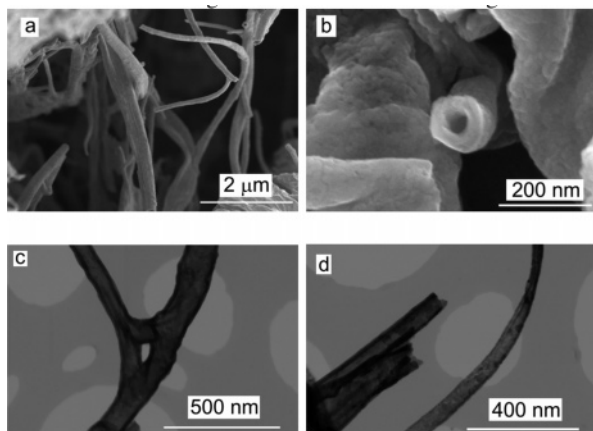


Figure 1. (a,b) FESEM (Hitachi S-4800) micrographs of a TiO₂ replica where the TiO₂ film was deposited at 150 °C and the paper was removed by air-anneal at 450 °C. (c,d) STEM micrographs of a TiO₂ replica.

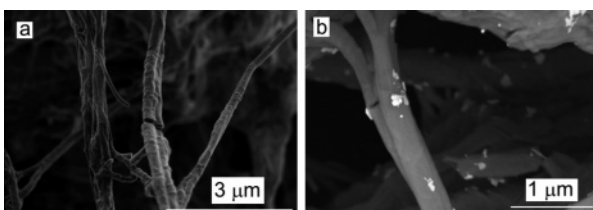


Figure 2. (a) FESEM micrograph of a TiO₂/cellulose composite prepared at 250 °C. (b) Backscattered electron image of Ag nanoparticles on the surface of the TiO₂/cellulose composite.

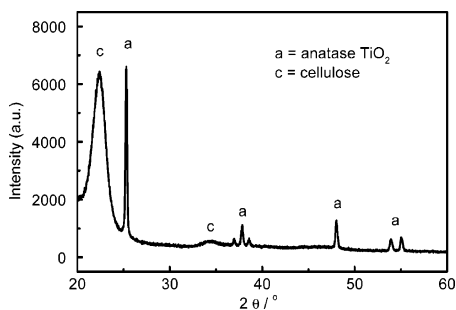


Figure 3. X-ray diffractogram of a TiO₂/cellulose composite prepared at 250 °C. The measurements were done on a Philips MPD 1880 powder X-ray diffractometer using Cu K α radiation.

To avoid the problem of fragility, TiO₂/cellulose composites were prepared by leaving the cellulose structure beneath the TiO₂ coating. The deposition temperature was chosen as 250 °C to obtain anatase structured film. Figure 2a shows a FESEM micrograph of a TiO₂/cellulose composite prepared at 250 °C. The morphology of the original paper has survived and become conformally coated with the TiO₂ film. The composite was mechanically robust and could be bent without rupturing, and its BET surface area was about 4 m²/g.

Figure 3 shows an X-ray diffractogram of a TiO₂/cellulose composite. The TiO₂ film is crystalline, showing the anatase reflections.¹¹ The reflections arising from the filter paper (cellulose, ref 12) are also seen. Crystalline TiO₂ films deposited by ALD at 250 °C from Ti(OMe)₄ and H₂O are known to be photocatalytically active.⁴ The mechanical stability of these anatase TiO₂/cellulose composites enables their use as efficient, lightweight, high surface

area photocatalysts. They may be interesting also in specialized filtering applications and as sensors.

The photocatalytic activity of the anatase TiO₂/cellulose composite was verified by photocatalytic reduction of Ag(I) to Ag.¹³ The composite was immersed for 5 min in a 0.1 M aqueous AgNO₃ solution and irradiated by UV light ($\lambda = 365$ nm, intensity 0.8 mW/cm²). To reduce all the adsorbed Ag(I) ions, the irradiation was continued for 5 min after rinsing and drying the composite. Figure 2b shows a backscattered electron image where the metallic Ag nanoparticles on the TiO₂-coated fibers can be seen clearly as bright features. Loading with noble metal particles is known to improve the charge separation in TiO₂, leading to higher photocatalytic activity.¹⁴ Silver is especially interesting due to its antimicrobial properties.

Thermogravimetric measurements (not shown) of the filter paper under nitrogen showed that the paper starts to lose weight only above 250 °C. This gives the possibility to deposit a wide range of materials on cellulose by ALD either directly or, if necessary, by depositing first a thin layer of TiO₂ or Al₂O₃¹⁵ on the filter paper. The latter option could also enable the use of more aggressive precursors such as ozone or oxygen that otherwise might decompose the fibers. An attractive feature of ALD is straightforward preparation of nanolaminates consisting of thin layers of two or more materials.⁸ When applied in replication of fibers, the nanolaminates will result in coaxial tubes.

In conclusion, it was shown that with ALD it is possible to accurately replicate cellulose structure of paper down to the nanofiber level. Thus, deposition temperatures considerably higher than room temperature can be successfully used for thin films on cellulosic materials. Anatase TiO₂/cellulose composite material was also prepared. Metallic Ag nanoparticles were formed on the TiO₂ surface by photocatalytic reduction of Ag(I) ions. The mechanical stability of the TiO₂/cellulose composite enables its use in various applications. This study opens new possibilities for the preparation of organic/inorganic composite materials by ALD.

Acknowledgment. Financial support from the Academy of Finland (Project no. 201564) and the Finnish National Technology Agency (TEKES, Technology programme Clean Surfaces 2002-2006) is gratefully acknowledged.

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JA0532887