Solvolthermally-synthesized anatase TiO$_2$ nanoparticles for photoanodes in dye-sensitized solar cells

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The reference intensity method (RIR) for quantification analysis

The commercial NR18-T and synthesised SANP nanoparticles were spiked with about 10% silicon to act as an internal standard to assess the degree of crystallinity. The actual weight ratio was (90.7 %:9.3 %) for NR18-T:Si and (90.3 %:9.7 %) for SANP:Si. While The calculated weight ratios obtained from the integrated intensities (after subtracting the background) of NR18-T: Si and SANP: Si was (90.3 %:9.7 %) and (90 %:10 %) respectively (Figure S1). Thus, the percentage decrease of crystallinity degree, which represents the amorphous weight ratio, can be calculated as:

\[
\text{Amorphous TiO}_2 \text{ (Wt\%)} = 100 \text{ (Wt\%)} - [\text{Si}_{\text{mass}} \text{ (Wt\%)} + \frac{\text{Si}_{\text{mass}} \text{ (Wt\%)} \times \text{crystalline TiO}_2 \text{XRD (Wt\%)}}{\text{Si}_{\text{XRD}} \text{ (Wt\%)}}]
\]

Or,

\[(90.7 \%-90.3 \%)/90.3 \% = 4 \% \text{ for NR18-T}\]

\[(90.3\%-90\%)/90\%=3 \% \text{ for synthesised SANP}\]

The calculated amount of amorphous phase (less than 3%) which can be raised from the broadened peaks compared to the best fitting due to the nanosize effect with different grain size ranges or very finely crystalline phase (different full-width half-maximum-FWHM).

**Figure S1**: The quantification of the crystallinity degree of NR18-T and synthesised SANP nanoparticles using the reference intensity method (RIR).
**Figure S2:** HRTEM images and SAED patterns of (a,b) SANP; and (c,d) NR18-T.

**Figure S3:** (a) XRD patterns of synthesised SANP with/without calcination; (b) HRTEM images of synthesised SANP without calcination, the morphology and internal microspores structure.
**Figure S4:** Particle size distribution of (a, b) SANP (c, d) NR18-T.

**Thickness optimization of SANP|D149 photoanode based DSCs**

DSCs solar performance was investigated for different SANP photoanode thicknesses sensitized with a metal-free D149 organic dye Table S1 (SANP photoanode structures 8 ± 0.5, 10 ± 0.5 and 12 ± 0.5 µm in thickness and 11 ± 0.5 µm bilayer photoanode structure consist of 6 µm SANP layer with 5 µm top commercial scattering WER2-O layer). As shown in Figure S7 a and b Table S2, DSCs based on SANP-10 µm showed the PCE, and IPCE due to the LHE leading to higher $J_{sc}$ compared to other devices. All devices showed similar $V_{oc}$ while there is a difference in the FF values due to owing different $\Phi_{ccr}$ in term of the charge recombination.
Table S1: Optimization of photoanode thickness based on synthesised SANP sensitized with D149.

| SANP|D149 (8 µm) | $J_{sc}$ (mA·cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|------|-------------|-----------------|--------------|--------|---------|
| 1    | 14.0        | 0.68            | 61.1        | 6.06   |
| 2    | 12.7        | 0.68            | 61.2        | 5.51   |
| 3    | 14.2        | 0.67            | 59.7        | 6.14   |
| 4    | 12.9        | 0.67            | 61.4        | 5.56   |
| Average | 13.5        | 0.68            | 60.8        | 5.82   |
| STDEV | 0.7         | 0.01            | 0.8         | 0.33   |

| SANP|D149 (10 µm) | $J_{sc}$ (mA·cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|------|-------------|-----------------|--------------|--------|---------|
| 1    | 17.1        | 0.67            | 63.6        | 7.02   |
| 2    | 16.5        | 0.68            | 63.2        | 6.85   |
| 3    | 17.2        | 0.65            | 63.8        | 6.72   |
| 4    | 16.7        | 0.66            | 63.2        | 6.80   |
| Average | 16.9        | 0.66            | 63.5        | 6.91   |
| STDEV | 0.3         | 0.01            | 0.3         | 0.12   |

| SANP|D149 (12 µm) | $J_{sc}$ (mA·cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|------|-------------|-----------------|--------------|--------|---------|
| 1    | 15.3        | 0.68            | 57.6        | 5.82   |
| 2    | 16.3        | 0.68            | 59.2        | 6.15   |
| 3    | 15.8        | 0.67            | 60.3        | 6.00   |
| 4    | 15.9        | 0.67            | 55.3        | 6.00   |
| Average | 15.6        | 0.67            | 57.7        | 6.08   |
| STDEV | 0.4         | 0.01            | 2.5         | 0.08   |

| SANP|WER2-O|D149 (11 µm) | $J_{sc}$ (mA·cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|------|------|-------------|-----------------|--------------|--------|---------|
| 1    |      | 14.9        | 0.69            | 58.6        | 5.80   |
| 2    |      | 13.7        | 0.68            | 55.3        | 5.58   |
| 3    |      | 13.7        | 0.69            | 56.4        | 5.75   |
| 4    |      | 14.9        | 0.69            | 55.4        | 5.71   |
| Average |      | 14.9        | 0.69            | 56.4        | 5.71   |
| STDEV |      | 0.6         | 0.01            | 1.5         | 0.10   |

Table S2: J-V parameters of devices based on optimized SANP sensitized with D149.

| Device | $J_{sc}$ (mA·cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|--------|-----------------|--------------|--------|---------|
| SANP-8 µm | 13.5±0.7        | 0.68±0.01    | 57.6±2.5 | 5.82±0.30 |
| SANP-10 µm | 16.9±0.3       | 0.66±0.01    | 63.5±0.3 | 6.91±0.13 |
| SANP-12 µm | 15.6±0.4       | 0.67±0.01    | 61.5±0.7 | 6.10±0.10 |
| SANP/WER2-O-11 µm | 14.9±0.7     | 0.69±0.01    | 56.5±1.5 | 5.71±0.10 |
Table S3: J-V parameters details of devices based on synthesized SANP, NR18-T and NR18-T/WER2-O sensitized with D149.

| Device | $J_{sc}$ (mA·cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|--------|----------------|----------|--------|--------|
| SANP|D149 (10 µm) | 1 | 17.1 | 0.67 | 63.7 | 7.02 |
| 2 | 16.5 | 0.68 | 63.2 | 6.85 |
| 3 | 17.2 | 0.65 | 63.9 | 6.72 |
| 4 | 16.7 | 0.66 | 63.3 | 6.80 |
| Average | | | | | 16.9 | 0.66 | 63.5 | 6.91 |
| STDEV | | | | | 0.3 | 0.01 | 0.3 | 0.12 |
| NR18-T|D149 (10 µm) | 1 | 14.0 | 0.65 | 60.3 | 5.53 |
| 2 | 15.0 | 0.67 | 55.0 | 5.57 |
| 3 | 15.1 | 0.67 | 57.3 | 5.81 |
| Average | | | | | 14.7 | 0.67 | 57.5 | 5.63 |
| STDEV | | | | | 0.6 | 0.011 | 2.6 | 0.15 |
| NR18/WER2-O|D149 (11 µm) | 1 | 16.0 | 0.65 | 57.7 | 6.04 |
| 2 | 15.6 | 0.68 | 55.2 | 5.86 |
| 3 | 16.1 | 0.64 | 52.7 | 5.44 |
| 4 | 15.1 | 0.68 | 55.9 | 6.19 |
| Average | | | | | 15.7 | 0.66 | 55.4 | 5.88 |
| STDEV | | | | | 0.4 | 0.02 | 2.0 | 0.32 |

Figure S5: (a) J-V characteristics measured under 1 sun illumination with an area of 0.16 cm$^2$ and; (b) The IPCE
Figure S6: Dye desorption measurements of (a) D149 on SANP, NR18-T and WER2-O films (three films for each, thickness $5.0\pm0.3$ µm; area= 1 cm$^2$); (b) The quantified LHE of D149 desorbed on SANP, NR18-T and WER2-O films.

Figure S7: The optical band gap ($E_g$) measurements (Tauc plot) of SANP, NR18-T and WER2-O films (10.0±0.3 µm thick).
Raman Analysis

The percentage of specific exposed (001) facets of anatase can be quantified from the relative intensity ratios of $E_g(1)$ and $A_{1g}$ vibrational modes in Raman spectra, [1-3] typically from the relative ratio of $E_g(1)$ at 144 cm$^{-1}$ and $A_{1g}$ at 513 cm$^{-1}$ vibrational modes ($A_{1g}/E_g(1)$). This is of interest as a possible explanation for the difference in IEP between SANP and the other TiO$_2$ materials.

Figure S8 shows Raman spectra of both samples, collected in the range of (100-800 cm$^{-1}$). Gaussian fits were applied for the ease of comparison to calculate the Full Width at Half Maximum (FWHM) of all vibration modes. Raman spectra of anatase TiO$_2$ is distinguished by six allowed vibrational modes centered at 144 cm$^{-1}$ ($E_g(1)$), 197 cm$^{-1}$ ($E_g(2)$), 399 cm$^{-1}$ ($B_{1g}$), 513 cm$^{-1}$ ($A_{1g}$), 519 cm$^{-1}$ ($B_{1g}$), and 639 cm$^{-1}$ ($E_g(3)$).[4] All active vibrational modes ($A_{1g} + 2B_{1g} + 3E_g$) were detected in both SANP and NR18-T, with the good agreement to previously reported values,[5] SANP showed less peak broadening compared to NR18-T which is correlated with smaller particle sizes, indicating better crystallinity compared to NR18-T.

![Figure S8: Raman measurements of SANP and NR18-T films (3 μm).](image-url)
XPS analysis

XPS spectra were measured in range (260-550 eV). Figure S9 shows the spectra of SANP and NR18-T where the peaks of Ti, O and C are observed for both samples. These peaks (Ti, O) are in good agreement with anatase TiO$_2$.[6] Whereas Figures S10 a,b show the high-resolution spectra of (Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$) at 458 eV and 464 eV respectively which correspond to Ti 2p representing the Ti$^{4+}$ oxidation state.[7] The O 1s peaks at 529 and 530.6 eV were assigned to Ti-O and OH respectively.[8]

**Figure S9:** XPS survey of SANP and NR18-T materials.
Figure S10: XPS spectra of (a,b) Ti 2p and (c,d) O 1s of; SANP and NR18-T.

Figure S11: EIS Nyquist plots fitting for devices based on SANP, NR18-T and NR18-T/WER2-O photoanodes sensitized with D149.
Figure S12: Dye desorption measurements of (a) N719 on SANP, NR18-T and WER2-O films (three films for each, thickness 5.0±0.3 µm; area= 1 cm²); (b) The quantified LHE of N719 desorbed on SANP, NR18-T and WER2-O films.

Table S4: J-V parameters details of devices based on synthesized SANP, NR18-T and NR18-T/WER2-O sensitized with N719 dye.

| SANP|N719 (10 µm) | $J_{sc}$ (mA·cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|---|---|---|---|---|---|
| 1 | 15.5 | 0.72 | 70.3 | 7.88 |
| 2 | 15.3 | 0.71 | 70.1 | 7.68 |
| 3 | 15.9 | 0.69 | 69.5 | 7.64 |
| Average | 15.6 | 0.71 | 69.9 | 7.73 |
| STDEV | 0.3 | 0.02 | 0.41 | 0.13 |

| NR18-T|N719 (10 µm) | $J_{sc}$ (mA·cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|---|---|---|---|---|---|
| 1 | 14.8 | 0.68 | 73.2 | 7.35 |
| 2 | 14.4 | 0.68 | 73.5 | 7.20 |
| 3 | 14.1 | 0.70 | 72.3 | 7.16 |
| Average | 14.4 | 0.69 | 73.0 | 7.23 |
| STDEV | 0.4 | 0.02 | 0.6 | 0.10 |

| NR18/WER2-O|N719 (15 µm) | $J_{sc}$ (mA·cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|---|---|---|---|---|---|
| 1 | 14.9 | 0.72 | 73.0 | 7.90 |
| 2 | 16.0 | 0.71 | 72.6 | 8.20 |
| 3 | 15.2 | 0.69 | 73.0 | 7.65 |
| Average | 15.37 | 0.71 | 72.8 | 7.91 |
| STDEV | 0.57 | 0.02 | 0.4 | 0.28 |
Figure S13: EIS Nyquist plots fitting for devices based on SANP, NR18-T and NR18-T/WER2-O photoanodes sensitized with N719.

References

1. Tian, F., Y. Zhang, J. Zhang, and C. Pan, Raman Spectroscopy: A New Approach to Measure the Percentage of Anatase TiO$_2$ Exposed (001) Facets. The Journal of Physical Chemistry C, 2012. 116(13): p. 7515-7519.

2. Chu, L., Z. Qin, and J. Yang, Anatase TiO$_2$ nanoparticles with exposed {001} facets for efficient dye-sensitized solar cells. Scientific reports, 2015. 5: p. 12143.

3. Yang, H.G., C.H. Sun, S.Z. Qiao, J. Zou, G. Liu, S.C. Smith, H.M. Cheng, and G.Q. Lu, Anatase TiO$_2$ single crystals with a large percentage of reactive facets. Nature, 2008. 453: p. 638.

4. Ohsaka, T., Temperature dependence of the Raman spectrum in anatase TiO$_2$. Journal of the Physical Society of Japan, 1980. 48(5): p. 1661-1668.

5. Šćepanović, M.J., M. Grujić-Brojčin, Z. Dohčević-Mitrović, and Z. Popović, Characterization of anatase TiO$_2$ nanopowder by variable-temperature Raman spectroscopy. Science of Sintering, 2009. 41(1): p. 67-73.

6. Shaban, M., J. Poostforooshan, and A. Weber, Surface–Initiated Polymerization on Unmodified Inorganic Semiconductor Nanoparticles via Surfactant–Free Aerosol–Based Synthesis toward Core–Shell Nanohybrids with Tunable Shell Thickness. V. 5. 2017. 18651-18663.

7. Hwang, J.-Y., S.-T. Myung, J.-H. Lee, A. Abouimrane, I. Belharouak, and Y.-K. Sun, Ultrafast sodium storage in anatase TiO$_2$ nanoparticles embedded on carbon nanotubes. Nano Energy, 2015. 16: p. 218-226.

8. Ni, J., S. Fu, C. Wu, J. Maier, Y. Yu, and L. Li, Self-supported nanotube arrays of Sulfur-doped TiO$_2$ enabling ultrastable and robust Sodium storage. Advanced Materials, 2016. 28(11): p. 2259-2265.