Electronic Supplementary Information For:

Hybrid nanoparticle/alkoxide ink for inkjet printing of TiO₂: templating effect to form anatase at 200°C

Josh Turner,^a Helen C. Aspinall,^a Simon Rushworth^c and Kate Black^{b*}

- a. Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, U.K.
- b. School of Engineering, University of Liverpool, Liverpool L69 3GH, U.K.
- c. Epivalence Ltd., The Wilton Site, Wilton, Redcar TS10 4RF, U.K.

E-mail: k.black@liverpool.ac.uk

We would like to thank EpiValence and the EPSRC for their financial support.

1. Experimental

Materials: Purified propan-2-ol (ⁱPrOH) was obtained from an MBraun MB-SPS 5-Solvent Purification System and stored over 3 Å "Molsiv" Molecular sieves (Type 3A, 1/16th inch pellets) in a clean, oven dried Schlenk flask (500 cm³). Karl-Fisher titration using a C30 Coulometric KF Titrator gave the H₂O content as 99.9 ppm (~0.01 %). The following chemicals were purchased from Sigma-Aldrich and used without further purification: titanium(IV) isopropoxide [TTIP] (\geq 97.0 %), 1,2-dimethoxyethane (anhydrous, 99.5 %, inhibitor-free), titanium(IV) oxide (anatase nanopowder, <25 nm particle size, 99.7 % trace metals basis).

Formulation of ink 1: Using standard Schlenk techniques, a Schlenk flask was charged with propan-2-ol (4.0 mL, mmol), 1,2-dimethoxyethane (0.78 mL, mmol) and titanium(IV) isopropoxide (0.22 mL, mmol).

Formulation of ink 2: Anatase nanopowder (0.0400 g) was added to a Schlenk flask, which was then charged with propan-2-ol (4.0 mL, mmol), 1,2-dimethoxyethane (0.78 mL, mmol) and titanium(IV) isopropoxide (0.22 mL, mmol) using standard Schlenk techniques. Prior to printing, the resulting solution was sonicated for 60 minutes.

Inkjet printing of samples: Printing was performed using a MicroFab JetLAB 4 Tabletop Printing Platform, fitted with a MicroFab MJ-ATP-01-080 drop-on-demand single jet dispensing device with an 80 μ m orifice diameter. Glass substrates (Thermo Scientific, Menzel-Gläser, 76 x 26 mm, 1.0 – 1.2 mm thickness) were manually cleaned in warm soapy water, rinsed with absolute EtOH, individually mounted into a slide box, and left to dry under ambient conditions. PET substrates (DuPont Teijin Films, Melinex-406, 71 μ m thickness) were cut to 76 x 26 mm rectangles and used as a substrate without further modification.

Characterisation of printed samples: A Leitz Instruments metalloplan metallurgical microscope, fitted with a Nikon CF Plan 2.5x objective lens and bright-field reflection illumination was used to image the printed samples. Profiles of the printed samples were obtained using an Ambios XP-Plus 200 Advanced Stylus Profiling System. Annealing was performed using a Carbolite MTF 12/38/250 horizontal tube furnace. Samples were placed in the tube furnace at the annealing temperature and removed after their denoted annealing time. There was no temperature ramp up or down process. Raman spectra were obtained using a Renishaw inVia Reflex Qontor Confocal Raman Microscope with a 532 nm laser. Baseline correction of the obtained spectra was performed within the software. A Rigaku Miniflex fitted with a Cu K α emission source was used to carry out XRD measurements. Baseline corrections were performed in Origin 2016 software.

2. Supplementary Data



Figure S1 Profile of printed 5 pass 1 cm² using Ink 2 (glass substrate) after annealing at 200°C 160 minutes



Figure S2 Raman spectra of drop-tested sample of Ink 2 (PET substrate) before and after annealing at 200°C 160 minutes