Inkjet-Printed TiO$_2$ Nanoparticles from Aqueous Solutions for Dye-Sensitized Solar Cells (DSSCs)

Ruth Cherrington,*[a] Darren J. Hughes,[a] S. Senthilarasu,[b] and Vannessa Goodship[a]

This work reports on the formulation of suitable ink for inkjet printing of TiO$_2$ by investigating the critical parameters of particle size, pH, viscosity, and stability. Aqueous suspensions of TiO$_2$ nanoparticles (Degussa, P25) were prepared with the addition of 25 wt% polyethylene glycol 400 as a humectant to minimize drying at the printer nozzles and reduce the likelihood of nozzle blockage. The inkjet-printed TiO$_2$ layers were assembled into dye-sensitized solar cells.

The current–voltage (I–V) characteristics were measured under one sun (air mass 1.5, 100 mW cm^{-2}) using a source meter (Model 2400, Keithley Instrument, Inc.), and the active area of the cell was 0.25 cm^2. The inkjet-printed TiO$_2$ photoanode produced a device with a short-circuit current (I_{sc}) of 9.42 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.76 V, and a fill factor (FF) of 0.49, resulting in a power conversion efficiency (PCE) of 3.50%.

Introduction

Dye-sensitized solar cells (DSSCs) provide an interesting application of nanotechnology that offers a potentially low-cost alternative to conventional commercial solar cells. Typically for DSSC production, mesoporous titanium dioxide (TiO$_2$) layers are deposited by screen-printing or doctor blading. Screen-printing inks usually require large amounts of binders and thickeners to produce the high viscosities of between 1000 and 10000 mPa s required for reproducible and reliable film production.[1] Viscosities can be increased with the addition of polymeric additives such as glycerol, ethylene glycol, or ethyl cellulose.[2] However, high-temperature curing in the range of 450–500 °C is required to completely remove these large amounts of material from the printed layers.[3] Screen-printed pastes can sometimes result in significant cracking and peeling of layers from the substrate. These are some of the major limitations of the screen-printing method and yet it is still one of the most reported methods of producing the nanostructured metal-oxide layer within DSSCs.[4,5] Several unconventional methods to produce porous TiO$_2$ photoanodes have been investigated in the literature including UV-sintering methods, which dramatically speed up the sintering time from hours to seconds,[6] novel sol-preparation methods to produce coated nanoparticles,[7] production of complex porous structures which improve electrical power conversion efficiencies,[8] emulsion templating to produce hollow spheres with improved photocatalytic activity,[9] and doctor-blade deposition techniques.[10,11]

Inkjet printing allows for the direct deposition of a liquid onto a substrate to produce a pre-determined pattern or shape, for which layer-by-layer printing can be used to increase the thickness. By controlling the amount and the location of the ink deposition, the production of undesirable waste materials during the manufacturing process is avoided. These advantages result in an environmentally friendly, low-cost production method that can be adapted for mass production. Successful inkjet printing requires careful optimization of the ink and substrate properties as well as the printer parameters. Inkjet printing inks require low-viscosity fluids (between 2 and 20 mPa s) to allow droplets to be ejected from the nozzle and achieve appropriate spreading of the droplets on the substrate.[12] Viscosity and surface tension are the two key factors that enable reliable flow through the inkjet nozzle to produce a good quality film. The ideal surface tension of ink must be high enough to be held in the nozzle and avoid premature droplet formation, but it must also be low enough to allow the droplet to spread over the substrate surface to result in the formation of a continuous film. A variety of solvents and additives are often used to optimize formulations to provide successful jetting, drop formation, wetting, and drying behavior alongside functional performance. The role of a solvent within inkjet ink is to act as a carrier to deliver the functional material to the substrate. The solvent is then removed by a drying mechanism. The carrier solvent is usually the largest constituent within inkjet ink and therefore has a large impact on the overall properties of the ink. The choice of solvent is also important to determine which ingredients can be added. One of the most important factors to consider when choosing a solvent is the evaporation rate. Slow-drying solvents minimize drying in

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the nozzles and therefore reduce the likelihood of nozzle blockage; however they require larger amounts of energy and drying time to be removed. A common solution for this is to use a mixture of solvents with a high and low evaporation rate. Several studies have found that the addition of a high-boiling-point solvent combined with a low-boiling-point solvent produces the uniform deposition of functional materials onto the surface of the substrate.[13,14]

With particle-based inks, it is necessary to ensure that particles and agglomerates are small enough to pass through the nozzles. Suspended particles within an ink formulation must be several times smaller than the nozzle diameter to avoid clogging and allow for a large number of particles to pass through the nozzle at a given time.[15] For piezoelectric printers, it is suggested that the maximum particle size is 1% of the nozzle diameter.[12] Titanium dioxide particles can undergo either organic or inorganic surface treatment to improve their dispersibility. Nanoparticle suspensions are generally thermodynamically unstable and only held in suspension by the electrostatic forces of steric stabilization. The addition of chemical dispersants keeps particles separated by overcoming the attractive forces between the particles. Ink formulations for piezoelectric inkjet printers need to meet a large number of requirements for them to be considered a good-quality product capable of producing reliable depositions. Manufacturers often keep ink formulations as highly guarded secrets. Successful formulations balance jetting, drop formation, wetting, and drying behavior alongside functional performance. Usually a functional material is dispersed in a solvent and at least one other component to make them jet processable. Most of the work found in the literature reports on the inkjet printing of TiO_2 nanoparticles from aqueous solutions, with few investigating the influence of additives within ink formulations.[13,16,17]

Results and Discussion

Upon aggregation within a nanoparticle suspension, the favorably high surface-area-to-volume ratio of the nanoparticles is diminished and inkjet printing may become a problem due to the blockage of nozzles. The particles were therefore measured to avoid any problems associated with this.

The average particle size was measured to be 1405 nm and was suspended in water alone, indicating that significant agglomeration occurs within the suspension. Therefore the use of a dispersing agent was investigated to reduce the particle size. Zetasperse 1200 from Air Products is a commercially available dispersing additive designed to wet, disperse, and stabilize polar pigments such as titanium dioxide. Up to 5 wt% of dispersing agent was added and the particle size distribution was measured using dynamic light scattering (DLS). It was observed that the average particle size reduced to 80 nm after the addition of 2 wt% dispersing agent (as shown in Figure 1a), however there was still a large spread of particle sizes and therefore filtration was necessary to remove any large agglomerates from the suspension. The stability of the suspensions was also investigated by measuring
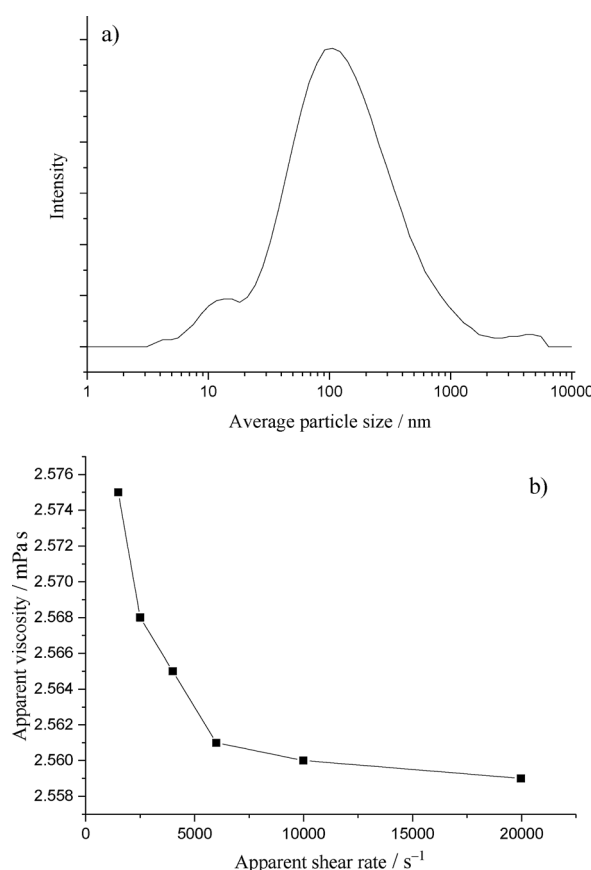

Figure 1. a) DLS obtained particle size distribution of the aqueous TiO_2 suspension. b) Flow curve (viscosity vs. shear rate) for TiO_2 aqueous ink with 25 wt% PEG 400.

the zeta-potential of the particles in diluted suspensions and was found to be 35.9 millivolts (mV), indicating good stability.

The inkjet printing process usually involves high jet speeds (typically more than 6 m s^{-1}); considering that the process is likely to be moved to high-throughput industrial applications, printing speeds are likely to be increased even more. This results in high shear rates in excess of 1000 s^{-1} and therefore it is important to investigate how inkjet fluids perform under these conditions. Figure 1b illustrates the rheological behavior of the TiO_2 ink formulation and clearly shows how the fluid viscosity decreases with an increasing rate of shear stress, which indicates shear thinning within the fluid. The average viscosity was 2.6 mPa s, which is lower than the 10–12 mPa s recommended for inkjet printing.

The jettable fluid formulation guidelines for dimatix printers suggest a surface tension in the range of 28–33 mN m^{-1} to enable reliable printing.[12] The surface tension was calculated to be an average of 26.34 mN m^{-1}, which is a little lower than recommended. This resulted in an average contact angle of 33.85° on fluorine-doped tin oxide (FTO)-coated glass. Prior to printing, the FTO glass was cleaned in a detergent solution using an ultrasonic bath for 15 min and then rinsed with water and ethanol. The TiO_2 ink was then printed directly
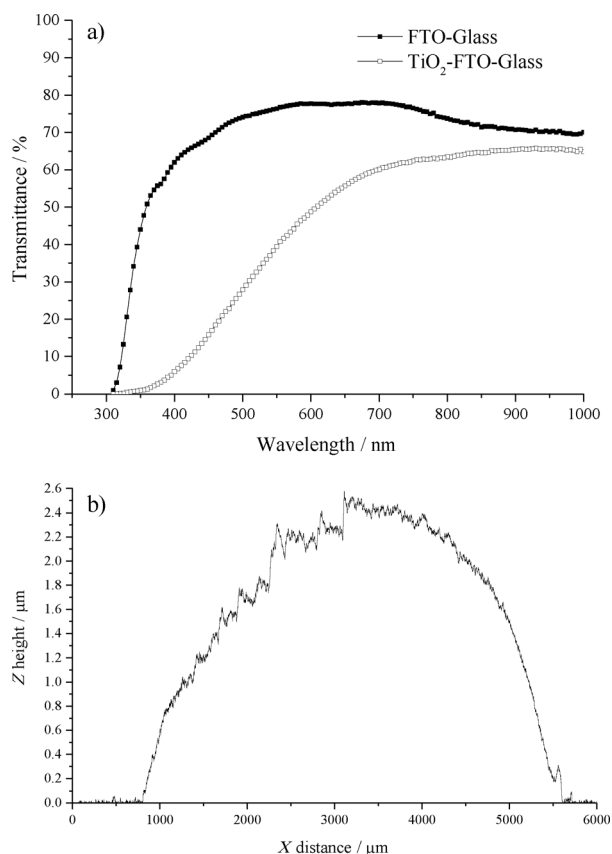
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Figure 2. a) Measured transmittance spectra of FTO-glass and inkjet-printed TiO$_2$-FTO-Glass. b) Surface profile of the printed samples showing roughness and thickness.

Figure 3. a) SEM image of inkjet-printed TiO$_2$ layer at low magnification. b) SEM image of inkjet-printed TiO$_2$ layer at high magnification.

onto the FTO glass. Details of the printing parameters can be found in the Experimental Section.

The transmittance of the TiO$_2$ film is shown in Figure 2 a, as well as the transmittance of the FTO glass that is used for comparison. The measured transmittance of the printed TiO$_2$ films reached 60 % at a wavelength of 700 nm, compared with 78 % for the FTO glass. This shows good transparency in the visible light range, which is advantageous for the application as a photoelectrode in DSSC applications. It can also be noted that the addition of the TiO$_2$ film does not significantly diminish the transmittance in comparison with the FTO glass.

It is well known that TiO$_2$ has three main crystal phases: anatase, rutile, and brookite. Anatase has the largest band gap energy of 3.23 eV and shows the highest photocatalytic activity.[18,19] X-ray diffraction (XRD) analysis was performed to determine the crystal phase of the printed films. The spectrum showed diffraction peaks at 29.57° and 56.55°, indicating TiO$_2$ in the anatase phase.[20]

The diameter of the printed samples (after two printed layers) was found to be 4818 μm, with an average Z-height of 1.70 μm and a maximum Z-height of 2.57 μm (shown in Figure 2 b). The SEM images (Figure 3 a,b), further show that the nanoparticles have built up to form a porous texture without any cracks. The texture of the photoanodes constitutes a key parameter for determining the performances of
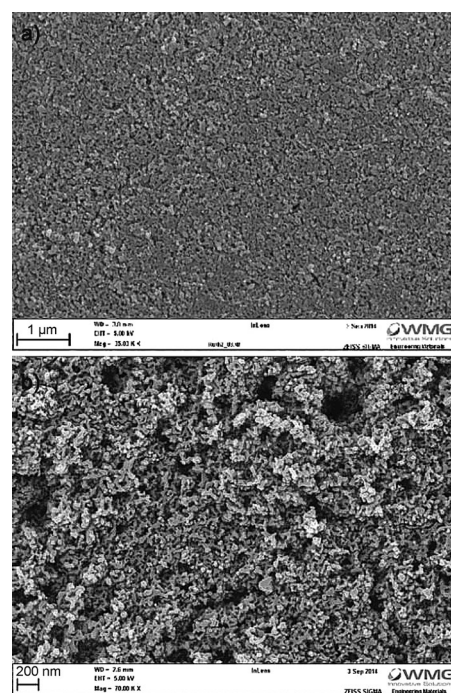
DSSCs. A rougher surface structure will generally result in the absorption of more dye molecules and subsequently result in the capture of more photon energy.[21] The images in Figure 3 show that the majority of particles retain the average size obtained from DLS, but that many of the particles are connected into larger agglomerates. The photocatalytic activity of TiO$_2$ increases as the particle size decreases toward the critical value of 10 nm. This will therefore have an influence on the amount of dye absorbed and therefore the overall conversion efficiency of the cell.

The inkjet-printed TiO$_2$ photoanodes were then made into cells and the current–voltage (I–V) characteristics were measured. Details of the cell preparation can be found in the Experimental Section. The devices produced a short-circuit current (I_{sc}) of 9.42 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.76 V, and a fill factor (FF) of 0.49, resulting in a power conversion efficiency (PCE) of 3.50 % as shown in Figure 4 a. However, it is important to note that although it is widely known that TiCl$_4$ treatment would improve the efficiency of the cells, it was not used in the manufacture of the cells.

Conclusions

Crack-free TiO$_2$ films were printed on FTO glass and used to produce the photoelectrode for DSSCs. The thickness of the TiO$_2$-printed films was investigated and found to be a maximum of 2.57 μm after annealing. The current–voltage (I–V) characteristics were used to evaluate the performance of the cell. A cell conversion efficiency of 3.50 % was measured, which demonstrates good efficiency in comparison to competing processes. For example, P25 photoanodes have
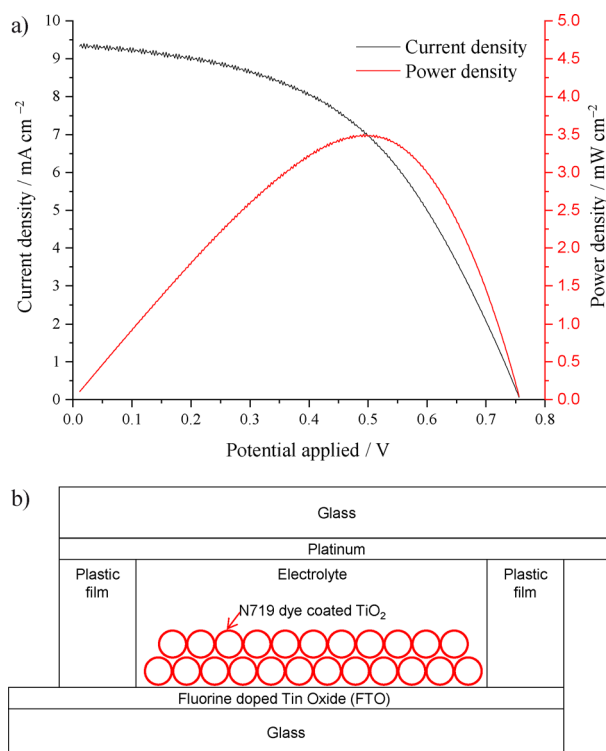
Figure 4. a) I–V characteristics of the inkjet-printed TiO$_2$ photoelectrode films. b) Schematic of the DSSC structure.

previously been processed by the screen-printing deposition route to produce a 5 μm thick layer and result in an efficiency of 1.6 %.[22] This slightly higher efficiency could be attributed to the high roughness measured, resulting in a high dye uptake. However, the resultant fill factor (FF) of 0.49 reported in this study is quite low and could have been improved by post-treating the FTO substrates and porous TiO$_2$ anodes with titanium tetrachloride (TiCl$_4$).[23] The processes used in this work are aimed at manufacturing under ambient conditions, and therefore alternative methods to improve the efficiency are subject to further research by the authors.

The photocurrent density value is governed by a number of factors including, the amount of dye chemisorbed onto the surface of the TiO$_2$. Future work will measure the chemisorption of the sensitized photoanodes using the method described by L. Cojocaru, et al., to show the effect of the dye loading on the I_{sc} values.[23] Electrochemical impedance spectroscopy will also be performed to better characterize the electronic processes involved in the fabricated cells.

The ink developed in this work was binder-free and only incorporated polyethylene glycol (PEG 400) as a humectant to enable printing. As a result, the TiO$_2$ photoelectrode was annealed at 250 °C, which is significantly lower than the 450 °C temperatures typically used. However, the printed films resulted in poor adhesion and therefore further work needs to be conducted on the optimization of binders to produce durable films for low-temperature annealing. Work will also continue to look at the printing of other materials and build-up of layers within the DSSC structure.

Experimental Section

TiO$_2$ nanoparticles (Aeroxide® P25) were dispersed in a premixed solution of deionized (DI) water and dimethylformamide (DMF), which was added as a drying agent to create a uniform distribution of nanoparticles as reported by Y. Oh, et al., 2011.[13] The specific surface area of the TiO$_2$ nanoparticles had a primary particle size of 21 nm as measured by transmission electron microscopy (TEM) and mean pore size of 35–65 m^{2}g^{-1} as measured using the Brunauer–Emmett–Teller (BET) method. Zetasperse 1200 from Air Products is a commercially available dispersing additive designed to wet, disperse, and stabilize polar pigments such as titanium dioxide. Zetasperse 1200 (2 wt %) was then added to the mixture to reduce the likelihood of agglomeration within the suspension.

The nanoparticles were introduced incrementally and continuously stirred using a large magnetic stirrer to produce a suspension containing 3 wt % of TiO$_2$. Polyethylene glycol (PEG 400, 25 wt %) was then added to minimize drying at the nozzles and reduce the likelihood of nozzle blockage. The isoelectric point (IEP) for TiO$_2$ (P25) is approximately 6; solutions with a pH near this point were observed to have significant agglomeration and large flocculates due to the large attractive van der Waals forces.[24] Therefore, the pH of the suspension was adjusted to approximately 4 by using Nitric acid (measured using pH indicator paper) to reduce the likelihood of forming agglomerated particles. Table 1 provides a summary of the ink composition.

The TiO$_2$ particle size and zeta potential were measured using a Zetasizer Nano ZS dynamic light scattering (DLS) particle size analyzer from Malvern Instruments, which has a measurement range of 0.3 nm (+/−2 %) to 10.0 μm (+/−2 %) diameter.

The surface tension and contact angle of the ink were determined using a Theta Lite Optical Tensiometer from Biolin Scientific. The rheological behavior of the inks was investigated using a microfluidic viscometer/rheometer from Malvern Instruments. A microfluidic flow chip with a channel depth of 50 μm was used to access the shear rate range.

Printing was performed using a Fujifilm-Dimatix DMP2831 materials printer that had sixteen 21.5 μm diameter nozzles for depositing 10 pL droplet volumes. The suspensions were passed through a 5 μm, followed by a 1.2 μm polyvinylidene fluoride (PVDF) filter to remove any large particulates and injected into a 1.5 mL cartridge. Squares of 5 mm diameter were printed onto

Table 1. Composition of TiO$_2$ ink.

Component	Function	Material[a]	Weight [%]
functional material	key component	TiO$_2$	3
solvent	dispersion medium	water	56
co-solvent	controls drying modifies surface tension	DMF	14
dispersing additive	stabilizes dispersion modifies surface tension improves wetting	Zetasperse 1200*	2
humectant	prevents ink drying in nozzles	PEG 400	25
other	pH buffer	Nitric acid	trace

[a] All materials (unless otherwise stated) were purchased from Sigma Aldrich. Zetasperse 1200 was received as a sample from Air Products and Chemicals, Inc.

a fluorine-doped tin oxide (FTO) glass substrate heated to 60 °C (TEC8, Pilkington with a sheet resistance of 8 Ω/sq, transmittance of 80 %, glass thickness of 2.3 mm). The Dimatix drop manager software has a standard waveform that has been found to work very well with model fluids and this was used as a starting point to monitor drop formation from the nozzles using the built-in camera. A jetting frequency of 5 kHz was set and the voltage waveform was adjusted to 10 V to produce suitable jetted drops. Printing and jetting were performed at room temperature. The printed films and were annealed at 150 °C for 30 min, followed by a final annealing step at 250 °C for a further 30 min after the final layer was deposited.

The following equipment was used to characterize the printed films: The transmittance of the film was measured using a Cary60 ultraviolet–visible (UV–Vis) spectrophotometer from Agilent Technologies, in the wavelength range of 300–1000 nm. The thickness of the printed layer was determined using a surface profiler (Ambios XP-100) that measures roughness and step height of a material within a precision of 1 nm. The printed films were analyzed using a Carl Zeiss Sigma Field Emission Gun - scanning electron microscope (FEG–SEM), with an operating voltage of 5 kV. X-ray diffraction (XRD) analysis of the printed TiO_2 was performed using an Empyrean diffractometer from PANalytical with a $Co_{K\alpha}$ wavelength (λ) of 0.17890 nm, and data were taken in the range of 20–95°.

The inkjet-printed TiO_2 photoelectrodes were made into cells (as in the schematic in Figure 4 b) by firstly soaking in a mixture solution of 20 mL of ethanol and 2 mg of N719 dye (ruthenizer 535-bisTBA, Solaronix) at room temperature for 24 h and dried in air. Surlyn film (Meltonix 1170 60 Series, Solaronix) was then cut to size and sandwiched between the TiO_2-coated glass and the platinum-coated glass (Solaronix). An iodide-based low-viscosity electrolyte with 50 mM of tri-iodide in acetonitrile (AN-50, Solaronix) was used as the electrolyte and injected into the void between the electrodes by vacuum back filling through a pre-drilled hole in the platinum-coated glass. The active area of cell was measured to be 0.25 cm^2. Current–voltage (I–V) characteristics, which were measured under one sun (AM 1.5, 100 mW cm^{-2}) using a source meter (Model 2400, Keithley Instrument, Inc.).

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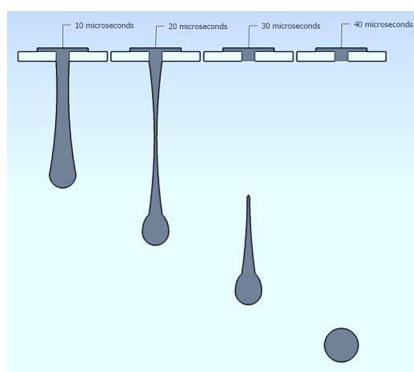
Water you waiting for? Digitally printed solar cells! TiO$_2$ nanoparticles are formulated into a functional ink and successfully deposited using a novel printing technique. The graphic illustrates how a droplet is formed from an ideal ink within a print head. The printed TiO$_2$ layers are assembled into dye-sensitized solar cells (DSSCs) resulting in high efficiency and ease of processing for use in future manufacturing techniques.