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Influence of yttrium dopant on the properties of anatase nanoparticles and the performance of dye-sensitized solar cells

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Abstract: TiO$_2$ mesoporous nanoparticles (NPs) doped with yttrium (Y) ions are fabricated via an environmentally friendly and facile solvothermal method to serve as photoanode for dye sensitized solar cells (DSSCs). X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy and N$_2$ adsorption–desorption tests are used to characterize the influence of yttrium dopant on the properties of TiO$_2$ NPs. The prepared Y–doped TiO$_2$ NPs have anatase phase and exhibit Ti–O–Y bonds. The photovoltaic performance is primarily associated with the morphological parameters of the NPs. At the optimum Y concentration of 3 at%, the short circuit current density has increased from 13.20 to 15.74 mA cm$^{-2}$, full sun solar power conversion efficiencies increased from 6.09% up to 7.61% as compared to the blank DSSC.

Key words: titanium dioxide; rare earth; mesoporous structure; specific surface area; photovoltaic performance

1. Introduction:
Dye-sensitized solar cells (DSSCs), invented by Grätzel [1], were designed as a sandwich structure which contains a photoanode, an electrolyte and a counter electrode. Over the last decade, the photoanode has been targeted with numerous efforts. Among these components, the photoanode not only transports photo-induced electrons but also acts as the matrix to adsorb organic dyes, which directly determines the photo-current density [3]. Among various candidates, TiO$_2$ has been identified as a promising photoanode material and has been widely investigated [3–5]. Generally, to effectively adsorb dyes, a large specific surface area (SSA) is necessary [6]; therefore, various technologies have been developed to enlarge the SSA, such as micelle [7,8], block copolymer [9] and ordered templates [10]. Unfortunately, all those approaches need post-processing [11,12], which retard their application. Therefore, it is highly desirable to find a facile way to enlarge the SSA of TiO$_2$ nano-powders. Mesoporous structure may be an option, not only offering higher surface area (providing sites for adsorbing organic dyes), but also possessing linked walls for the diffusion of photo-induced electrons.

Rare earth elements (REEs) have been employed extensively in photocatalysis [13–15] and selective catalytic reduction [16] to improve the electron–hole ($e^–h^+$) separation and to narrow the optical band gap for light harvesting of semiconductors [17–22]. Typically, researchers synthesized TiO$_2$ with Y doping and revealed that Y doping was helpful to the formation of oxygen vacancies for NO oxidation [16] and photocatalysis [17]. Besides, the role of REEs in DSSC photoanodes has been discussed in several other publications [23-26]. Light harvesting enhancement by dye
adsorption or other ways and electron transport improvement are major aims to incorporate REEs into DSSCs. Oh et al. [23] synthesized a Eu(III)–complex as an ultraviolet (UV) light–harvesting coadsorbent of DSSC and obtained a high short circuit photocurrent densities ($J_{SC}$) of 17.72 mA/cm$^2$ while that of the reference DSSC was 15.53 mA/cm$^2$. G. B. Shan [24] synthesized Er$^{3+}$/Yb$^{3+}$ co–doped LaF$_3$–TiO$_2$ nanocomposite and applied it as external up-conversion layer in the photoelectrode to harvest near infrared (NIR) light, improving the photocurrent with 2.4%. Zalas and Klein [25] fabricated TiO$_2$ films with lanthanide ions and reported that the RE–containing layer might act as an energy barrier preventing electron back-transfer. Zhang et al. [26] increased the density of oxygen vacancies of TiO$_2$ surface for dye adsorption by La doping and provided a power conversion efficiency (PCE) of 6.72%, which was a 13.5% improvement compared with that of references cell. However, to the best our knowledge, no report on mesoporous structure particles with REE doping for DSSC has been found. As is known, Y(III) has one occupied 4d orbital, which easily produces several electron configurations [27]. Besides, Y has the smallest ionic radius among REEs [28], which is relatively close to the Ti$^{4+}$ radius, thus, the substitution of Ti by Y seems feasible. Hence, in the present work, Y was adopted as the dopant, and the irregular mesoporous structure of the nano-powders was achieved via a facile way. The effect of irregular mesoporous structure by Y doping TiO$_2$ was reflected in the enhanced performance of DSSCs, which may open the way for further photoanode material research in DSSCs field.

2. Experimental
2.1. Preparation of Y-doped TiO$_2$ powders:

Y-doped TiO$_2$ nanoparticles (NPs) were synthesized by modifying the reported method for blank TiO$_2$ NPs [29]. A stock solution of Ti$^{4+}$ (0.5 M) was prepared by mixing titanium isopropoxide (TTIP) and triethanolamine (TEOA) (1 M), followed by adding distilled water. A small amount of yttrium nitrate (Y(NO$_3$)$_3$·6H$_2$O) was initially added into the above mixture (Y$^{3+}$/Ti$^{4+}$ molar ratio= 0.6 at%, 1.8 at%, 3.0 at%, 4.2 at% and 5.4 at%, and TTIP:TEOA molar ratio = 1:2). The mixture was transferred into a Teflon-lined autoclave, aged at 100 °C for 24 h to get gelation (the first aging). Then, the second aging treatment was performed at 140 °C for 72 h to nucleate and grow TiO$_2$ particles doped with Y ions. The obtained Y–doped TiO$_2$ powders were assigned as X%Y–TiO$_2$, where X represents the initial molar ratio of Y/Ti as determined by the weighed quantities of TTIP and yttrium nitrate. The molar ratio in the NPs can deviate from this initial ratio. For comparison, pure TiO$_2$ was prepared using the same procedure without Y$^{3+}$. TTIP hydrolysates were identified as amorphous TiO$_2$ using the transmission electron microscope (TEM) in combination with selected area electron diffraction (SAED), as shown in Fig. S1. The SAED pattern indicated that TiO$_2$ was in the amorphous state before further heat treatment.

2.2 Photoanode preparation:

The pastes (Y–doped or not), made from the above powders, were deposited on the surface of fluorine-doped tin oxide (FTO) conductive glass using the doctor blade technique (FTO, sheet resistance: 15 Ω). The film thickness could easily be tailored by tuning the paste’s viscosity and the depositing time. The deposited films were dried
at 130 °C and subsequently annealed at 500 °C for 1 h in air to remove residual organic compounds as well as to improve the bonding between the TiO$_2$ film and the FTO substrate. The annealed samples were immersed into a solution containing 40 mM TiCl$_4$ for 30 min at 70 °C, rinsed using deionized water, and then sintered at 500 °C. Finally, the film was dipped into an acetonitrile and ethanol (volume ratio=2:1) solution containing 0.5 mM cis-bis (isothiocyanato) - bis (2,2'-bipyridyl-4,4'-dicarboxylato) -ruthenium(II) -bis-tetrabutyl-ammonium (N719) dye, and kept at room temperature for 24 h.

2.3. Y-doped TiO$_2$ nanoparticles characterizations and photovoltaic performance

The morphology of the obtained samples was studied using a transmission electron microscope (TEM) (HitachiH-700). The crystal structure of the specimen was identified by X–ray diffraction (XRD) using a Bruker D8 advance diffractometer with Cu Kα radiation. The N$_2$ adsorption-desorption tests were measured using micromeritics ASAP 2020 at 77 K with N$_2$ physical adsorption, temperature–programmed reduction/desorption (TPR/TPD) and Mossbauer effect spectroscopy (MES) methods. The specific surface area (SSA) was calculated based on the Brunauer–Emmett–Teller (BET) method. Desorption pore volume (for pores of diameter 1.7–300 nm) and pore width, measured by the Barrett–Joyner–Halenda (BJH) method. X-ray photoelectron spectrum (XPS) measurements were performed on a thermo scientific X-ray photoelectron spectroscopy made in UK (ESCALAB 250Xi). The XPS binding energy (BE) was internally referenced to the C 1s peak (w = 285 eV). The adsorbed dye of the photoanode was desorbed in a mixed solution of water and
ethanol (volume ratio = 1:1) containing 0.1 M NaOH, and then measured with an 
UV–Vis spectrometer (SHIMADZU, UV-2550). The current-voltage (I–V) measurements were performed on a Keithley 2400 power source under irradiation of 1 Sun whose intensity of the incident light was air mass (AM) 1.5 G. This instrument was equipped with a 300 W solar simulator (Solar Light Co., INC.), which served as the light source. In order to gain better understanding of the electrical properties, the electrochemical impedance spectrum (EIS) was recorded under light irradiation via an electrochemical workstation (Zahner, IM6ex).

3. Results and Discussion:

3.1. Investigation of pure and doped nanoparticles

Figure 1 shows the XRD diffraction pattern of pure TiO$_2$ and X%Y–TiO$_2$. It is clear that, according to JCPDS 65–5714, the as-prepared pure TiO$_2$ and X%Y–TiO$_2$ nanoparticles (NPs) are in the anatase phase. However, the diffraction peak of sample X%Y–TiO$_2$ is obviously broader, besides, the peak intensities of the X%Y–TiO$_2$ are weaker than those found for pure TiO$_2$, which can possibly be attributed to the presence of foreign ions in the crystal lattice [30]. As depicted in Fig. S2, small shifts in peaks are observed reflecting an expansion of the unit cell volume. The lattice parameters and the unit cell volumes of pure TiO$_2$ and X%Y–TiO$_2$ are calculated from equation for tetragonal system:

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}}$$  \hspace{1cm} (1)
Where $d_{hkl}$ is the interplanar spacing, which is determined from the anatase diffraction peaks of 101 and 200 for pure TiO$_2$ and X%Y–TiO$_2$. As shown in Table 1, a universal trend of the elongation of each axis and increase of unit cell volume are observed with the increase of the Y concentration. When the initial Y molar ratio is 3%, the lattice volume expands from 137.35 Å$^3$ (non doped NPs) to 138.30 Å$^3$. The expansion of the TiO$_2$ lattice may be attributed to the difference in ionic radii of Y$^{3+}$ (0.089 nm) and Ti$^{4+}$ (0.068 nm), which indicates that the Y ions are incorporated into TiO$_2$ lattice. Besides, the crystallite size ($D$) is determined from Debye–Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

(2)

Where $\lambda$ is the CuK X–ray wavelength (1.5406 Å), $k$ is a constant (in this study $k=0.943$), $\beta$ is the full–width at half maximum ($FWHM$) and $\theta$ is the diffraction angle. The general observation from the data shown in Table 1 is that smaller crystallite size is obtained in all Y–doped samples. Obviously, 3%Y–TiO$_2$ NPs exhibit the smallest average size of 25.11 nm (that of non doped NPs is 28.41 nm). Upon further increasing the Y doping concentration, the Y–doped samples show a tendency for larger particle sizes again. M. Khan et al. [14] fabricated Y doped anatase using hydrothermal method which exhibited a reduced particle size and larger BET specific surface area compared to bare TiO$_2$. Besides, L. Cheng et al. [31] synthesized Y doped SnO$_2$ by the electro–spinning method and suggested that Y doping distorts the crystal lattice and subsequently prevents the growth of crystallites. Since smaller particles
usually manifest larger specific surface area (SSA), this is in good accordance with the relationship between our particle size and SSA results as indicated in Table 1.

X–ray photoelectron spectrum (XPS) is adopted to further investigate the chemical state of the elements and explore how the doped yttrium cations interact with TiO$_2$. The results are summarized in Fig. 2. Fig. 2a depicts the full scan XPS spectra of binding energy ($BE$). In Fig. 2b, the peak position of the O 1s core levels of 3%Y–TiO$_2$ shifts to higher energy compared with those of undoped TiO$_2$, indicating that the chemical environment of the elements has been changed. [32,33] Further, the O1s spectrum shows that two different oxygen binding energies exist in the as-prepared Y doping TiO$_2$, as compared with the binding energy of oxygen in pure TiO$_2$. The O1s peak of 3%Y–TiO$_2$ is divided into two different peaks which are located at 529.49 and 530.32 eV. These can be attributed to Ti–O and Y–O binding energy, respectively, as compared to that of pure TiO$_2$ shown in Fig.2b and Y–O binding energy in the literature (529.5 eV). [33] The spectrum for the Y 3d region of 3%Y–TiO$_2$ is shown in Fig. 2c. The $BE$ of Y 3d$_{5/2}$ and Y 3d$_{3/2}$ for 3%Y–TiO$_2$ is about 157.58 and 159.63 eV, respectively, with a spin–orbit splitting of 2.05 eV. These results are giving the evidence that the oxidation state of the Y ions is mainly trivalent. [34] Since oxidized yttrium was not observed in the XRD diagrams of X%Y–TiO$_2$ although the concentration of Y is more than 3 at% (as shown in Fig. 1), it is certain that some Y ions have been successfully substituted Ti ions in the TiO$_2$ lattice during the solvothermal process, and some Ti–O bonds in pure TiO$_2$ shown in Fig. 2b have
been replaced by Y–O bonds. Besides, the \textit{XPS} analysis result indicates that the actual Y amount in 3\%Y–TiO\textsubscript{2} is 1.21 at\%.

The \textit{TEM} study was done to examine the effect of Y doping on the morphology of anatase, as shown in Fig. 3. The average particle size of the \textit{NPs} is 10–40 nm, which is in agreement with the average value of the crystallite size determined by \textit{XRD} (as shown in Table 1). As shown in Fig. 3b and Fig. 3e, in contrast to the regular structure of pure TiO\textsubscript{2} \textit{NPs}, 3\%Y–TiO\textsubscript{2} \textit{NPs} possess a more irregular mesoporous structure. The accumulated 3\%Y–TiO\textsubscript{2} \textit{NPs} with irregular structure (see Fig. 3e) have an enhanced surface area and linked framework that will facilitate the diffusion of photo-induced electrons. The Selected area electron diffractions (\textit{SAED}) shown in insets of Fig. 3a and 3d clearly indicate the poly–crystallinity circles in anatase of TiO\textsubscript{2} and 3\%Y–TiO\textsubscript{2}. Fig. 3c and 3f show that (101) planes have slightly expanded in 3\%Y–TiO\textsubscript{2} (3.46 Å) compared to those in pure TiO\textsubscript{2} (3.45 Å). This agrees favorably with the 101 interplanar spacing calculated from 101 diffraction angle of TiO\textsubscript{2} and 3\%Y–TiO\textsubscript{2} (see Table S2), indicating also that Y ions have been doped into the TiO\textsubscript{2} lattice. Finally, by comparing the microstructure of pure TiO\textsubscript{2} (Fig. 3g) with that of 3\%Y–TiO\textsubscript{2} (Fig. 3h), lattice distortion can be detected, indicating oxygen vacancy and substitution of Y for Ti in 3\%Y–TiO\textsubscript{2} lattice. In other words, the \textit{XRD}, \textit{XPS} and \textit{TEM} analysis results indicate that Y ions have entered into the TiO\textsubscript{2} lattice and substituted Ti sites.

The N\textsubscript{2} adsorption–desorption isotherms and pore size distributions of pure and doped nanoparticles are recorded and depicted in Fig. 4. It is shown in Fig. 4a that the
isotherms of TiO$_2$ and X%Y–TiO$_2$ are identified as type V, a typical characteristic of mesoporous materials according to the International Union of Pure and Applied Chemistry (IUPAC) classification system. The pore size distribution (Fig. 4b) of 3%Y–TiO$_2$ ranges from 5 to 48 nm, which is broader than that of TiO$_2$ (5 to 35 nm). The hysteresis loop appears to be type H2, indicating that the pores are formed by accumulated NPs due to the high surface activity of the as–prepared NPs. Effects of Y doping on the BET surface area and pore parameters are summarized in Table 1. The mesoporous NPs with 3 at% dopant offer a high specific surface area and a pore volume of 142 m$^2$/g and 0.564 cm$^3$/g, respectively, being 36.6% and 121.5% higher than that of pure TiO$_2$ NPs. An increase of SSA and pore volume in the sequence 3%Y–TiO$_2$ - 1.8%Y–TiO$_2$ - 0.6%Y–TiO$_2$ - TiO$_2$ is observed, while a large decrease in 4.2%Y–TiO$_2$ and 5.4%Y–TiO$_2$ occurs. However, all NPs with Y doping have higher SSA and pore volume compared with reference sample. The smaller size (see Table 1) and irregular structure (see Fig. 3e) in doped NPs may account for the increase of SSA and pore volume for block X%Y–TiO$_2$. TiO$_2$ powders with higher SSA and larger pore volumes can enhance the efficiency of DSSC because more surface sites are available to adsorb organic dye, resulting in the enhancement of light harvest capability and increasing the amount of excited electrons, which move through the interconnected porous network.

3.2. Photovoltaic performance

The characteristic current–voltage (I–V) curves for pure and Y–doped TiO$_2$ and the effect of Y/Ti molar ratios on the relationship between specific surface area and
conversion efficiency are depicted in Fig. 5. The detailed photovoltaic parameters, including energy conversion efficiency, open-circuit voltage ($V_{OC}$), fill factors ($FFs$) and short circuit photocurrent densities ($J_{SC}$) are summarized in Table 2. The dye adsorption has been measured and is also listed in Table 2: the amount of dye increased as the $SSA$ increased. The $SSA$ substantially enhances the dye adsorption from $0.79 \times 10^{-7}$ (pure) to $1.26 \times 10^{-7}$ mol/cm$^2$ (3%Y–TiO$_2$). Clearly, compared with the pure TiO$_2$ based DSSC, a general increase of $J_{SC}$ has been observed for the X%Y–TiO$_2$ based DSSC. In addition, we also measured the incident photo-current efficiency ($IPCE$) spectra of the pure and X%Y–TiO$_2$ based DSSCs as shown in Fig. S4. The $IPCE$ results are consistent with the photocurrent of the DSSCs. As shown in Fig. 5b, the irregular structure and small particle size due to the Y incorporation into the TiO$_2$ matrix could provide high $SSA$ and thus increase the amount of excited electrons because of larger dye–adsorption, leading to the enhancement of $J_{SC}$. The highest $J_{SC}$ value (15.74 mA/cm$^2$) has been achieved by 3%Y–TiO$_2$ based DSSC. Further increasing Y/Ti molar ratios over 4.2% leads to $J_{SC}$ reduction, which can be attributed to a larger internal resistance [26]. Furthermore, a red shift of the absorption edge is observed in the UV–Vis absorption spectra of TiO$_2$ and Y–doped TiO$_2$ (Fig. S3). The absorption threshold shifts from 395 nm (undoped) to 405 nm (3%Y–TiO$_2$); so, the optical band gap decreases from 3.14 eV to 3.06 eV (see Table 1). The probable reason is that Y doping induces a part of the Y 4d states to extend into the TiO$_2$ conduction band resulting into narrowing of the band gap of anatase [14,35]. This may promote the transport of electrons. As listed in Table 2, Y doping also
results in a slight increase of $V_{OC}$, which may be due to a small upward shift of the Fermi level upon Y doping [35], since the voltage produced under illumination corresponds to the difference between the electrons in the Fermi level of TiO$_2$ NPs and the chemical potential of the holes in the hole conductor (electrolyte). [36] It should be noted that Y doped TiO$_2$ DSSC devices have higher fill factor ($FF$) values. The $FF$ reflects the quality of the TiO$_2$ film and the external electrical and electrochemical losses during the operation of the DSSCs [37,38]. The N$_2$ absorption-desorption measurement, BET, dye amount, $I-V$ characteristics curves jointly demonstrate that the doping of Y plays an important role in the SSA, dye adsorption and the efficiency of DSSCs (see Table 2).

To study the difference between the interfacial characteristics of the photo–electrodes, the electrochemical impedance spectra (EIS) of DSSCs based on pure TiO$_2$ and X%Y–TiO$_2$ have been measured in a frequency range from 0.01 Hz to 3 MHz under simulated solar light with an intensity of 100 mW/cm$^2$ ($AM$ 1.5). Results are shown in Fig. 6. According to Quintana et al. [39], the hemisphere in the intermediate-frequency region represents the transport resistance ($R_{ct}$) associated with the charge transfer across the TiO$_2$ film and the TiO$_2$/redox electrolyte interface. Experimental data have been fitted to the model as depicted in Fig. 6c represented by the equivalent circuit. The EIS parameters of the TiO$_2$ and X%Y–TiO$_2$ based DSSCs are listed in Table 2. A decrease of $R_{ct}$ in the sequence TiO$_2$ - 0.6%Y–TiO$_2$ - 1.8%Y–TiO$_2$ - 3%Y–TiO$_2$ is observed, while an increase occurs when the initial Y molar ratio is over 4.2%, which is consistent with the $J_{SC}$ and the energy conversion
efficiency of the obtained solar cells. S. Phadke et al. [40] explained the EIS of DSSCs in terms of electron transport energetics/kinetics of the photoelectrochemical processes and the pore–channel openness and interconnection of the photoanode. They proved that the incorporation of a hierarchical, interconnected network of pores in the TiO$_2$ electrode improves the charge transport. As shown in Table 2, the larger transport resistance of TiO$_2$ based DSSC as compared to that of X%Y–TiO$_2$ based DSSC can be due to the linked and irregular mesoporous structure of the latter: this enhances the diffusion of photo–induced electrons (see Fig. 3). In addition, the electron lifetime ($\tau_e$) can be calculated from the Bode plots (Fig. 6b), using the following equation:

$$\tau_e = \frac{1}{2\pi\omega_{\text{max}}}$$

(3)

Where $\omega_{\text{max}}$ is the frequency at which the intermediate-frequency peak appears in the Bode plot. Table 2 summarizes $\omega_{\text{max}}$, $\tau_e$ and $R_{\text{ct}}$ of TiO$_2$ and X%Y–TiO$_2$. The $\tau_e$ value first increases to 20.47 ms and then decreases. Among these cells, 3%Y–TiO$_2$ cell has the highest $\tau_e$ value (20.47 ms) and lowest $R_{\text{ct}}$ value (19.38 Ω), resulting in the highest efficiency of energy conversion. It can be deduced from the EIS results that Y doping is prolonging the lifetime of the injected electron and reduces the charge transport resistance significantly: hence, it improves the photovoltaic performance of the solar cell. From the results mentioned above, we conclude that a small particle size and irregular mesoporous structure caused by the Y incorporation into the TiO$_2$ matrix is responsible for the high $\tau_e$, the low $R_{\text{ct}}$, the high $V_{OC}$, the high $J_{SC}$, the high $FF$ and therefore the higher conversion efficiency of X%Y–TiO$_2$ based DSSCs.
4. Conclusion:

Mesoporous Y–doped TiO$_2$ nanoparticles (NPs) have been successfully synthesized via a facile strategy. Y doping leads to smaller particle size and expansion of the TiO$_2$ lattice compared with the reference sample. Transmission electron microscopy indicates the linked and irregular mesoporous structure for the photo-induced electron diffusion of doping NPs. It is found that a Y doping concentration of 3 at% yields the best performance in terms of short circuit current density and efficiency. The parameters that correlate best with this performance increase are the specific surface area, the pore volume, the electron lifetime and the transport resistance. A DSSC with mesoporous 3%Y–TiO$_2$ NPs, which have the highest specific surface area and pore volume (being 36.6% and 123% higher than that of pure TiO$_2$), demonstrates ~53% decrease of transport resistance and ~216% increase of electron lifetime compared with the reference DSSC. Such doping effectively improves the photocurrent from 13.20 to 15.74 mA·cm$^{-2}$, photovoltage from 703 to 706 mV, yielding a high energy conversion of 7.61%. Finally, we hope that the present work is a good starting point for understanding the properties of mesoporous Y–doped NPs and DSSCs. We intend to study the electronic behavior related to the morphology of doped photoanode in DSSCs, both experimentally and theoretically.

Acknowledgements

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References


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<th>Sample</th>
<th>TiO$_2$</th>
<th>0.6%Y-TiO$_2$</th>
<th>1.8%Y-TiO$_2$</th>
<th>3%Y-TiO$_2$</th>
<th>4.2%Y-TiO$_2$</th>
<th>5.4%Y-TiO$_2$</th>
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Table 2 Detailed parameters of X%Y-TiO$_2$ based DSSC devices.

<table>
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<tr>
<th>DSSC Device</th>
<th>Film thickness ($\mu$m)</th>
<th>Photovoltaic performance</th>
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<tr>
<td></td>
<td>$V_{OC}$ (mV)</td>
<td>$J_{SC}$ (mA/cm$^2$)</td>
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<td>TiO$_2$</td>
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Figure Captions:

Fig. 1 XRD diffractogram of TiO$_2$ and X%Y-TiO$_2$

Fig. 2 X-ray photoelectron spectroscopy spectra of TiO$_2$ and 3%Y-TiO$_2$ (a) Full scan XPS spectrum, (b) O 1s spectrum and (c) Y 3d core levels of 3%Y-TiO$_2$. For O 1s and Y 3d spectra the orange and grey lines are obtained by a curve fitting method.

Fig. 3 TEM images of TiO$_2$ (a, b, c and g) and 3%Y-TiO$_2$ (d, e, f and h) at different magnifications. SAED patterns from TiO$_2$ and 3%Y-TiO$_2$ nanoparticles are shown as inset in a, d.

Fig. 4 (a) N$_2$ absorption desorption isotherms of TiO$_2$ and X%Y-TiO$_2$ powders (b) The corresponding pore size distribution curves

Fig. 5 (a) I-V curves of the DSSC devices based on pure TiO$_2$ and X%Y–TiO$_2$ (b) Effect of Y/Ti molar ratios on the relationship between specific surface area and conversion efficiency. The insets are TEM images of bare TiO$_2$ and 3%Y–TiO$_2$ from Fig. 3.

Fig. 6 EIS spectra of TiO$_2$ and X%Y-TiO$_2$ based DSSCs; (a) Nyquist plots, (b) Bode plots and (c) the equivalent circuit.
Fig. 1 XRD diffractogram of TiO$_2$ and X\%Y-TiO$_2$
Fig. 2 X-ray photoelectron spectroscopy spectra of TiO$_2$ and 3\%Y-TiO$_2$ (a) Full scan XPS spectrum, (b) O 1s spectrum and (c) Y 3d core levels of 3\%Y-TiO$_2$. For O 1s and Y 3d spectra the orange and grey lines are obtained by a curve fitting method.
Fig. 3 TEM images of TiO$_2$ (a, b, c and g) and 3%Y-TiO$_2$ (d, e, f and h) at different magnifications. SAED patterns from TiO$_2$ and 3%Y-TiO$_2$ nanoparticles are shown as inset in a, d.
Fig. 4 (a) N\textsubscript{2} absorption-desorption isotherms of TiO\textsubscript{2} and X\%Y-TiO\textsubscript{2} powders (b) The corresponding pore size distribution curves
Fig. 5 (a) $I-V$ curves of the DSSC devices based on pure TiO$_2$ and X%Y–TiO$_2$ (b)

Effect of Y/Ti molar ratios on the relationship between specific surface area and conversion efficiency. The insets are TEM images of bare TiO$_2$ and 3%Y–TiO$_2$ from Fig. 3.
Fig. 6 EIS spectra of TiO$_2$ and X%Y-TiO$_2$ based DSSCs; (a) Nyquist plots, (b) Bode plots and (c) the equivalent circuit.
Graphic Abstract