Supasan Pattanaargson Wanichwecharungruang et al.

Organic–inorganic hybrid polysilsesquioxane nanospheres as UVA/UVB absorber and fragrance carrier

This work was performed at Drexel University with funding provided by ArtCraft Glassware. SEM by Murat Kurtoglu, color and design by Pavel Gogotsi (Drexel University).

Title: Synthesis of quasi-oriented α-MoO₃ nanobelts and nanoplatelets on TiO₂ coated glass

Using a simple yet efficient wet-chemical method followed by calcination, various morphologies of α-MoO₃ structures are produced, including nanobelts (shown above).
Synthesis of quasi-oriented $\alpha$-MoO$_3$ nanobelts and nanoplatelets on TiO$_2$ coated glass

Murat E. Kurtoglu,$^{a,b}$ Travis Longenbach$^a$ and Yury Gogotsi$^{a,*}$

Received 19th February 2011, Accepted 24th March 2011
DOI: 10.1039/c1jm10752f

We report on a new method to produce quasi-oriented $\alpha$-MoO$_3$ nanobelts on TiO$_2$ coated glass substrates. Using a simple yet efficient wet-chemical method with subsequent calcination, various morphologies of $\alpha$-MoO$_3$ including oriented nanobelts, rods and platelets were produced. The crystal morphology can be controlled by changing the substrate and/or the process parameters. Some applications of the resulting structures were demonstrated by coating them with TiO$_2$ and carbon. The photocatalytic activity of the TiO$_2$ coated $\alpha$-MoO$_3$ nanobelts was several times higher than that of the smooth TiO$_2$ coatings prepared on soda-lime glass. A very thin layer (20–30 nm) of carbon coated on nanobelts by sputtering resulted in a highly light absorbing film with an average reflectivity of 4%, while fluorosilane coated nanobelts showed superhydrophobic properties.

Introduction

One-(1-D) and two-dimensional (2-D) nanostructures are receiving a lot of attention due to their unique electronic, chemical, optical and mechanical properties that differ from thin films or bulk materials.$^{1,2}$ In particular, high surface area metal oxide nanostructures offer significant potential in several application areas such as gas sensors, piezoelectric devices, and catalysis.$^3$ While nanotubes and nanowires have been very extensively studied,$^4$ nanobelts received less attention until recently.$^5$ In particular, $\alpha$-MoO$_3$ nanobelts have been utilized in several applications including field emission devices,$^7$ gas sensors,$^8$ as positive templates,$^9$ Li-ion battery electrodes because of their layered structure,$^{10,11}$ as well as the synthesis of MoS$_2$ nanotubes$^{12}$ and MoO$_2$ nanorods.$^{13}$

There are two common phases of molybdenum trioxide (MoO$_3$): a thermodynamically stable orthorhombic phase ($\alpha$-MoO$_3$) and a monoclinic phase ($\beta$-MoO$_3$). $\alpha$-MoO$_3$ has a layered atomic structure with layers stacked along [010] by van der Waals bonding and each layer is composed of two sub-layers forming corner-sharing octahedra along [001] and [100]. It can form a variety of morphologies due to this unusual crystal structure that favors anisotropic growth. Consequently, a rich variety of nanostructures including nanorods,$^{14,15}$ nanowires,$^{16}$ nanotubes,$^{17}$ and nanobelts$^5$ have been reported for $\alpha$-MoO$_3$.

Several methods have been used for the synthesis of $\alpha$-MoO$_3$ nanobelts. Li et al. reported field emission properties of $\alpha$-MoO$_3$ nanobelts which were prepared by heating a piece of molybdenum sheet at high temperatures in a chamber and evaporating the molybdenum trioxide onto a silicon single crystal.$^7$ Several other authors have published hydrothermal processes to produce $\alpha$-MoO$_3$ nanobelts.$^{18-21}$ Lou et al. reported fork-like $\alpha$-MoO$_3$ structures by capping the (001) planes with TiO$_2$ in a hydrothermal process.$^{22}$ However, hydrothermal processes are not applicable to the synthesis of coatings on a large surface area. Recently Xie et al. suggested a method in which $\alpha$-MoO$_3$ nanobelts were formed by placing a molybdenum sheet on a glass substrate and heating this system to 480 °C on a heater plate for 2 days.$^{23}$ While this is the simplest process reported thus far for the production of $\alpha$-MoO$_3$ nanobelts, which can be applied to relatively large areas, it is still a very slow process with a prolonged, energy-inefficient annealing step. Here, we report the synthesis of quasi-oriented $\alpha$-MoO$_3$ nanobelts on TiO$_2$ coated glass substrates of any dimension using a very simple wet chemical approach followed by annealing at a temperature as low as 400 °C with a short dwell time (ca. 30 min).

Experimental

To produce $\alpha$-MoO$_3$, molybdenum pentachloride (MoCl$_5$) (Alfa-Aesar, 99.6%) was dissolved in N,N-dimethyl formamide (DMF) (Sigma-Aldrich, anhydrous, 99.8%), which yielded a green transparent solution. 150 μl of this solution was dropped onto a TiO$_2$ coated (ca. 70 nm) glass slide (2 x 2 cm) using a micropipette. TiO$_2$ coating of the glass slides was done via a sol–gel method as reported previously.$^{24}$ Briefly, 120 g ethyl alcohol (200-proof, Electron Microscopy Sciences) and 15 g Ti-(O-i-C$_3$H$_7$)$_4$ (Alfa-Aesar, 98%) were mixed and subsequently stirred with a magnetic stirrer for 30 min. Then, a mixture of 0.96 ml deionized water (18 MΩ cm), 0.52 g HCl (Fisher Science, 38%), 1 g poly (ethylene glycol) (Sigma-Aldrich, M.W. = 2000) and 6.3 g...
ethyl alcohol was added drop-wise to the main solution. The solution was stirred for 2 h. Then, 9.6 g acetylacetone (Sigma-Aldrich, 98%) and 5 ml of deionized water were added to the prepared sol and stirred for an additional hour. The film was prepared by dip-coating (MTI Dip Coater HL-01). For this purpose, a glass microscope slide (Erie Scientific) was dipped into the prepared solution and withdrawn at a constant speed of 100 mm min$^{-1}$ followed by calcination at 400 °C for 30 min. After the deposition of the MoCl$_5$-DMF mixture on TiO$_2$ coated glass slides, the mixture turned from green to brown with increasing wait time and humidity, which is an indication of hydrolysis. Coated samples were placed into a furnace, which was preheated to 500 °C, within 10 min from the deposition of the MoCl$_5$-DMF mixture and calcined for 30 min. The same procedures were repeated on a plain glass microscope slide and TiO$_2$ coated quartz slides to evaluate the substrate effect. Samples were characterized by scanning electron microscopy (Zeiss Supra 50VP), transmission electron microscopy (JEOL JEM 2100), UV-Vis spectrophotometry (Thermo Scientific Evolution 600), and X-ray diffraction analysis (Siemens D500).

**Results and discussion**

SEM images show that the substrates were covered with belt-like anisotropic crystals with their long end directed upwards, as shown in Fig. 1a-1b. Obtained nanobelts were typically 6 to 8 µm in length and less than 0.4–0.5 µm in width. The typical thickness of the nanobelts was approximately 50 nm. XRD analysis (Fig. 1d) was in agreement with the previously reported $\alpha$-MoO$_3$ patterns, strong anisotropy was evident from the relative intensities of the peaks, particularly the (021) peak, which is similar to the reported XRD patterns of the aligned MoO$_3$ structures.$^{7,25}$ As seen from the TEM image and the respective SAED pattern (Fig. 1c), the nanobelts were single crystalline and had a principal growth direction along <001> and the sideways growth along <100>.

Our experiments have shown that the obtained morphology is strongly dependent on the type of substrate, the solvent used for dissolving MoCl$_5$, and the heating rate. When plain soda-lime glass was used as a substrate, rod-like structures with their growth direction parallel to the substrate were obtained (Fig. 2a). XRD analysis (Fig. 2b) of the structures shows that these crystals were mainly composed of $\alpha$-MoO$_3$ with (0k0) planes aligned parallel to the surface. Some sodium molybdate formation (Na$_2$MoO$_4$) was also evident from the diffraction pattern. Thus, this approach allows the synthesis of adherent $\alpha$-MoO$_3$ coatings on glass. We assume that sodium diffusion was responsible for the change in the $\alpha$-MoO$_3$ growth habit.

When TiO$_2$ coated quartz substrates were used, nanoplatelets (Fig. 2c) with their (0k0) planes perpendicular to the substrate

![Fig. 1](image-url) (a) Low- and (b) high-magnification SEM images of oriented MoO$_3$ nanobelts on soda-lime glass substrates (calcined at 500 °C). (c) TEM image and single crystal SAED pattern (inset). (d) XRD spectrum of the nanobelts (■: Na$_2$MoO$_4$).
were observed. The nanoplatelets were more robust to handling (scratching, peeling off etc.) compared with nanobelts due to a smaller aspect ratio and the intersecting plates forming a rigid structure. Therefore, despite their smaller aspect ratio and lower surface area, they may be more suitable for many practical applications as a coating when durability and wear resistance is required.

In order to better understand the growth process, we prepared a set of samples on glass slides and calcined them by heating at the rate of 50 °C min⁻¹ to 350 °C and 400 °C. Samples were taken out of the furnace at each temperature and quenched in air. At 350 °C, formation of plate-like structures was evident on the surface (Fig. 3a), whereas nanobelts were formed at 400 °C (Fig. 3b).

Based on the observations above, it can be concluded that anisotropic growth of α-MoO₃ nanobelts with their (0k0) planes perpendicular to the substrate plane were favored on TiO₂. The low lattice mismatch between the (010) plane of α-MoO₃ (a = 3.963 Å, b = 3.696 Å, c = 13.856 Å) and the (001) plane of anatase TiO₂ (a = b = 3.785 Å, c = 9.513 Å) (Fig. 4a) favors the preferential nucleation of the (010) planes of α-MoO₃ to the (001) planes of TiO₂. However, growth along [010] occurs through the creation of van der Waals bonds, which limits the growth rate compared to other principal growth directions, in which the growth occurs through the creation of ionic bonds (Fig. 4b). Accordingly, planar growth rates along the principal axes of α-MoO₃ decrease in the following order: (001) > (100) > (010). Since there is an excess supply of the α-MoO₃ precursor due to the fast heating rates, growth proceeds along the fastest direction, i.e. [001]. When the heating rate was decreased to 5 °C min⁻¹, nanoplatelets were formed instead of nanobelts. The TiO₂ (anatase) films deposited on glass are polycrystalline and there is a mixture of faces exposed in random directions. Typically, an anatase crystal has a tetragonal prism structure consisting of eight (011) and two (001) faces (Fig. 4c). (001) planes of TiO₂ laying parallel to the surface cannot nucleate nanobelts since (a) growth will be restricted by the compressive stress induced on the substrate due to fast heating and (b) the α-MoO₃ supply is provided in the direction perpendicular to the film plane. The growth starts from the TiO₂ film surface and proceeds outwards since heterogeneous nucleation is typically faster than homogeneous nucleation. Thus, those (001) planes of TiO₂, which are oriented at an angle to the substrate, act as preferred nucleation and growth sites for the formation of α-MoO₃ nanobelts. A schematic of the proposed mechanism is shown in Fig. 4d-e.
It is important to note that the rate of nucleation and growth should be carefully controlled to sustain the desired growth. For example, when samples were heated with a speed of \(5 \degree C \text{ min}^{-1}\), nanobelts were not observed. This can be explained by the high nucleation density due to the slow evaporation of DMF (b.p. \(= 153 \degree C\)), during which nuclei are created, but growth is limited as the temperature is well below the crystallization temperature. The solvent used to dissolve MoCl\(_5\) was also one of the determining parameters on the obtained structures, as suggested by several authors.\(^{28,29}\) When 2-propanol was used as a solvent in place of DMF, hydrolysis occurred quickly, as evident from the dark blue color of the deposited solution only a few minutes after coating. Dimethyl sulfoxide gave similar results to DMF while methanol produced results similar to 2-propanol. In the case of 2-propanol, the resulting structure is a film composed of fine crystals of \(\alpha\)-MoO\(_3\), indicative of a high nucleation rate (Fig. 3c). On the other hand, it was quite surprising to observe nanoplatelets on TiO\(_2\) coated quartz (Fig. 2c) rather than nanobelts, similar to the ones obtained on TiO\(_2\) coated soda-lime glass. There are only two differences between TiO\(_2\) coated quartz and glass substrates. The first is the high alkali content of soda-lime glass. In particular, sodium can diffuse easily through TiO\(_2\) films\(^{30,31}\) and may react with MoCl\(_5\) to form NaCl and/or Na\(_2\)MoO\(_4\), although this amount should be lower compared to
an uncoated surface. The second is the thermal expansion of the substrate. Quartz has one of the lowest coefficients of thermal expansion (CTE) (ca. 0.5 × 10⁻⁶ °C⁻¹)¹² while soda lime glass has a very high CTE (ca. 7.6 × 10⁻⁶ °C⁻¹)¹³. Thus, coatings on a glass substrate tend to experience a lower compressive stress than the ones on quartz. However, we believe that the alkali content is more important, as evidenced by the decrease in nanobelt density with increasing TiO₂ coating thickness (not shown). Increasing the TiO₂ thickness from ca. 80 nm to 300 nm significantly decreased the nanobelt density per unit of surface area; a thicker titania film led to a decrease in sodium content. It is important to note that no major morphological differences were detected with the TiO₂ films on glass and quartz, which might have led to different MoO₃ structures. Although the exact mechanism is still under investigation, some sodium diffusion through the TiO₂ film appears to be necessary to obtain highly anisotropic α-MoO₃ structures. It is possible that the NaCl crystals may be acting as capping agents to ensure an anisotropic growth of MoO₃ structures, as suggested recently by these authors.¹⁴

One-dimensional nanostructures attract great attention in solar cells and photocatalytic applications for light trapping as well as in electrochemical applications⁵⁴ due to their high surface area and surface roughness. α-MoO₃ nanobelts grown on an inexpensive glass substrate by such an easy method can be utilized as templates to produce active structures for solar cells and photocatalysis. To demonstrate the light trapping ability, obtained α-MoO₃ nanobelts were sputter coated with carbon. As can be seen from the total reflection spectra (Fig. 5), the reflection of carbon-coated nanobelts was less than 4%, compared to 20% for carbon-coated glass. Nanoplatelets on quartz samples also produced low reflection values (less than 7%).

For photocatalytic applications, α-MoO₃ nanobelts were first coated by SiO₂ using dip coating and then again dip coated with TiO₂. The resultant film was much more active compared to the film coated on plain glass, possibly due to its much higher surface area (Fig. 6). Approximately 10 times more dye was decomposed within the first 2 h by the TiO₂-coated nanobelts compared to the conventionally prepared TiO₂ film on glass. Although we used a dip-coating process, a gas phase deposition method should be more suitable as it is difficult to prepare a uniform coating on these structures by liquid phase deposition methods.

It is known that hydrophobic surfaces exhibit superhydrophobic behaviour when they are patterned, although patterning a surface is not very straightforward in most cases. In order to demonstrate the ease of forming a patterned superhydrophobic surface with this method, contact angle measurements were performed by the Sessile drop method on plain, carbon-coated, and fluorosilane coated α-MoO₃ nanobelts. Fluorosilane coating was prepared by soaking nanobelt coated glass in a 10 mM octadeyl-fluorosilane-hexane solution for 30 min followed by drying at 200 °C for 10 min. The plain nanobelt film was superhydrophilic with a contact angle of zero, possibly due to the hydration of the nanobelts, which also resulted in the nanobelt film peeling off the surface, most probably due to stresses associated with the intercalation. After coating with carbon or fluorosilane, the films became stable and did not show any sign of peeling or delamination after soaking in water for at least a day. The carbon coated film was hydrophobic with a contact angle of 105° (Fig. 7a), whereas fluorosilane coated film attained a superhydrophobic state with a contact angle of 154° (Fig. 7b).

![Fig. 5](image_url) Total reflection spectra and photographs of (a) MoO₃ nanobelts, (b) MoO₃ nanoplatelets, (c) carbon-coated MoO₃ nanobelts, (d) carbon-coated MoO₃ nanoplatelets, and (e) carbon-coated glass.

![Fig. 6](image_url) (a,b) SEM images of the TiO₂ coated MoO₃ nanobelts and (c) a plot showing photocatalytic degradation of methylene blue (under UV light irradiation) by TiO₂ coated MoO₃ nanobelts, TiO₂ film and a glass substrate.
photo-catalysis and superhydrophobic surfaces. Coatings can be utilized in several applications, such as solar cells, substrate, annealing temperature and the heating rate. Such morphology of the films depends on the composition of the glass obtain nanobelts or plate-like structures in which the substrates. Depending on the substrate used, it was possible to in summary, we have demonstrated a simple yet effective method to produce large aspect ratio z-MoO3 structures on TiO2 coated substrates. Depending on the substrate used, it was possible to obtain nanobelts or plate-like structures in which the morphology of the films depends on the composition of the glass substrate, annealing temperature and the heating rate. Such coatings can be utilized in several applications, such as solar cells, photo-catalysis and superhydrophobic surfaces.

Conclusions

Acknowledgements

This work was supported by Gurallar ArtCraft Glassware. Authors are thankful to the Centralized Research Facility of Drexel University for use of SEM, TEM, and XRD; Dr Craig Johnson for assistance with TEM and Dr Volker Presser for the contact angle measurements.

Notes and references