Synthesis of rutile Nb:TiO₂ free-standing thin film at the liquid-air interface

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A free-standing niobium doped rutile TiO_2 film was synthesised via a hydrothermal method without the use of a template at the liquid- air interface. SEM images revealed that the film is 10 µm thick, with rutile rods creating a stable and merged structure, that maintains flexibility and can be shaped within a two minutes window of being removed from the solution.

Free-standing films at the liquid-air interface were previously composed of either graphene[1-3] or polymer composites[4, 5]. While there are only a few reporting fabrication of metal oxide free- standing films[6-9], most of them grow free-standing films using surfactant tempalting. Prinz *et al.* report a method of growing InGaAs/GaAs free-standing films that were fabricated while de-bonding from the substrate. Yang *et al.* describe a surfactant-templated synthesis of oriented mesoporous silica films grown at the air-water interface. He *et al.* reports a synthesis

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of free-standing TiO_2-NT arrays by a two-step anodization of Ti sheets. The synthesis of first free-standing inorganic film fabricated without using any kind of external templating and forming a film was reported by Xia *et al.*[10-12] using one-step hydrothermal synthesis of free-standing rutile TiO_2 film. This report focuses on the synthesis of niobium doped rutile TiO_2 free-standing film that is flexible and can be shaped when first taken from the solution.
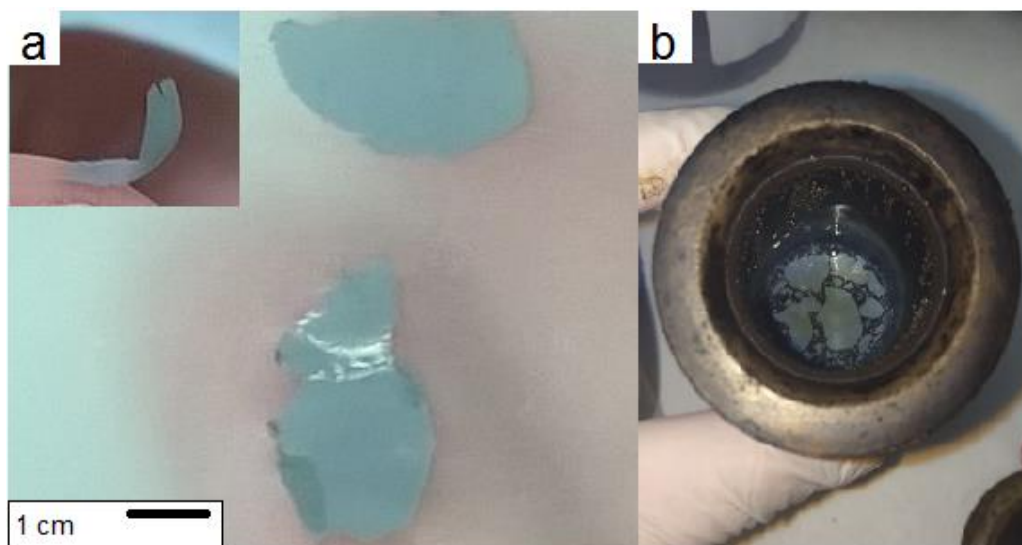

Figure 1. Image showing niobium doped titania self-assembled film (a) on the flat surface, insert shows same foil after bending and (b) as-synthesised film inside the autoclave.

Self-assembled niobium doped rutile TiO_2 free-standing films were synthesised *via* a single step hydrothermal method. Although different conditions were investigated, the film assembly formed only at 10 atom.% Nb:Ti ([Ti(OBu)$_4$] and niobium powder, -325 mesh) and the precise concentration of [Ti(OBu)$_4$] of 0.12 mol/L. Any variation from these conditions resulted in obtaining a loose powder. The rutile film forms at the liquid-air interface and their size is dependent on the diameter of the synthesis vessel. In this experiment a Parr autoclave with a Teflon liner, with a diameter of 2.5 cm was used, the biggest obtained pieces were 2 cm in diameter.

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The free-standing film is opaque (fig.1), blue in colour and is similar in physical properties to the silica films grown by Yang *et al.;* flexible enough to withstand bending as well as transferring and moulding onto cylindrically shaped objects. Although the Nb:TiO$_2$ film is most flexible shortly after being removed from the solution, after drying in air it behaves like a ceramic material and breaks if bent. It can be stored either in common solvents (ie. water, isopropanol, acetone) or air and both the colour and shape is stable for over a year. Annealing the film in air at 500 °C for 12 h results in a loss of colour, due to the oxidation of Ti^{3+} responsible for blue colour to Ti^{4+}, yet the formed macro structure remains unchanged and does not disintegrate into a powder form.

Niobium is present in two separate species within the film, one being doped into the titania lattice and other being a Nb$_2$O$_5$ phase. X-ray diffraction (**see supporting information, Fig. S1**) showed that the primary phase is rutile TiO$_2$ with a minor presence of Nb$_2$O$_5$ as a secondary phase formed due to the excess of niobium in the starting solution. In order to confirm that niobium is substitutionally incorporated into the rutile TiO$_2$ lattice the Rietveld refinement was performed on the XRD data collected from the free-standing film and pristine rutile TiO$_2$ prepared by the same method. Since the Nb^{5+} ion radius is 0.03 Å larger that of Ti^{4+} an expected unit cell expansion was observed from 62.29 Å^3 for undoped TiO$_2$ (a = 4.5906 Å, c = 2.9557 Å, R$_{wp}$ = 5%) to 62.93 Å^3 for Nb doped TiO$_2$ (a = 4.6098 Å, c = 2.9616 Å, R$_{wp}$ = 10%).

EDX analysis shows that even though the starting solution contains 10 atom.% Nb:Ti, the dopant level in the TiO$_2$ lattice is 3.5 atom.%. This was confirmed by the HR-TEM images of the powder co-precipitated along with the free-standing film (fig.2). Small amounts of the Nb$_2$O$_5$ phase are present on the Nb doped rutile TiO$_2$ rods. Close TEM examination of the rods shows that the main reflections found in all the investigated rods were rutile TiO$_2$ (111) and (110), with the (110) plane going along the longer edge of the crystallites.
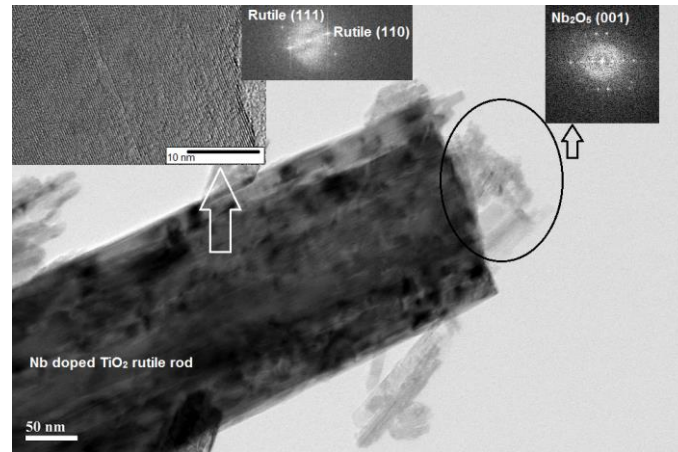
Figure 2. HR TEM picture of the Nb:TiO$_2$ powder precipitated from the same solution along with the free-standing film.

SEM images revealed that free-standing film is built of chrysanthemum-like assembled rods with clear centres (**Fig. 3**). This allows one "chrysanthemum" to grow into the side of another and form a solid structure. This characteristic distinguishes the Nb doped TiO$_2$ film from templated silica film[7] or graphene sheets formed due to its amphiphilicity[13, 14]. Hong *et al.* report the formation of rutile TiO$_2$ mesocrystals, which are partially linked by an organic medium and partially by the nanocrystals themselves[15]. Linking of the crystallites occurs through a homoepitaxial self-assembly[16]. As explained by Xia *et al.* growth of the TiO$_2$ free-standing films at the gas-liquid interface, without use of templates or surfactants, is possible due to the formation of layer of organic compounds, generated during hydrolisis of titanium (IV) butoxide. The nucleation of the nanorods occurs at the interface rather than in the solution, due to the surface tension. The surface tension present due to the thin organic layer supports seeding and nucleation processes, due to the lower net interfacial energy compared to the solution-particle interfacial energy[17]. As the growth continues, rods assemble into the „chrysantemums", which furter merge together creating continous film. The presence of the thin organic layer prevents growth in one direction, which explains why one of the sides of the film is flat, while the other, submerged into the growth solution, is irregular.
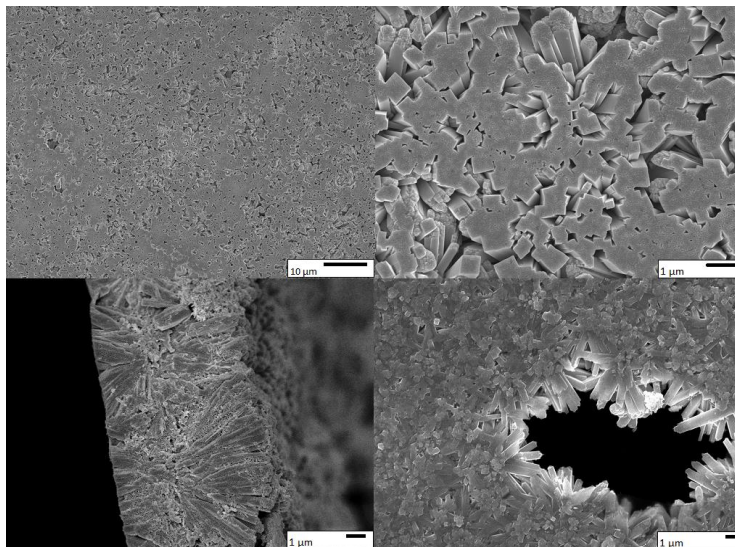
Figure 3. Top-down and cross-sectional SEM images of the free-standing film.

It was observed that after removal from the solution, the film was flexible when handled for a short time. Although neither FT-IR nor UV-vis absorption spectroscopy showed difference between flexible and brittle state (**see supporting information, Fig. S2 and S3**), it was surmised that the $Nb:TiO_2$ rods were formed while the space between them remained in liquid form. The newly formed film became more brittle after several minutes in air which is likely be the due to the evaporation of the solution between the $Nb:TiO_2$ rutile rods encouraging irreversible covalent bond formation.

Despite successful doping of niobium into the titania lattice, which has perviously shown to increases electrical conductivity[18], the resistivity of the film was too high to perform Hall effect measurements. Such high resistivity was most likely an effect to the pores and micro gaps between the rods.

Yang *et al.* assign the flexibility of their silica film to the thin organic-inorganic composite nature of it. Though the flexibility of the $Nb:TiO_2$ film might be explained by its macroporous structure. As the elements of the two "chrysanthemums" overlap and create a continuous film, the rods can rub each other, without breaking the structure. The dense packing of the rods,

creating homogenous membrane makes it a suitable candidate for gas separation application, with a novel approach to improve CO_2 reforming performance[19]. Moreover, decoration of the free-standing TiO_2 film with a conductive layer may lead to nanosized, flexible electrodes for photo-electrochemical[20], gas sensors or solar panels applications.

In conclusion, this report presents a one-step hydrothermal method of synthesising a free-standing niobium doped rutile TiO_2 film at the water-air interface without the use of surfactants or other templates. The film after formation has a degree of flexibility and can be shaped within first few minutes of removal from the solution.

Experimental

All chemicals used in this experiment were used without further purification; 1 ml of technical grade titanium (IV) butoxide (Sigma Aldrich), (10 atom % Nb:Ti) niobium powder, -325 mesh (Alfa Aesar), 12.5 ml of deionised water and 12.5 ml of 37% HCl (Sigma Aldrich) were mixed together and stirred until obtaining homogenous mixture. The whole mixture was then transported into the Parr autoclave and heated to 180°C for 20 h. After cooling and leaving the vessel in the fume hood for at least 12h, the obtained foil was carefully taken out from the autoclave and washed with water and dried in air.

Characterisation

For identification of the crystal structure of the foil X-Ray diffraction (XRD) was used. This was carried out on a *Bruker GADDS D8* diffractometer with a Cu Kα X-Ray source and readings were taken over the $10° < 2θ < 75°$ range. In order to determine unit cell parameters, Rietveld refinement was used to fit the collected data using GSAS and EXPGUI software. Energy dispersive X-ray spectroscopy (EDX- obtained by using a JEOL JSM-6301F Field Emission SEM) was used to determine the Nb:Ti atomic ratio on the C-coated samples. Scanning electron microscopy imaging was used to determine foil morphology and thickness using a *JEOL JSM-6301F Field Emission SEM* at accelerating voltage of 5 keV, on Au-coated samples. Absorbance was measured using a *SHIMADZU UV-3101PC* UV-vis-NIR scanning spectrophotometer. FT-IR spectrum was taken using *Perkin Elmer FTIR spectrometer 100.* Electrical properties were measured at room temperature on an Escopia HMS-3000 set up in the Van der Pauw configuration. Measurements were carried out using a current of 1 µA and a 0.58 T permanent magnet on ≈ 1 x 1 cm squares with silver paint (Agar Scientific) used as ohmic contacts, integrity of which was tested prior to measurements.

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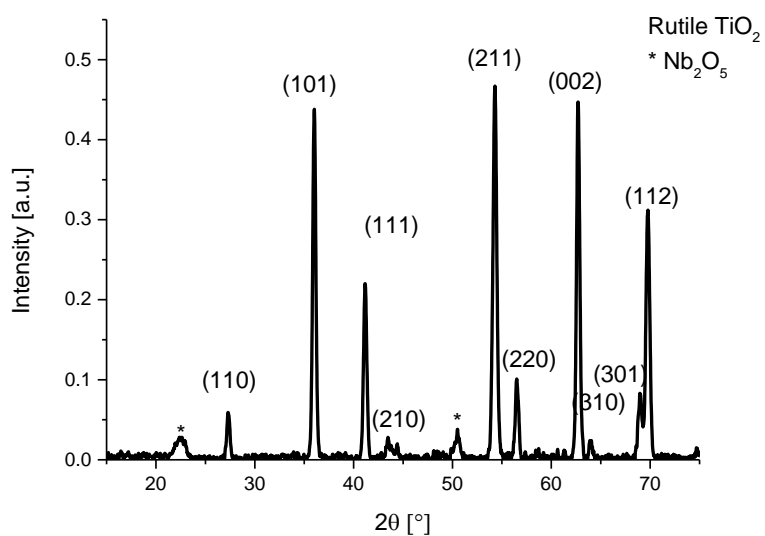
Supporting Information

Figure S1. XRD pattern of niobium doped rutile titania free-standing film. The rutile TiO₂ reflection positions with appropriate values (*hkl*) are shown in brackets.
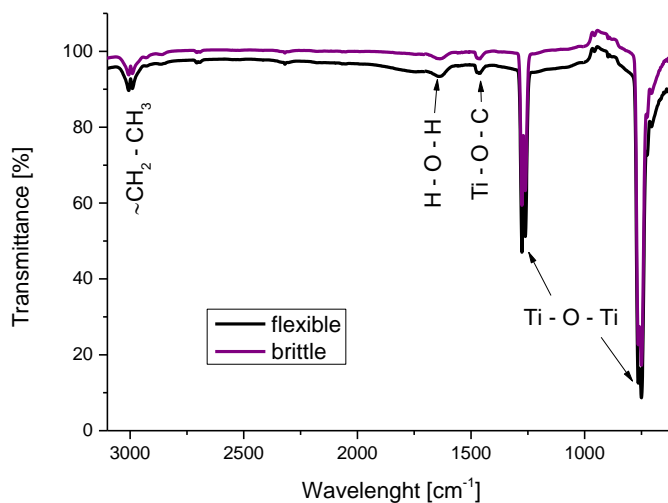
Figure S2. FT-IR spectra of of the Nb:TiO$_2$ free standing film. 1st scan was taken immediately after taking the film out of the synthesis vessel and washing it with DI water, when the film is flexible. 2nd scan were taken after 10 min when the film loses its initial flexibility.

The FT-IR spectra of the Nb:TiO$_2$ rutile free-standing film show two distinctive bands at 1275 to 1260 cm^{-1} and 765 to 759 cm^{-1} characteristic for the Ti – O and Ti – O – Ti framework bond.[1, 2] The 3006 – 2989.92 cm^{-1} band shows stretching vibrations of unhydrolysed –CH$_2$ – CH$_3$ chains,[3] the 1637.84 cm^{-1} band can be ascribed to the bending vibration of chemically adsorbed H$_2$O molecules[1] and the 1462 cm^{-1} band shows the presence of Ti – O – C asymmetric vibrations.[4]
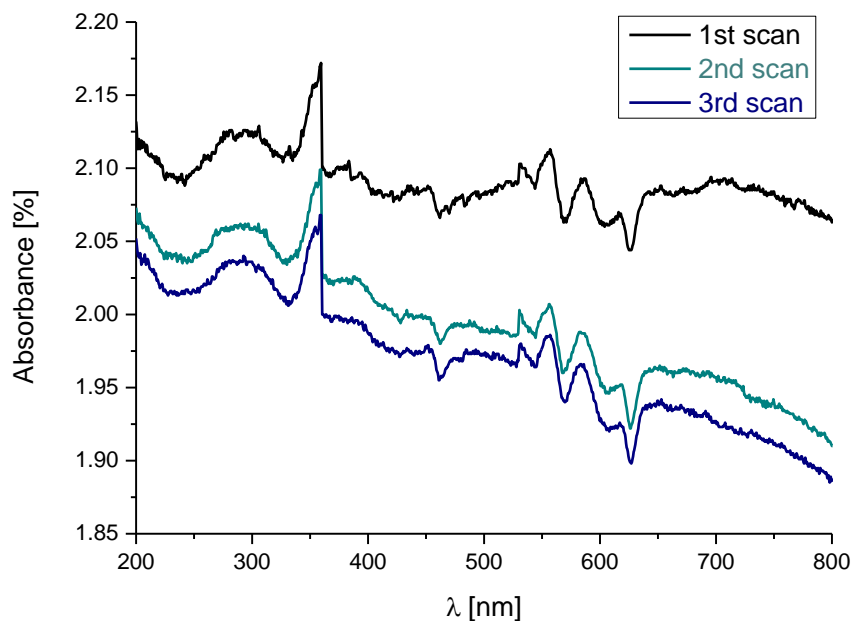
Figure S3. Absorption spectra of the Nb:TiO$_2$ free standing film. 1st scan was taken immediately after taking the film out of the synthesis vessel when film is flexible. 2nd and 3rd scans were taken after 5 and 10 min respectively when film loses its initial flexibility.

Supporting references

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