

Facile one-pot hydrothermal synthesis of nanorice-like TiO_2 for an efficient dye-sensitized solar cell (DSSC)

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Highly crystalline TiO_2 powder consisting of morphologically rice-like nanoparticles is synthesized by a simple hydrothermal process using a premixture of titanium isopropoxide, ethanol and aqueous ammonia. An efficient mechanism decoupling hydrolysis and condensation promotes the formation of a rice-like morphology. As the average particle size and BET properties of nanorice-like TiO_2 were found to be quite similar to a commercially available TiO_2 (Degussa P25), their photoelectric properties were compared as a DSSC electrode. Under 1 sun irradiation the photovoltaic efficiency of nanorice-like TiO_2 was measured to be c. 20% higher in contrast to the mediocre efficiency (~5.45%) of P25. We suggest that together with a generally exploited reference, such nanorice-like TiO_2 could also be adopted as a model material for various applications.

1. Introduction

A part from traditional pigment applications, nanocrystalline TiO_2 intrinsically possesses multifunctional attributes enabling it to be deployed in environmental photocatalysts (for treating polluted air or wastewater, self-cleaning windows, antimicrobial coatings); and in efficient electrodes for photovoltaic cells, photo-electrochromics and gas sensing devices.¹⁻³ Several physical techniques and chemical approaches have been successfully used to prepare

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¹ X. Chen and S.S. Mao, Titanium dioxide nanomaterials: Synthesis, properties, modifications, and applications. *Chem. Rev.* **107** (2007) 2891–2959.

² M.R. Hoffmann, S.T. Martin, W.Y. Choi and D.W. Bahnemann, Environmental applications of semiconductor photocatalysis. *Chem. Rev.* **95** (1995) 69–96.

³ O. Carp, C.L. Huisman and A. Reller, Photoinduced reactivity of titanium dioxide. *Progr. Solid State Chem.* **32** (2004) 33–177.

various crystal forms of anisotropic nanosize crystalline TiO₂ materials.^{1–2} Among these chemical approaches, low-temperature hydrothermal (HT) synthesis is widely preferred because of its simplicity, low cost, and amenability to readily control the physicochemical properties of the material; e.g., crystallinity, size and morphology of particles; and desirable Brunauer–Emmett–Teller (BET) features (surface area; pore shape; size and volume). Such controlled desired physicochemical properties of the material can be achieved by a tailored combination of the reaction variables, viz. time, temperature, type of precursors (pristine or chemically modified), type of solvent, pH, modulating agent etc.

Here we report a simple and facile low temperature HT synthesis of highly crystalline nanorice-like TiO₂ powder, whose pore size and volume is relatively larger than the commonly exploited model TiO₂ powder Degussa P25, yet both these TiO₂ powders have more or less comparable average particle sizes and BET surface areas. These TiO₂ nanoparticles differ in their shapes (P25 is nearly spherical); shape-dependent, superior charge-transfer properties of nanorice-like TiO₂ are exploitable in an easily implemented, low-cost DSSC device technology, which could well fulfil our future needs of clean energy.⁴ Under global light illumination (1 sun, AM 1.5 G), and identical electrode fabrication and DSSC assembly conditions, a cell made of nanorice-like anatase easily gave a solar to electric conversion efficiency (η) of *c.* 6.5%, an enhancement of *c.* 20% with respect to that of a reference cell made of the commercially available and commonly exploited benchmark TiO₂ (Evonik, formerly Degussa P25).

2. Materials and methods

Titanium isopropoxide (TTIP, 97%), ethanol (EtOH, 99.9%) and ammonia solution (NH₃, 28–32 wt% in water) were obtained from commercial sources and used as received. A premixture was made by simply diluting pristine TTIP with EtOH (1:6 molar ratio) inside a Teflon vessel (~100 mL), and after 10 minutes of mild magnetic stirring *c.* 70 mL of aqueous solvent (pH ~12, adjusted by NH₃) of triply deionized water (Millipore, 18 M Ω cm) was carefully poured to this premixture. Within a few seconds, a white slurry was formed, which was stirred for *c.* 10 min. Then the HT reaction was carried out at 150 °C for 12 h and the resulting white product was collected by centrifugation and lavish washing with deionized water. The final TiO₂ powder was obtained by drying the white product at 100 °C for 4 h, followed by grinding.

Crystalline phase and average particle size were determined using X-ray diffraction (XRD; PRO-MPD, Philips). BET properties were measured by N₂ adsorption–desorption at 77 K (ASAP-2010, Micromeritics). Specific BET surface area (S_{BET}), pore size (D_{p}) and pore volume (V_{p}) were determined from the N₂ adsorption isotherms using BET and Barrett–Joyner–Halenda (BJH) methods. Morphological features were examined by field-emission scanning electron microscopy (SEM; XL30S FEG, Philips).

TiO₂ electrodes were prepared by screen printing a mesoscopic TiO₂ paste made with the procedure given in ref. 5. Platinum (Pt) counter electrodes were prepared by depositing a

⁴ M. Grätzel, Solar energy conversion by dye-sensitized photovoltaic cells. *Inorg. Chem.* **44** (2005) 6841–5851.

⁵ K.P.S. Parmar, E. Ramasamy, J. Lee and J.S. Lee, Rapid (~10 min) synthesis of single-crystalline, nanorice TiO₂ mesoparticles with a high photovoltaic efficiency of above 8%. *Chem. Commun.* **47** (2011) 8572–8574.

hexachloroplatinic acid-based paste onto conducting FTO glass substrates (TEC-10). TiO₂ and Pt-electrodes were sintered at 500 and 400 °C respectively for *c.* 30 min. The redox electrolyte consisted of 0.5 M 1-butyl-3-methylimidazolium iodide, 0.05 M I₂ and 0.5 M 4-tert-butylpyridine in acetonitrile.

The N719 dye adsorption capacity of the electrodes was measured by immersing them overnight into a 0.1 M NaOH solution (of EtOH:water 1:1) and calculating the concentration of N719 dye (extinction coefficient $\sim 1.41 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) by light absorbance (peak at 515 nm) using UV-Vis spectroscopy (UV-2401PC, Shimadzu).

The current–voltage characteristics of the assembled DSSC were measured in the dark and under 1 sun (100 mW cm⁻², AM 1.5 G) illumination with a Peccell PEL-L11 solar simulator. Electrochemical impedance spectra (EIS) were measured under 1 sun in the open-circuit condition using a Reference 600 potentiostat (Gamry Instruments).

3. Results and discussion

Several crystalline TiO₂ powders were synthesized, however here we present one typical TiO₂ (obtained by a premixture of 1 mole of TTIP with 3.5 moles of EtOH), which is closely comparable to P25 in its average particle size, BET surface area and pore characteristics, yet shows much better parametric performance as an electrode film for a DSSC. In the XRD pattern (Fig. 1a) it is clearly seen that the synthesized TiO₂ is highly crystalline and is pure anatase (JCPDS Card No. 04-0477), whereas P25 is biphasic, consisting of about 73% anatase and 27% rutile, as estimated by the intense (101) peaks of its anatase and rutile phases.⁶ The average particle size of the prepared TiO₂ is comparable with that of P25 (Table 1), estimated from the XRD (101) peak using Scherrer's equation.⁶ Both TiO₂ and P25 powders were found to be mesoporous in nature (Fig. 1b) with comparable BET surface areas (Table 1). The mesoscopic nature of the powders is clearly indicated by their N₂ adsorption–desorption (H3-type, IV-type; BDDT classification) hysteresis loops, and BJH pore-size distributions (see inset to Fig 1b) are typical for nanoparticles having disordered cylindrical pore structures. As shown in Fig. 1b, N₂ capillary cohesion of as-prepared TiO₂ powder occurred at relatively higher pressure, indicating that its pore features are larger than those of P25 (Table 1).

SEM images (Fig. 2) show the nanoparticles of the synthesized anatase and biphasic P25 powders. It can clearly be seen that the P25 nanoparticles are nearly isotropic in shape, whereas the synthesized TiO₂ nanoparticles are rice-like; anisotropic growth of the particles is highly expected from ongoing hydrolysis–polycondensation reactions of a molecularly modified pristine monomeric precursor (Ti(OPr)₄) reacting with EtOH. When pristine Ti(OPr)₄ is mixed with EtOH, it is possible that some of the less electronegative OPr ligands are replaced by the more electronegative OEt ligands, hence forming a new chemical precursor Ti(OPr)_{4-x}(OEt)_x.⁷⁻⁸ The difference in electronegativity of the two ligands should promote an efficient decoupling

⁶ H. Jensen, K.D. Joensen, J.-E. Jørgensen, J.S. Pedersen and E.G. Søgaard, Characterization of nanosized partly crystalline photocatalysts. *J. Nanoparticle Res.* **6** (2004) 519–526.

⁷ C. Sanchez, J. Livage, M. Henry and F. Babonneau, Chemical modification of alkoxide precursors. *J. Non-Crystalline Solids* **100** (1988) 65–75.

⁸ U. Schubert, Chemical modification of titanium alkoxides for sol–gel processing. *J. Mater. Chem.* **15** (2005) 3701–3715.

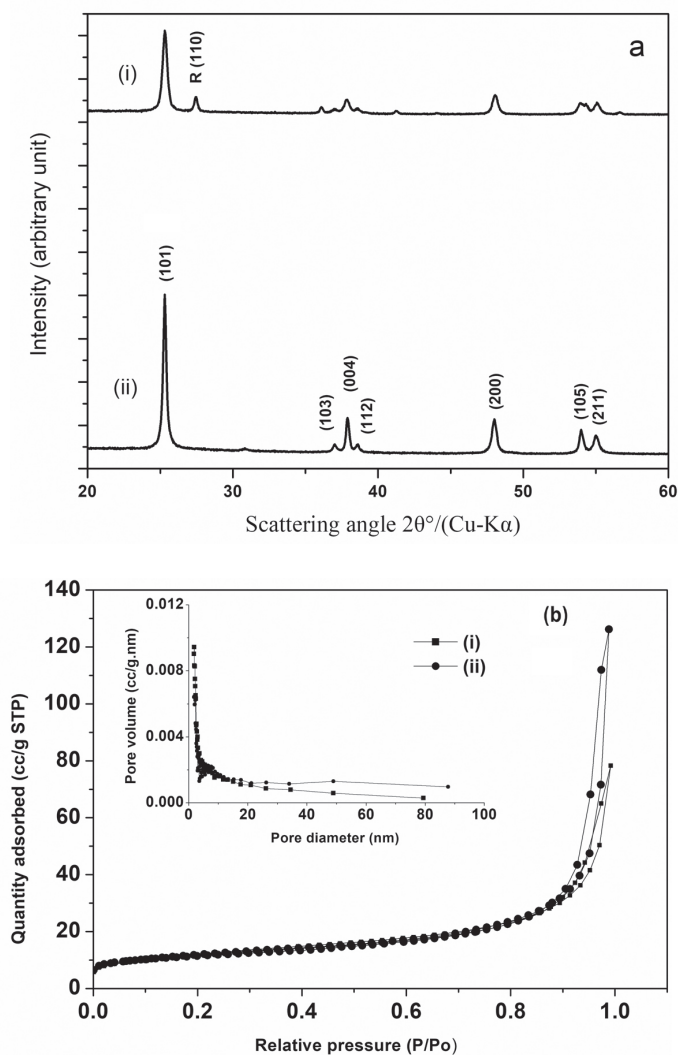


Figure 1. (a) XRD patterns and (b) N_2 adsorption–desorption BET curves (inset; pore-size distributions) of (i) Degussa P25 and (ii) synthesized TiO_2 . R ($2\theta = 27.460$) represents the rutile-phase.

Table 1. Structural and textural BET features and DSSC parameters of isotropic P25 and rice-like anatase TiO_2 .

Mean	particle size /nm	$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	$V_{\text{P}} / \text{cc g}^{-1}$	D_{P} / nm	V_{OC} / V	$J_{\text{sc}} / \text{mA cm}^{-2}$	FF ^a	η^b (%)	Dye loading /mol cm^{-2}	f_{p} / Hz
P25	19.5	42.3	0.12	13.1	0.79	9.45	73	5.3	0.57	20.6
TiO_2	18.9	43.6	0.20	21.9	0.85	10.78	71	6.5	0.57	15.5

^a Fill factor.

^b Efficiency—the fraction of incident power converted to electricity.

between hydrolysis and polycondensation reactions.⁷ Inevitably, a less electronegative ligand is removed quickly by the OH[−] group during hydrolysis, whereas a more electronegative ligand is mainly replaced by the OH[−] group during the polycondensation process and, consequently, decoupling between hydrolysis and condensation reactions occurs, playing a key role in the creation of the anisotropic shape of the nanoparticles.

In any suitable potential application, nanorice-like TiO₂ should demonstrate better performance due to its high crystallinity, pure phase and, more importantly, distinct anisotropic shape of its nanoparticles (Figs 1 and 2), though having comparable S_{BET} and average particle size (Table 1) to those of a routinely exploited biphasic and isotropic material (P25). We have tested the performance of a DSSC made of a nanorice-like TiO₂ powder and a reference P25 TiO₂ powder. The DSSC assembly parameters were first optimized for the spheroidal P25, and the same parameters were then taken as the starting point for the nanorice-like TiO₂.⁵

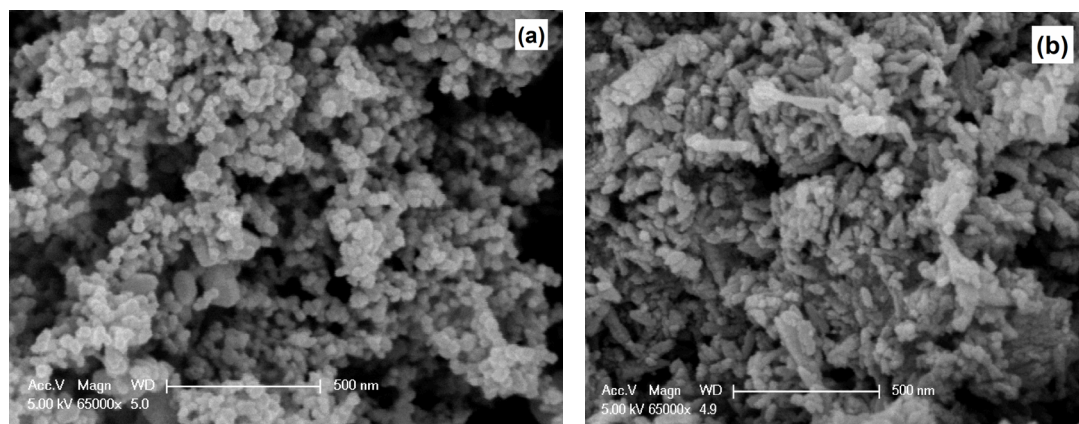


Figure 2. SEM images of: (a) Degussa (Evonik) P25; and (b) nanorice-like anatase TiO₂.

Fig. 3(a) shows the measured photocurrent–voltage (V – I) characteristics of the DSSC. It is evident that under identical standard 1 sun illumination and fabrication conditions of the electrode, open circuit voltage (V_{oc}) and short-circuit photocurrent density (J_{sc}) of a nanorice-like TiO₂ electrode are much improved compared with a P25 electrode, although P25 gave a slightly better fill factor (FF) due to its advantageous compact electrode film made of spheroidal nanoparticles; however, the efficiency η of the nanorice-like TiO₂ electrode was much higher (*c.* 20% enhanced), in contrast to the biphasic and isotropic P25 electrode.

As evident from Fig. 3(a), the higher open circuit voltage (V_{oc}) of the nanorice-like TiO₂ electrode could be attributed to its pure phase and enriched crystallinity (i.e., sharp/intense XRD peaks). On the other hand, along with crystallinity, the enhanced J_{sc} of the nanorice-like TiO₂ electrode might be due to factors like more dye adsorption and better electron conductivity. However, very little difference was observed in the adsorbed amounts of photosensitizer (N719 dye) (Table 1) in the interconnected mesoporous networks of isotropic P25 and anisotropic nanorice-like TiO₂, which could be understood in terms of a comparable BET surface area of the powder samples employed for electrode fabrication (Table 1).

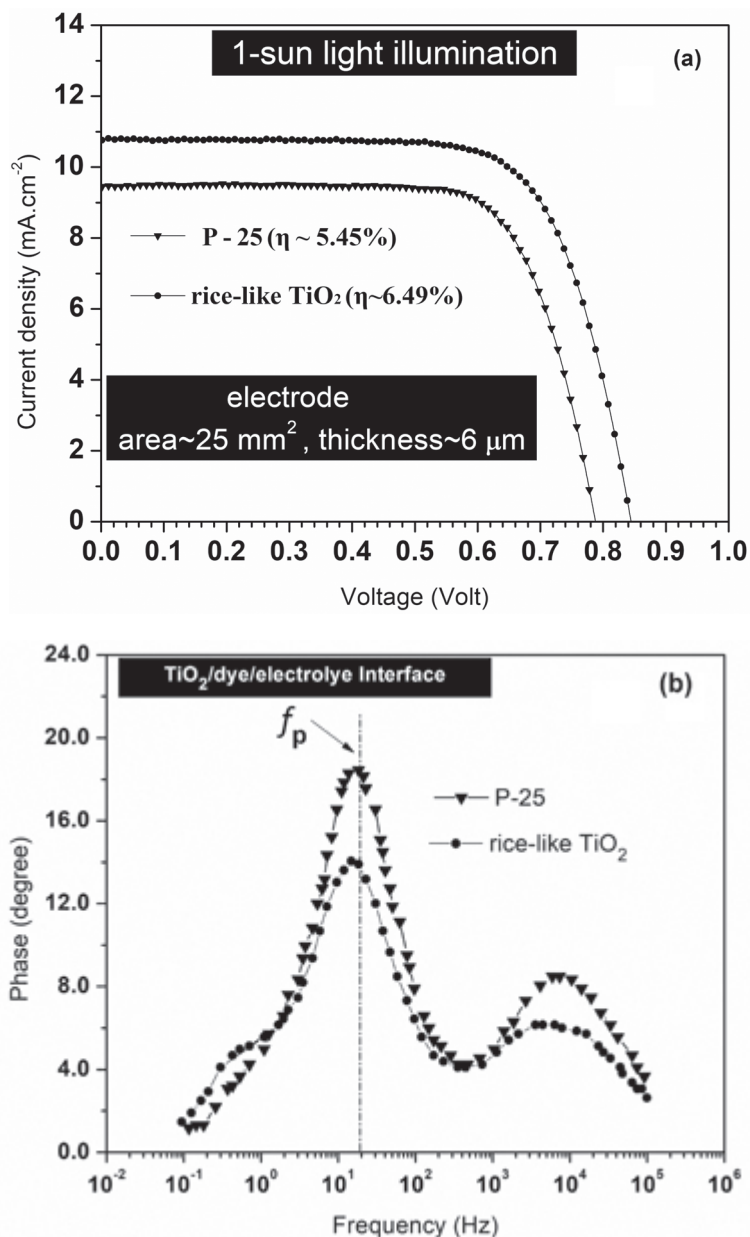


Figure 3. (a) Photocurrent–voltage characteristics and (b) Bode phase plots of nanorice-like anatase TiO_2 and P25 (see Table 1).

Therefore, in contrast to isotropic and biphasic P25, it seems obvious that the higher J_{sc} of nanorice-like TiO_2 electrode is favoured by enriched crystallinity, a pure phase and, more importantly, shape anisotropy that could possess a better charge conductivity in relation with a higher lifetime (τ_{el}) for electrons dye-injected into the conduction band (CB) of the mesoporous

oxide film structure to the back conducting fluoride-doped tin oxide (FTO) glass substrate.⁹ τ_{el} was estimated from Bode phase plots of electrochemical impedance spectroscopy (EIS) results of the electrodes (Fig. 3b). The peaks of characteristic frequency $f_p = 1/(2\pi\tau_{el})$ for the oxide/dye/electrolyte interface for anisotropic and isotropic electrode films were at 15.52 and 20.58 Hz respectively, thus indicating an improved τ_{el} (c. 25%) of dye-injected charge carriers into the anisotropic rice-like anatase TiO₂ film compared to that of the biphasic and spheroidal P25 film. An improved τ_{el} is an obvious consequence of a well crystallized anisotropic charge-conducting geometry providing suppressed charge recombination due to fewer defects and traps in the film.⁵

4. Conclusion

Crystalline nanorice-like anatase TiO₂ powder can be well synthesized in a one-pot HT reaction simply by taking advantage of the electronegativity difference of the attached ligands. The average particle size and exposed BET surface area of the resulting nanorice-like TiO₂ powder are quite similar to those of a commercially available benchmark (reference) TiO₂ powder (Degussa P25). The reported HT synthesis process is very convenient, easy and readily scalable. Moreover the synthesized nanorice-like TiO₂ material showed good performance in a DSSC. Thus, such nanorice-like TiO₂ could be potentially adapted as a reference material in numerous applications, whenever and wherever possible.

Acknowledgment

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⁹ A. Sacco, Electrochemical impedance spectroscopy: Fundamentals and application in dye-sensitized solar cells. *Renewable Sustainable Energy Rev.* **79** (2017) 814–829.