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# A hybrid nanoparticle/alkoxide ink for inkjet printing of TiO<sub>2</sub>: a templating effect to form anatase at 200 °C†

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A reactive ink (Ink 1) containing Ti(OPr)<sup>i</sup><sub>4</sub> in Pr<sup>i</sup>OH with dimethoxyethan as a kinetic stabiliser deposits TiO<sub>2</sub> by inkjet printing. A hybrid ink (Ink 2) consists of Ink 1 with the addition of anatase NPs, which act as seeds for the formation of anatase TiO<sub>2</sub> at 200 °C. Printing of anatase on PET is also reported.

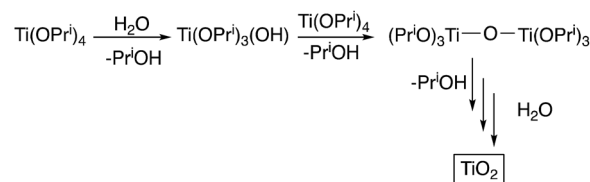
TiO<sub>2</sub>, particularly in the form of anatase thin films, continues to attract significant interest, due to applications such as photocatalysis.<sup>1</sup> Anatase thin films are typically prepared by sol-gel or chemical vapour deposition (MOCVD or ALD) techniques.<sup>2,3</sup> As-deposited thin films from sol-gel synthesis are found to be amorphous and require annealing at >350 °C in order to form anatase. CVD techniques require sophisticated equipment, and although plasma enhanced CVD deposition of anatase at 100 °C has recently been reported,<sup>4</sup> most CVD preparations of anatase require either a high substrate temperature (>300 °C) or high temperature annealing step.<sup>5</sup>

Inkjet printing is an alternative method for thin-film deposition and has the advantages of being both low-cost and low-waste, as well as enabling direct patterning.<sup>6,7</sup> A major challenge in inkjet printing is the formulation of a stable ink with the correct chemical and rheological properties. To date, most published methods for inkjet printing of anatase have used colloidal TiO<sub>2</sub> solutions.<sup>8</sup> As-deposited films are amorphous and require annealing at >375 °C to convert the printed films to anatase.<sup>9</sup> Suspensions of pre-formed anatase nanoparticles have also been used as inks; these inks often require the addition of high molecular weight stabilisers in order to keep the nanoparticles in suspension. A high-temperature (>350 °C) processing step is therefore required in order to remove the stabiliser and to sinter the nanoparticles to form a continuous film.<sup>10</sup> In some cases a lengthy heat-treatment is required after each printing pass before a final high temperature annealing stage.<sup>11</sup>

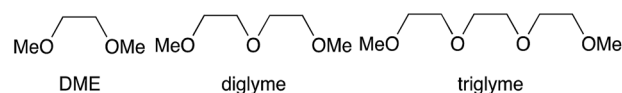
As an alternative to inks containing pre-formed TiO<sub>2</sub>, we present a series of reactive inks that contain a metalorganic Ti precursor that reacts under ambient laboratory conditions with

atmospheric moisture and surface OH groups to form TiO<sub>2</sub>. The aim of this work is to avoid the need for high temperature treatments and thus to develop a process for printing anatase TiO<sub>2</sub> that is compatible with temperature-sensitive, flexible substrates such as polyethylene terephthalate (PET).<sup>12,13</sup>

Ti(OPr)<sup>i</sup><sub>4</sub> has been chosen as the reactive component of the ink: as it is readily available at relatively low cost, and has been extensively studied as a precursor for deposition of TiO<sub>2</sub> by sol-gel techniques.<sup>14</sup> Ti(OPr)<sup>i</sup><sub>4</sub> reacts with H<sub>2</sub>O (and with Si-OH groups on the surface of a glass substrate) by a sequence of protonolysis/condensation reactions to form TiO<sub>2</sub>:



In addition to optimising rheological properties, an ink formulation that is stable enough to have an acceptable shelf-life and not to cause blockages in the printer is required. The ink formulation however needs to be reactive enough to produce TiO<sub>2</sub> once printed under ambient conditions. Pr<sup>i</sup>OH was chosen as the carrier solvent as it is chemically compatible with Ti(OPr)<sup>i</sup><sub>4</sub> and it also has compatible rheological properties for inkjet printing. However, a solution of Ti(OPr)<sup>i</sup><sub>4</sub> in Pr<sup>i</sup>OH reacts within seconds with small traces of H<sub>2</sub>O to form insoluble TiO<sub>2</sub>, and this behaviour results in rapid blocking of the printer head. A variety of glycol ethers as kinetic stabilisers has therefore been investigated:



These glycol ethers are Lewis bases with the ability to coordinate to Ti(OPr)<sup>i</sup><sub>4</sub>, resulting in kinetic stabilisation by blocking access of H<sub>2</sub>O to vacant coordination sites at Ti.<sup>15</sup> In optimising

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the ink formulation, we aimed to achieve a printable ink with: a reasonable level of Ti loading, a rate of reaction with ambient atmosphere that is compatible with printing multiple passes in rapid succession, and a convenient level of shelf-stability.  $\text{Ti}(\text{OPr}^i)_4$  concentrations from 0.05 M to 0.15 M, and glycol ether:  $\text{Ti}(\text{OPr}^i)_4$  ratios from 2.5 : 1 up to 10 : 1 have been investigated.

DME was identified as the optimum kinetic stabiliser: as its boiling point (85 °C) is close to that of  $\text{Pr}^i\text{OH}$  (83 °C), resulting in evaporation of both carrier solvent and stabiliser at similar rates post-deposition. The complimentary evaporation rates minimises surface tension driven Marangoni effects due to compositional changes, and results in good uniformity of deposited material.<sup>16</sup> The optimised formulation for the stabilised  $\text{Ti}(\text{OPr}^i)_4$  ink (designated as **Ink 1**) is given in Table 1. Ageing studies show a 1.34% increase in viscosity of **Ink 1** after four weeks stored at room temperature (Fig. 1), indicating good ink stability.

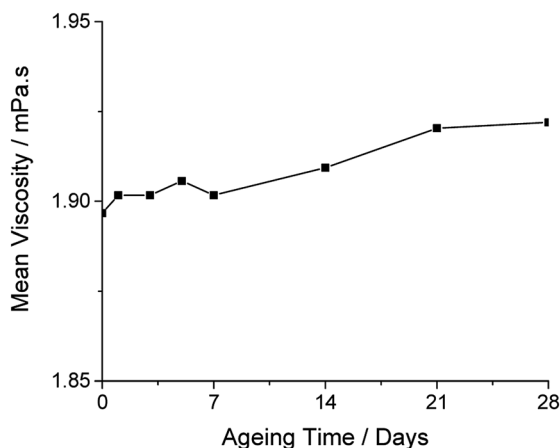
The waveform generated for pure  $\text{Pr}^i\text{OH}$  is also suitable for **Ink 1**. The print speed, step width and substrate temperature has been optimised by printing a single pass track onto a glass substrate (see Fig. 2).

The Ti loading in **Ink 1** (0.15 M) is too low to print a film of viable thickness with a single pass (theoretically *ca.* 46 nm), and so a 1 cm × 1 cm square using 1 and 5 passes was printed (Fig. 3) along with more complex architectures such as “ $\text{TiO}_2$ ”.

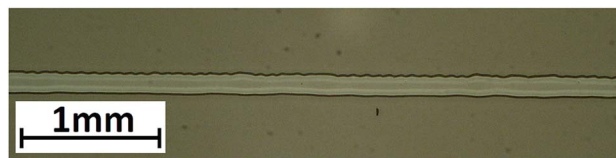
Raman and XRD spectroscopy show that the as-deposited films are amorphous and require annealing at 450 °C in order to produce the desired anatase phase as shown in Fig. 4.

**Table 1** Optimised  $\text{Ti}(\text{OPr}^i)_4$  ink formulation (**Ink 1**); carrier solvent  $\text{Pr}^i\text{OH}$

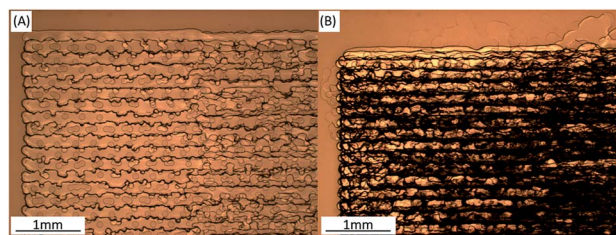
$[\text{Ti}(\text{OPr}^i)_4]/$ M	[DME]/ M	Density/ $\text{g cm}^{-3}$	Viscosity/ $\text{mPa s}$	Surface tension/ $\text{mN m}^{-1}$
0.15	1.5	0.799	1.89	20.57



**Fig. 1** Ageing data of viscosity over time for **Ink 1** over a 28 day maturation time held at room temperature.



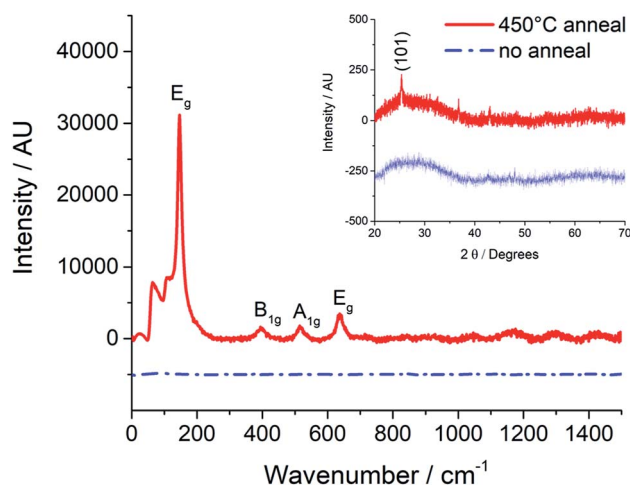
**Fig. 2** Printed track using **Ink 1** at ambient temperature with 10 mm  $\text{s}^{-1}$  print speed and 0.1 mm step size.



**Fig. 3** Optical micrographs of 1 cm<sup>2</sup> print with **Ink 1** on glass substrate (A) 1 pass; (B) 5 pass.

**Ink 1** displays the desired shelf-stability (Fig. 1) combined with good printability and an appropriate rate of reaction to form  $\text{TiO}_2$  under ambient conditions. However, as seen with traditional sol-gel methods, annealing at 450 °C is required in order to form anatase<sup>17</sup> (Fig. 4). Note that this processing temperature does not meet the stated aim of printing onto thermally-sensitive, flexible substrates.

Anatase can be deposited by inkjet printing with an ink containing pre-formed anatase nanoparticles (NPs); however in order to form a continuous film using a NP ink, a high temperature sintering step (>350 °C) is required. UV sintering of hybrid NP/titanium(IV) bis(ammonium lactate)dihydroxide ink can be achieved at 150 °C.<sup>18</sup> It is reasoned that in a hybrid ink consisting of anatase NPs and reactive  $\text{Ti}(\text{OPr}^i)_4$ , the NPs could act as templates for the formation of anatase on hydrolysis of



**Fig. 4** Raman and XRD (inset) spectra of an as deposited amorphous  $\text{TiO}_2$  film and an anatase film after annealing at 450 °C for 40 minutes (**Ink 1** on a glass substrate).



Ti(OPr<sup>i</sup>)<sub>4</sub>. This templating effect would obviate the need for a high temperature sintering step. Carboxylic acid functionalized anatase NPs have been chemically cross-linked by reaction with diamines to form thin films.<sup>19</sup> The novel aspect of the work presented here, is that a reactive organometallic framework, such as Ti(OPr<sup>i</sup>)<sub>4</sub>, and anatase NPs have not previously been combined and printed to enable the reduction of post processing temperatures.

The starting point for a hybrid ink is **Ink 1**, to which anatase NPs (Sigma Aldrich; <25 nm) are added in various proportions (0.5–5 wt%). A 0.1 M Ti concentration of NPs produces an ink with good printability (eg viscosity and surface tension) and is here designated as **Ink 2** (see Table 2). Prior to printing, **Ink 2** was sonicated for 1 h to give a homogeneous dispersion of NPs (DLS studies show that sonication for > 1 h resulted in formation of aggregates of NPs) and the dispersion remained stable, without the addition of stabilisers, for up to 72 h. Ageing studies showed that after 4 weeks the ink viscosity increased by only 1.55%, indicating good ink stability (Fig. 5). As the inks were sonicated before each measurement, the initial decrease was likely caused by viscosity being measured before the solution had cooled to 20 °C.

**Ink 2** was printed onto a glass substrate using printing parameters similar to those used for **Ink 1**. Optical microscopy showed that **Ink 2** produced a denser film than **Ink 1**, due to the increased Ti loading. Profilometry measurements showed that after annealing at 200 °C, a 5-pass print with **Ink 2** had a mean thickness of ca. 1600 nm (see S1†).

Table 2 Optimised hybrid nanoparticle/Ti(OPr<sup>i</sup>)<sub>4</sub> ink formulation (Ink 2); carrier solvent Pr<sup>i</sup>OH

[Ti(OPr <sup>i</sup> ) <sub>4</sub> ]/ M	[Ti] NPs/M	[DME]/ M	Density/ g cm <sup>-3</sup>	Viscosity/ mPa s	Surface tension/ mN m <sup>-1</sup>
0.15	0.1	1.5	0.804	1.90	20.70

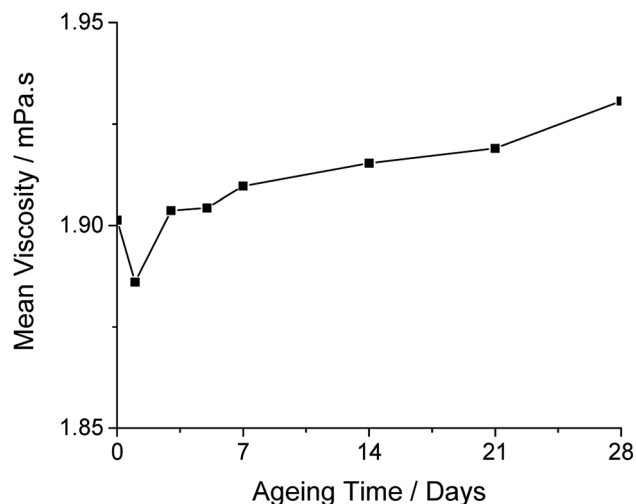


Fig. 5 Ageing data of viscosity over time for Ink 2 over a 28 day maturation time held at room temperature.

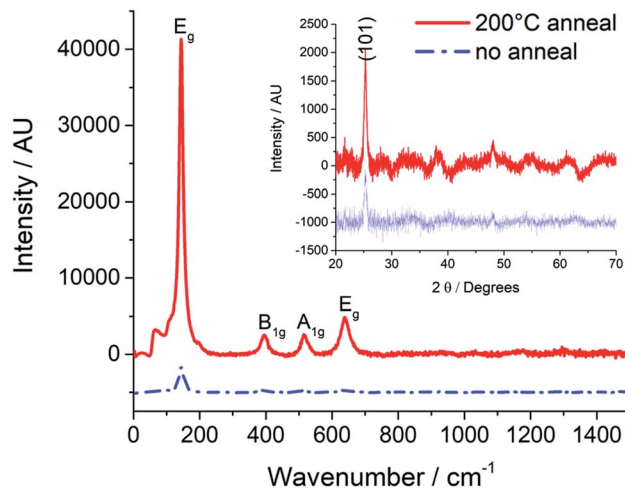


Fig. 6 Raman and XRD (inset) spectra of drop-tested sample of Ink 2 (glass substrate) before and after annealing at 200 °C for 160 minutes.

The main objective for **Ink 2** was to form a thin film of anatase without the requirement for high temperature post processing. Raman and XRD spectroscopy (Fig. 6) of a drop-tested film of **Ink 2** shows that the as-deposited film contains a small amount of anatase, consistent with anatase NPs in a matrix of amorphous TiO<sub>2</sub>. However, on annealing at 200 °C for 160 min, there is a marked increase in the Raman and XRD intensities for peaks assigned to anatase (Fig. 6). This annealing temperature is 250 °C lower than that required to form anatase from **Ink 1** (Fig. 4). The reduction in annealing temperature is consistent with the NPs acting as templates for the conversion of amorphous TiO<sub>2</sub> to anatase.

PET is a flexible material with a melting point of 250 °C.<sup>20</sup> The annealing temperature of **Ink 2** is substantially below the melting temperature of PET and as such represents a step closer to enabling inkjet printing of metal oxides on thermally sensitive, flexible substrates. Single and multiple-pass prints of 1 cm × 1 cm squares directly onto PET without the need for prior treatment of the substrate surface were achieved. A more complex architecture (3-pass print of “TiO<sub>2</sub>”) as shown in Fig. 7 was also printed. The prints adhered well to the surface and survived over 10 cycles of bending. Raman spectroscopy of a drop-tested sample of **Ink 2** on a PET substrate confirmed that



Fig. 7 3-pass “TiO<sub>2</sub>” print with Ink 2 on a PET substrate.



conversion to anatase occurred after annealing at 200 °C for 160 minutes, as observed for **Ink 2** on a glass substrate (see S2†). As this is above the glass transition temperature,  $T_g$ , of the PET substrate, minor deformation of the substrate was observed. Further reduction in processing temperature, minimising PET deformation, could be achieved by the optimisation of NP to organometallic ratio.

In conclusion, we have demonstrated for the first time that the combination of anatase NPs with a reactive organometallic component,  $(\text{Ti}(\text{OPr}^i)_4)$  gives a novel hybrid ink that enables the inkjet printing of anatase  $\text{TiO}_2$  onto thermally sensitive flexible substrates.  $\text{Ti}(\text{OPr}^i)_4$  reacts with ambient atmospheric moisture to form a matrix of amorphous  $\text{TiO}_2$ , and anatase NPs promote conversion of this matrix to anatase at the relatively low temperature of 200 °C.

## Conflicts of interest

There are no conflicts to declare.

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