Solar Cells

Increasing the Efficiency of Organic Dye-Sensitized Solar Cells over 10.3% Using Locally Ordered Inverse Opal Nanostructures in the Photoelectrode

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3D inverse opal (3D-IO) oxides are very appealing nanostructures to be integrated into the photoelectrodes of dye-sensitized solar cells (DSSCs). Due to their periodic interconnected pore network with a high pore volume fraction, they facilitate electrolyte infiltration and enhance light scattering. Nonetheless, preparing 3D-IO structures directly on nonflat DSSC electrodes is challenging. Herein, 3D-IO TiO₂ structures are prepared by templating with self-assembled polymethyl methacrylate spheres on glass substrates, impregnation with a mixed TiO₂:SiO₂ precursor and calcination. The specific surface increases from 20.9 to 30.7 m² g⁻¹ after SiO₂ removal via etching, which leads to the formation of mesopores. The obtained nanostructures are scraped from the substrate, processed as a paste, and deposited on photoelectrodes containing a mesoporous TiO₂ layer. This procedure maintains locally the 3D-IO order. When sensitized with the novel benzothiadiazole dye YKP-88, DSSCs containing the modified photoelectrodes exhibit an efficiency of 10.35% versus 9.26% for the same devices with conventional photoelectrodes. Similarly, using the ruthenium dye N719 as sensitizer an efficiency increase from 5.31% to 6.23% is obtained. These improvements originate mainly from an increase in the photocurrent density, which is attributed to an enhanced dye loading obtained with the mesoporous 3D-IO structures due to SiO₂ removal.

1. Introduction

Novel strategies to enhance the efficiency in dye-sensitized solar cell (DSSC) are attracting a renewed interest in this research topic, which expands from new electrolyte formulations to new sensitizers and, less explored, the use of photonic inorganic

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structures.^[1] Since pioneering works by O'Regan and Grätzel who introduced the use of a mesoporous TiO₂ film in the photoelectrode of DSSCs in 1991,^[2] research on this type of solar cells has been continuously and intensively pursued. Recently, a power conversion efficiency (PCE) of 13% has been achieved with DSSCs using purely organic dyes,^[3] while the highest value (14.6%) has been obtained by using a complex mixture of sensitizers and coadsorbents in a tandem structure.^[4] A DSSC is typically composed of a dye-sensitized photoelectrode, a counter electrode, and an electrolyte serving as a redox shuttle for regenerating the sensitizer. Accordingly, in the last few years the highest PCE values of DSSCs were achieved by synthesizing more efficient sensitizers,^[5] by developing specific electrolytes,^[6] and by designing novel mesoporous photoelectrodes. The latter can either enhance the light scattering or increase the electron mobility to facilitate the charge transport to the electrodes.^[7]

N-type mesoporous photoelectrodes with a pore size around 20 nm are generally obtained by sintering TiO₂ nanoparticles (NPs) deposited on an appropriate substrate. However, the disordered particle assembly and tight packing in the film reduce electron transport and ion diffusion of the redox species from the electrolyte solution, respectively. In this regard, novel strategies are being proposed for engineering TiO₂ photoelectrodes and achieving structures of better controlled morphology.^[8] 3D inverse-opal (3D-IO) photonic crystals are one particular interesting example of easily accessible, highly ordered materials.^[9a,b] 3D-IO nanostructures show a face-centered cubic periodic pore network containing interconnected macro- and mesopores of controllable porosity with a pore volume fraction of up to \approx 55%.^[9c] Due to these appealing features, 3D-IO TiO₂ appears to be a promising candidate for use as a photoanode in DSSCs. Fully connected pores with extended diameters could facilitate the infiltration of the electrolyte solution and enhance light scattering, i.e., reduce losses due to photons nonabsorbed by the sensitizer. Furthermore, 3D-IO structures can promote electron transport since the highly ordered TiO₂ network provides more efficient transport channels compared to conventional electrodes made of sintered NPs. In particular, this type of macroporous electrodes can be of great benefit for the development of DSSCs with polymer or gel electrolytes, which possess a high viscosity.^[10]

So far, hierarchically porous materials and 3D-IO TiO₂ photoanodes are prepared within a self-assembled synthetic opal template by sol-gel hydrolysis of metal alkoxide precursors or by infiltration of TiO₂ NPs.^[11] The obtained structure is then converted into an inverted opal structure by means of either thermal or chemical treatment.[11a-d] However, these approaches bear several shortcomings and it remains highly challenging to obtain a high-quality 3D-IO TiO₂ structure suitable for use in DSSCs. First, due to the necessity of using a smooth and clean surface in the self-assembling process of the 3D opal template, the implementation of standard fabrication methods for photonic structures on the comparably rough blocking layer covering the transparent electrode of DSSCs is often not possible.^[11b,12] Besides, cracks induced by the free-volume shrinkage appear inevitably during the template removal process due to the incomplete infiltration of metal precursors or TiO₂ NPs into the template. This phenomenon is known to deteriorate the contact with the underlying blocking layer and to negatively impact the integrity and continuity of the 3D-IO film.^[10,11b,13] Therefore strategies have to be developed to minimize cracks in IO structures. Although efforts have been made to find alternatives to the sol-gel method by using TiO₂ colloidal NPs or atomic layer deposition techniques, a shrinkage of 10-30% in volume and crack formation are still observed.^[13,14] Finally, despite the fact that IO TiO_2 materials reveal a very large surface/mass ratio due to their hollow 3D structure, the absolute specific surface area for a given film thickness is lower than in sintered films of TiO2 NPs. This effect is a consequence of the larger pore size, on the order of hundreds of nm for 3D-IO structures, and leads to a decrease of the dve loading and hence the efficiency of the DSSCs.^[10,15] For the above mentioned reasons, the reported PCEs of solar cells containing 3D-IO TiO₂ structures lie in the range of 3–7% when they are directly employed as scaffold for the sensitizer in the working electrode, [14a, 16] in the range of 3–9% when used as a scattering layer.^[1e,12,17] The highest efficiency reported so far (9.2%) has been obtained by Yu and co-workers using four alternating layers of sintered TiO2 NPs (with added reduced

graphene oxide for improving electronic transport) and 3D-IO with optimized macropore size as the photoanodes.^[1e]

Here, we report a new method to prepare photoelectrodes incorporating locally ordered 3D-IO TiO₂ nanostructures, which overcomes the cited drawbacks. The straightforward and scalable fabrication procedure of mesoporous 3D-IO TiO₂ nanostructures is based on self-assembly of template beads on a glass substrate, calcination, and etching. The obtained nanostructures are then scraped from the surface, formulated as a paste, and deposited by doctor blading for effective screening and study of different photoanode configurations. The obtained photoelectrodes were sensitized with a new organic dye (YKP-88) containing a benzothiadiazole chromophore group. As we have shown earlier with another benzothiadiazole-based dye using a standard TiO₂ photoanode, this family of molecules can lead to outstanding PCE values.^[18] For comparison the well-known commercial ruthenium dye N719 has been used as a sensitizer, and in all cases the standard iodine/iodide redox couple was applied in the electrolyte. We demonstrate that the use of the locally preserved 3D-IO TiO₂ nanostructures, playing the role of a scattering and sensitization layer on top of the conventional mesoporous TiO₂ photoelectrode, significantly enhances the device performances with both dyes compared to conventional electrodes. Whereas in the case of N719 a PCE increase from 5.31% to 6.23% is achieved, in the case of YKP-88 a maximum PCE value of 10.35% associated with a high current density (J_{sc}) of 19.86 mA cm⁻² was reached. These performances rank among the best results reported for DSSCs with fully organic dyes and iodine-based electrolytes and to the best of our knowledge, this is the highest PCE ever achieved employing locally ordered inverse opal TiO₂ nanostructures in the photoanode.

2. Results and Discussion

2.1. Preparation of Mesoporous 3D-IO TiO₂ Photoanodes

Figure 1 illustrates the experimental procedure for the fabrication of the mesoporous 3D-IO TiO₂ structures developed in this study. An inverse-opal structure was produced by first generating a self-assembled 3D opal using a colloidal array of



Figure 1. Schematic diagram of the preparation of mesoporous 3D-IO TiO₂ nanostructures.





monodisperse polymethyl methacrylate (PMMA) spheres (450 nm, Figure S1, Supporting Information) as a sacrificial template and next infiltration of the TiO₂ precursor solution (TiCl₄) to form the 3D-IO skeleton after a calcination step. With the goal to increase the specific surface a small amount (3–8 mol%) of tetraethyl-orthosilicate was added to the TiO₂ precursor solution. This approach implies that the 3D-IO skeletons are further treated with a 10% hydrofluoric acid (HF) solution to remove the SiO₂ part and hence increase the roughness of the walls. A subsequent annealing step at 500 °C affords the final mesoporous 3D-IO TiO₂ structures.

Figure 2 shows scanning electron microscopy (SEM) images of the as-prepared 3D-IO structures. For comparison, pristine 3D-IO TiO₂, only infiltrated with the TiCl₄ precursor, was also fabricated (cf. Figure 1a,b). It reveals a skeleton of densely packed TiO₂ NPs and regular arrays of interconnected macropores with a diameter of 300 nm. The macropores shrank by 33% compared to the original PMMA spheres during the thermal template removal. The mesoporous 3D-IO TiO₂ structure (5 mol% SiO₂ removed, Figure 2c,d) shows marked differences: It exhibits a much thinner skeleton with interconnected macropores of 320 nm in diameter and the TiO₂ NPs are packed in a looser way due to the removal of the SiO₂. This has important consequences on the specific surface area (vide infra).

To get more detailed structural information of the 3D-IO structure, transmission electron microscopy (TEM) images were acquired. The mesoporous 3D-IO TiO₂ structure (5 mol% SiO₂ removed) can be clearly observed on the low magnification image in **Figure 3a**. At higher magnification (Figure 3b,c), the randomly distributed mesopores can distinguished as lighter spots on the skeleton of the 3D-IO TiO₂. We emphasize that these features are found neither in the case of pristine 3D-IO

TiO₂ (Figure S2a–c, Supporting Information) nor in the case of 3D-IO TiO₂ with 5 mol% SiO₂ before etching (Figure S2d–f, Supporting Information). The pore size distribution after SiO₂ removal lies in the range of 2.5–17.5 nm with an average pore size of 7.8 nm (Figure 3d). The crystallinity of the as-prepared mesoporous 3D-IO TiO₂ structures was investigated by means of high-resolution TEM (HRTEM) and selected-area electron diffraction (SAED). As shown in Figure 3e, the TiO₂ nanostructures exhibit inter-reticular distances of 2.43 and 3.52 Å, which correspond to the (101) and (103) planes of anatase TiO₂, respectively. This is further confirmed by SAED (Figure 3f), which reveals Debye–Scherrer rings characteristic of anatase TiO₂ in a wide area.^[19] These results indicate that a good crystallinity of the anatase phase is obtained, which is highly beneficial for efficient electron transport.

To estimate the specific surface area, N₂ adsorption–desorption isotherms of the pristine 3D-IO TiO₂ and of mesoporous 3D-IO TiO₂ nanostructures have been measured on powders obtained after scratching from the surface (Figure S3, Supporting Information). The specific Brunauer–Emmet–Teller (BET) surface areas of pristine 3D-IO TiO₂ and mesoporous 3D-IO TiO₂ (5 mol% SiO₂ removed) are 20.9 and 30.7 m² g⁻¹, with a total pore volume of 0.06 and 0.13 cm³ g⁻¹ and a pore diameter of 12.7 and 17.3 nm, respectively. The specific surface area of the mesoporous 3D-IO TiO₂ calculated using the BET equation is thus 1.5 times higher than that of pristine 3D-IO TiO₂, its pore volume per mass unit is two times greater, and furthermore the pore size is effectively enlarged by 36% due to the SiO₂ removal.

Generally, the increase of the specific surface area of 3D-IO materials requires the use of smaller template particle sizes and porous packing of the NPs in the skeleton.^[11a] However,



Figure 2. SEM images of a,b) pristine 3D-IO TiO₂ and c,d) mesoporous 3D-IO TiO₂ (5 mol% SiO₂ removed).



Figure 3. a–c) TEM images at different magnification of mesoporous 3D-IO TiO₂ (5 mol% SiO₂ removed); d) mesopore size distribution; e) HRTEM image; f) selected area electron diffraction (SAED) pattern.

it is more challenging to synthesize monodisperse template nanospheres (PMMA or polystyrene) with sizes below 200 nm than for intermediate sizes (300–500 nm). In our approach we propose another strategy, which does not require the use of small-sized template NPs. According to the above results, the surface area and pore volume of mesoporous 3D-IO TiO₂ structures were successfully enhanced due to the removal of SiO₂ from the initially obtained skeleton. First, as proven by the SEM images, this step has an influence on the macroskeletal structure, which becomes much thinner and looser than in the pristine 3D-IO TiO₂. We attribute this to small SiO₂ NPs that were randomly formed in the 3D-IO TiO₂ skeleton. Moreover, as demonstrated by the TEM images, removal of SiO₂ also induces the formation of additional mesopores in the skeleton, which further increase the surface area and pore volume.

The mesoporous 3D-IO TiO2 structures were scraped from the substrate (cf. Figure S4, Supporting Information), suspended in a paste and deposited by doctor-blading onto photoelectrodes containing TiO₂ NPs (P25, Solaronix). In this configuration, the locally preserved 3D-IO nanostructures can act as both a scattering layer and additionally as mesoporous layer for dye sensitization. This procedure bears several advantages over other methods of reporting the 3D-IO structure onto the photoelectrode: the integrity of the mesoporous 3D-IO TiO₂ structure is only kept locally, but the whole film exhibits a good contact with the lower layer of TiO₂ NPs and crack formation is prevented. As shown in Figure 4a, the as-prepared layer is continuous on a very large scale. When zooming in (Figure 4b,c), the locally intact tightly packed 3D-IO TiO₂ structures with big pore size in the layer can be clearly seen. This is further confirmed in the cross-section view of the photoanode (Figure 4d). Compared with the underlying mesoporous layer of TiO₂ NPs (\approx 11 µm in thickness), the upper mesoporous layer made of 3D-IO TiO₂ nanostructures (5 μ m) appears much more porous due to the inverse opal structure that is maintained locally

during the transfer process. Besides, the SEM images indicate a very good contact between the two layers, which is in stark contrast to the poor contact properties usually observed in conventional direct 3D-IO synthesis methods due to the incomplete infiltration of metal precursors.^[10,11b,13]

2.2. Synthesis and Characterization of the Organic Photosensitizer

Another key element to develop efficient DSSCs is the dve itself. Until 2010, high performance devices have mostly been fabricated by employing ruthenium complexes,^[20] but the limited natural availability of ruthenium, the usually low molar extinction coefficients of Ru-complexes^[21] and their suspected toxicity have pushed the scientific community to develop alternative dyes such as Zn-porphyrin dyes. This class of dyes showed very competitive performances and great progress has been made by combining them with cobalt-based electrolytes, leading to PCEs up to 13%.^[22] However, the synthesis of these dyes requires multistep synthetic routes with very low overall yields and currently fully organic sensitizers appear as the most promising materials related to the mass-market development of this technology. Indeed they can be prepared and purified in only few steps, their energy band gap and absorption properties can be tuned relatively easily,^[23] and they can lead to efficient and robust solar cells even under harsh operating conditions.^[24]

In this context, our group reported in 2015 several dyes based on a benzothiadiazole chromophore unit that combine high efficiency and long-term stability in solar cells when ionic liquid is used as the electrolyte.^[19] Following this research axis, here we report a new organic dye named YKP-88, which is obtained in 21% yield after only six synthetic steps (**Figure 5**).

For the preparation of this dye, it is necessary to synthesize the electron-donating unit (3) consisting of a fused triphenylamine



Figure 4. a–c) Top-view, d) cross-section view SEM images of a photoanode containing a \approx 11 µm thick layer of TiO₂ NPs and a \approx 5 µm layer of mesoporous locally ordered 3D-IO TiO₂ (5 mol% SiO₂ removed). Substrate: fluorine-doped tin oxide (FTO)-coated glass.

with a thiophene through the formation of an indene ring. The synthesis of this synthon is achieved in three steps thanks to a Neigishi coupling of commercially available products followed by a cyclization reaction and a Buchwald–Hartwig coupling between diphenylamine and compound (2). The intermediate (3) is subsequently stannylated by action of butyllithium and trimethyl tin chloride and then directly involved in a Stille coupling with bromo-formylbenzyl-benzothiadiazole.^[25] From the resulting compound (5) YKP-88 is obtained through a simple Knoevenagel reaction. The dye was characterized optically by UV–vis spectroscopy in solution and after grafting on TiO₂ and electrochemically by means of cycling voltammetry to determine the position of the Highest Ocuupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy levels.

As shown in **Figure 6**, the UV–vis spectrum of YKP-88 shows several absorption bands in the UV region corresponding to π – π * transitions of the different aromatic and heteroaromatic rings. The strong absorption feature located in the visible at 529 nm, with a molar absorption coefficient of 28 100 M⁻¹ cm⁻¹, is attributed to an internal charge transfer (ICT) band, resulting in a red-pinkish color in solution. Once the dye is grafted on TiO₂, the absorption spectrum of the ICT band is blueshifted shifted by 16 nm and broadened. Such a shift is often observed with organic dyes and it can be attributed to the deprotonation of the carboxylic acid function after grafting on the TiO₂ surface whereas the broadening of the spectrum and the disappearance of the discrete features related to the π – π * transitions can be attributed to the formation of aggregates. The energy



Figure 5. Schematic diagram of the synthesis of YKP-88.







Figure 6. UV-vis spectra of YKP-88 measured a) in dichloromethane (10^{-5} M) and b) after adsorption on a 2 μ m thick TiO₂ mesoporous layer.

level position of the frontier orbitals determined by cyclic voltammetry (cf. **Table 1**) are compatible with those of the conduction band of the oxide (at \approx -4.1 eV) and of the potential of the I^-/I_3^- redox couple used in the electrolyte (at \approx -4.95 eV):^[1b] the $\Delta E_{\rm inj}$ (0.6 eV) and $\Delta E_{\rm reg}$ (0.35 eV) are large enough to ensure a good injection of the photoexcited electrons in the oxide and the regeneration of the photo-oxidized dye molecules by the redox mediator.

2.3. Photovoltaic Properties

The locally ordered, mesoporous 3D-IO nanostructures modified photoelectrodes were immersed in a dyeing bath constituted of YKP-88 and chenodeoxycholic acid (CDCA) in acetonitrile/tert-butanol solution. The use of CDCA was motivated by its capacity to decrease dye aggregation, which is detrimental for the solar cell performance.^[26] The sensitized electrodes were assembled with Pt counter electrodes and the devices were filled with a classical iodide/ tri-iodide-based liquid electrolyte. Pristine photoelectrodes embedding 3D-IO TiO₂ nanostructures and conventional TiO₂ NPs based photoelectrodes (with a thickness of 12 µm for the mesoporous layer and 4 µm for the scattering layer, Solaronix) were also prepared for comparison. To be fully comparable, the total thickness and area of all the photoanodes used in this work were fixed to 16 μ m and 0.36 cm², respectively.

Table 1. Optoelectronic properties of YKP-88.

Dye	$\lambda_{abs}{}^{a)}$ [nm] ε [M ⁻¹ .cm ⁻¹]	$\lambda_{onset}^{a)}$ [nm]	E _g ^{b)} [eV]	λ _{max} TiO ₂ ^{c)} [nm]	λ_{onset} TiO ₂ ^{c)}	E _g TiO ₂ ^{b)} [eV]	HOMO ^{d)} [eV]	LUMO ^{d)} [eV]
					[nm]			
YKP-88	315 (27800)	623	1.99	371	632	1.96	-5.30	-3.50
	374 (32700)			513				
	529 (28100)							

^{a)}Measured in dichloromethane (10⁻⁵ M); ^{b)}Calculated from 1241/ λ_{onset} , ^{c)}Measured on a 2 μ m thick mesoporous layer of TiO₂; ^{d)}Measured by cyclic voltammetry in dichloromethane with tetra-butylammonium hexafluorophosphate and using ferrocene/ ferrocenium couple as a reference.

The photovoltaic parameters short-circuit photocurrent (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), and PCE of the best DSSCs sensitized with YKP-88 and the mean values obtained from five devices are shown in **Table 2**. Alongside we report those obtained for devices sensitized using the well-known ruthenium dye N719 used as a reference. The photocurrent density–voltage characteristics of the best performing cells with YKP-88 are shown in **Figure 7**a and those of DSSCs using N719 in Figure S5 in the Supporting Information. Importantly, the mesoporous photoanode with local 3D-IO nanostructures (5 mol% SiO₂ removed) that revealed the highest porosity shows the best values of J_{SC} (19.86 mA cm⁻²) and V_{OC} (0.74 V) leading to the highest PCE of 10.35%. This value ranks among the highest reported to date for DSSCs fabricated with an iodine-based electrolyte. The photovoltaic parameters with the N719

Table 2. Photovoltaic parameters of different DSSCs sensitized with YKP-88 or N719 (highest performances and mean values with standard deviation over five devices).

Photoanodes [Dye]	$J_{\rm sc}$ [mA cm ⁻²]	V _{oc} [V]	FF [%]	PCE [%]
Pristine 3D-IO TiO ₂	18.67	0.70	67.9	8.83
(YKP-88)	$18.86\pm0,32$	0.68 ± 0,02	67.8 ± 0,9	8.70 ± 0,20
Mesoporous 3D-IO TiO ₂	19.86	0.74	70.6	10.35
(5 mol% SiO ₂ removed) (YKP-88)	19.55 ± 0.40	0.74 ± 0.01	70.7 ± 0.8	10.21 ± 0.30
TiO ₂ NPs (Solaronix)	18.29	0.73	69.0	9.26
(YKP-88)	18.25 ± 0.08	0.73 ± 0,01	$68.8 \pm 0,5$	9.24 ± 0.10
Pristine 3D-IO TiO ₂	12.70	0.59	69.7	5.23
(N719)	$12.55\pm0,15$	0.55 ± 0,05	68.3 ± 1.4	5.11 ± 0,20
Mesoporous 3D-IO TiO ₂	13.43	0,63	73.3	6.23
(5 mol% SiO ₂ removed) (N719)	13.34 ± 0,11	$\textbf{0.60} \pm \textbf{0,04}$	72.3 ± 1.0	$\textbf{6.16} \pm \textbf{0.07}$
TiO ₂ NPs (Solaronix)	11.47	0.62	74.3	5.31
(N719)	11.37 ± 0.10	0.59 ± 0.04	73.1 ± 1.2	5.23 ± 0.08







Figure 7. a) Photocurrent density-voltage curves (AM 1.5 illumination, active area 0.36 cm²) for solar cells containing mesoporous local 3D-IO TiO_2 (5 mol% SiO₂ removed), pristine local 3D-IO TiO_2 , and conventional TiO_2 NPs modified photoanodes sensitized with YKP-88 dye. The photographs show the photoanodes modified with b) mesoporous local 3D-IO TiO_2 (5 mol% SiO₂ removed), c) pristine local 3D-IO TiO_2 , and d) conventional TiO_2 NPs after dye loading.

sensitizer are significantly lower. The photocurrent density only reaches 13.43 mA cm⁻² leading to a maximum PCE of 6.23%.

Globally, both YKP-88 and N719 sensitized solar cells show very similar trends: the I_{sc} values of the electrodes with mesoporous 3D-IO TiO₂ (5 mol% SiO₂ removed) are significantly enhanced compared to electrodes with pristine 3D-IO TiO2 nanostructures and the lowest values are obtained with conventional electrodes based on TiO2 NPs. The highest gain of the mesoporous 3D-IO nanostructures is achieved in the J_{SC} value, indicating an improvement of the light harvesting properties of the solar cell. In order to verify this hypothesis, we determined the dye loading of the different electrodes. We found that the number of YKP-88 molecules adsorbed on the mesoporous electrodes is almost the same for devices based on pristine 3D-IO TiO₂ and on TiO₂ NPs with 195.6 \pm 1.3 and 199.0 \pm 2.0 nmol, respectively. However, for devices based on the mesoporous 3D-IO TiO2 (5 mol% SiO2 removed) nanostructures, a slightly higher value 208.1 \pm 1.4 nmol was found and the photoelectrode appears a bit darker than the other two types (Figure 7b-d). These findings can be understood on the basis of the above-mentioned N2 adsorption-desorption measurements (Figure S3, Supporting Information); after SiO_2 removal in the mesoporous 3D-IO TiO₂ structure the specific surface area is enlarged by 46.9% compared to the pristine 3D-IO TiO2. Furthermore, the SiO₂ removal also generates additional mesopores in the skeleton (Figure 3c), which help to further increase the loading of dye molecules. In addition to the improvement in the dye loading the locally ordered, mesoporous 3D-IO nanostructures can also influence the light management in the DSSCs. Several theoretical approaches report a variety of possible

effects, such as multiple scattering at disordered regions, Bragg diffraction, dielectric mirror effects, and resonant modes, which could enhance the effective optical path of light within the active layer.^[27] We cannot exclude that some of these effects also contribute to the enhancement of light absorption in the solar cells with the mesoporous 3D-IO nanostructures locally intact.

To conclude this section, our novel approach gives access to modified photoanodes with locally intact mesoporous 3D-IO TiO₂ nanostructures showing improved solar cell characteristics, in particular enhanced photocurrent density. The crucial importance of the SiO₂ removal step is visible by the comparison with pristine 3D-IO modified electrodes, which lead to a much lower J_{SC} improvement than the mesoporous 3D-IO modified ones with respect to conventional ${\rm TiO}_2~{\rm NPs}$ based electrodes. We explored this point in more detail by preparing electrodes embedding local 3D-IO TiO₂ nanostructures with 3 and 8 mol% SiO2. In addition, modified layers obtained by mixing the mesoporous 3D-IO TiO₂ nanostructures with TiO₂ NPs (P25) using a weight ratio of 3:1 were also prepared and tested (Figure S6, Supporting Information). Here again the total thickness of the photoanodes was fixed at 16 um. The photocurrent density-voltage characteristics are shown in Figure 8a and



Figure 8. a) Photocurrent density–voltage curves (AM 1.5 illumination, active area 0.36 cm²) for different mesoporous 3D-IO TiO₂ modified photoanodes sensitized with YKP-88 dye. Comparison of the obtained PCE and J_{SC} values (including error bars) of photoelectrodes modified with mesoporous 3D-IO TiO₂ using different amounts of SiO₂ b) without and c) with the addition of TiO₂ NPs (P25) into the IO structure using a weight ratio of 3:1 (IO:TiO₂ NPs).

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Table 3. Photovoltaic parameters of DSSCs fabricated using different mesoporous 3D-IO modified photoelectrodes and sensitized with YKP-88 dye (highest performances and mean values with standard deviation over five devices).

Photoanodes	J _{sc} [mA cm ⁻²]	V _{oc} [V]	FF [%]	PCE [%]
Mesoporous 3D-IO TiO ₂ (3 mol%	19.64	0.72	69.5	9.86
SiO ₂ removed)	19.52 ± 0.12	0.72 ± 0.02	68.9 ± 0.06	9.81 ± 0.05
Mesoporous 3D-IO TiO ₂ (3 mol%	18.51	0.73	70.7	9.60
SiO ₂ removed):P25 NPs = 3:1	18.62 ± 0.11	0.73 ± 0.02	70.3 ± 0.4	9.59 ± 0.03
Mesoporous 3D-IO TiO ₂ (5 mol%	19.86	0.74	70.6	10.35
SiO ₂ removed)	19.55 ± 0.40	0.74 ± 0.01	$\textbf{70.7} \pm \textbf{0.8}$	10.21 ± 0.3
Mesoporous 3D-10 TiO2 (5 mol%	19.04	0.73	69.1	9.58
SiO ₂ removed):P25 NPs = 3:1	18.89 ± 0.15	0.73 ± 0.01	69.0 ± 0.1	9.49 ± 0.09
Mesonorous 3D IO TiO, 18 mal%	10.20	0.73	68.4	9.54
SiO ₂ removed)	18.89 ± 0.21	0.73 ± 0.01	68.8 ± 0.4	9.46 ± 0.08
Mesoporous 3D-IO TiO ₂ (8 mol%	18.50	0.73	69.8	9,40
SiO_2 removed):P25 NPs = 3:1	18.67 ± 0.17	0.75 ± 0.02	69.0 ± 0.8	9.35 ± 0.05

the corresponding photovoltaic parameters are summarized in **Table 3** and compared in Figure 8b,c. This comparison shows that the best PCE value of the 3D-IO TiO₂ based devices is obtained with 5 mol% of SiO₂ initially incorporated and subsequently removed. Both lower (0.3 mol%) and higher (0.8 mol%) amounts of SiO₂ lead to lower values even though it should be underlined that all the solar cells show high performances above 9.4%. It appears clearly that the variation of the PCE is mainly driven by the J_{SC} , as the V_{OC} and FF values are almost constant for all devices.

When 25 wt% of NPs TiO₂ (P25) were mixed to the different mesoporous 3D-IO TiO₂ nanostructures, it can be observed that the J_{SC} and by consequence the PCE values are slightly decreased, while otherwise the same trends are observed as for the other cells, i.e., without added NPs. Figure S7 in the Supporting Information shows the top view SEM images of the corresponding modified photoanodes. TiO2 NPs are filling the 3D-IO nanostructures, decreasing the effective pore size in the whole IO layer. This effect is particularly noticeable in the case of the mesoporous local 3D-IO nanostructures with 8 mol% SiO₂ removed (Figure S7c, Supporting Information). Moon and co-workers studied the effect of electrolyte ion diffusion in 3D-IO structures based and conventional P25 based photoelectrodes using as here iodine-based electrolytes. The electrolyte/ electrode heterojunction is an important factor determining the device performance and the study showed that the electrolyte ion-diffusion coefficient in the 3D-IO structure based photoanode was 1.5 times higher than in the P25 electrode.^[9] Accordingly, in our case, the introduction of TiO₂ NPs may hinder the electrolyte diffusion and thus decreases the performance.

Figure 9 shows SEM images of mesoporous $3D-IO TiO_2$ structures with 3 and 8 mol% SiO₂ removed and top views of the corresponding photoanodes. The morphology of the

3D-IO TiO₂ structure obtained with 3 mol% SiO_2 (Figure 9a) shows a denser skeleton compared to that using 5 mol% SiO_2 (cf. Figure 2c,d), indicating a smaller available surface area for grafting dyes. In case of the 3D-IO obtained with 8 mol% of SiO_2 (Figure 9b), the structure becomes unstable due to the excess holes after removal of the large amount of SiO_2 from the skeleton, which makes the whole structure more fragile.

As visible in the top-view images (Figure 9c,d) when using 3 mol% SiO₂, the local 3D-IO nanostructures appears well intact in the blend similarly to 3D-IO TiO₂ with 5 mol% SiO₂ removed (Figure 3) while with 8 mol% SiO₂, the original morphology is not preserved. The more fragile nanostructures presented in Figure 9b are probably compressed during the processing. As a consequence these electrodes lead to a lower J_{SC} despite the fact that they have a larger number of mesopores.

Finally, to investigate in more detail the origin of the better solar cell performances

of cells sensitized with YKP-88 as compared to N719, we measured their photocurrent response (incident photon-toelectron conversion efficiency, IPCE). From the spectra presented in Figure 10a it can be evidenced that in the visible and near ultraviolet wavelength region, i.e., between 350 and 750 nm, YKP-88 is highly efficient and reaches a maximum IPCE of 80% in nearly the whole range of wavelengths. To the contrary, N719 shows a much lower IPCE maximum of 65% and this value is only obtained for a limited wavelength range. Further understanding of the high photocurrent generation with YKP-88 and concomitant elevated V_{OC} has been gained by means of charge extraction (CE) and transient photovoltage (TPV) measurements (see Figure 10b,c). It should be reminded here that the V_{oc} of a DSSC is determined by the quasi-Fermi-level of the metal oxide semiconductor, which is dependent on its conduction band edge (E_c) and electron density. The electron density is itself influenced by the rate of recombination between semiconductor electrons and oxidized electrolyte species.

Electron lifetimes measured at identical electron densities using TPV measurements are in good agreement with the cell voltages listed in Table 2, where longer electron lifetimes correspond to larger device voltages. The electron lifetime of YKP-88 is significantly higher than that of N719 indicating that recombination processes between electrons of the oxide and redox species of the electrolyte are less prone to occur. This could be explained by the presence of the lateral alkyl chains on this dye that may prevent redox species in the electrolyte to approach the TiO₂ surface. Furthermore, the charge density is not similar in both devices, indicating that the conduction band potentials of the electrodes are different after grafting the two different dyes and that its value is lower with N719.







Figure 9. SEM images of mesoporous 3D-IO TiO₂ structures obtained with a) 3 and b) 8 mol% SiO₂ removed and top views of the corresponding photoanodes c) 3 mol% and d) 8 mol%.

3. Conclusion

We have reported a versatile method to synthesize mesoporous 3D-IO TiO₂ nanostructures and to incorporate them in photoelectrodes suitable for application in DSSCs. Their specific surface area and porosity can be strongly increased by adding a small amount of silica precursor during the synthesis and subsequent removal of the formed SiO₂ domains. After scraping from the substrate the obtained 3D-IO nanostructures have been integrated into conventional DSSC photoelectrodes while preserving locally their structural properties. These photoelectrodes have been sensitized with a new purely organic dye (YKP-88) as well as with the ruthenium complex dye N719 used as a standard for comparison. The addition of the locally ordered mesoporous 3D-IO nanostructures in the photoelectrodes leads to a significant efficiency gain of 17% for the organic dye YKP-88 and of 12% for the ruthenium dye N719 compared to standard DSSC electrodes of the same total thickness (16 μ m) containing a TiO₂ mesoporous layer and a scattering layer. In the case of YKP-88, the resulting DSSCs employing classical iodine-triiodide liquid electrolyte reached a maximum value of 10.35% when applying locally ordered, mesoporous 3D-IO nanostructures obtained by removing 5 mol% SiO₂. Both lower and higher SiO₂ contents led to slightly lower efficiencies, even though still ranging between 9.40% and 9.86%. These performances rank among the best published for this class of devices and 10.35% is the highest value reported for DSSCs using inverse opal nanostructures as photoactive component in the photoelectrode. In this work we have also demonstrated that the improved efficiency of our devices is mainly related to an enhanced photocurrent generation originating from a higher dye loading on the mesoporous 3D-IO electrodes and a lower rate of recombination. The presented approach is of great versatility and can be applied for generating electrodes with 3D inverse opal structures of various types of metal oxides. As an example we applied the same procedure to the synthesis of NiO 3D-IO structures

(cf. Figure S8, Supporting Information), NiO being an important candidate for the fabrication of p-type photoelectrodes for use in tandem DSSCs, quantum dot (QD), and perovskite solar cells. Another salient and generalizable feature of our approach is the efficient and nondestructive transfer of the obtained 3D-IO nanostructures to the photoelectrode of interest. Therefore, this study paves the way for new works aiming at the development of more efficient photoelectrodes for use in DSSCs, perovskite solar cells or photocatalytic devices.

4. Experimental Section

Materials: Titanium (IV) chloride (TiCl₄, ≥99%) was purchased from Fluka Analytical, ethyl cellulose (5 mol% in toluene/ethanol), terpineol (anhydrous), and tetraethyl-orthosilicate (99.999% trace metals basis) were purchased from Sigma-Aldrich, microscopy glass slides were purchased from VWR International France. Platisol T, P25 NPs, and standard photoelectrodes were laronix. Deionized water (R > 18 MΩ) was used for

purchased from Solaronix. Deionized water (R $> 18~\text{M}\Omega)$ was used for all experiments.

Synthesis of Mesoporous 3D-IO TiO2 Structures: The fabrication process of the 3D-IO TiO_2 nanostructures is shown in Figure 1. First, monodispersed PMMA spheres with a diameter around 450 nm (Figure S1, Supporting Information) were synthesized from methyl methacrylate according to a published method.^[28] For the selfassembling of the PMMA opal film, the glass slides were first cleaned by immersion into a concentrated H₂SO₄ solution for at least 2 h, followed by ultrasound treatment in deionized water. The monodisperse PMMA spheres were then self-assembled on the as-cleaned glass substrates through the vertical deposition process (step A in Figure 1) at 50 °C in an oven until all the liquid was evaporated. Then the substrates (step B in Figure 1) were sintered at 120 °C for 40 min aiming to reduce the distance between the PMMA spheres and enhance the mechanical strength of the PMMA opal array. Subsequently, the interstitial spaces between the PMMA spheres were filled by immersion in a 4.5×10^{-3} M TiCl₄ solution (volume ratio of ethanol/deionized water = 1:1) containing 0, 3, 5, or 8 mol% of tetra-ethyl-orthosilicate (step C in Figure 1). After drying in ambient air for one day, the films were annealed in a furnace with a ramp of 1 °C min⁻¹ to 500 °C and kept at this temperature for 3 h to completely remove the polymer spheres by calcination and crystallize the TiO₂ network, then cooled down to room temperature naturally. 3D-IO TiO₂ nanostructures mixed with different amounts of SiO_2 (step D in Figure 1, TiO_2 -SiO₂) were obtained. To obtain the mesoporous 3D-IO TiO₂ nanostructure, the samples were scraped from the glass substrates, and etched using a 10% HF solution for 30 min. This step was followed by washing with ethanol and centrifugal cleaning for three times (10 000 rpm for 5 min); finally the obtained powder was dried at 70 °C in an oven.

Synthesis of the Dye YKP-88,86-Bromo-4,4'-bis(4-hexylphenyl)-4Hindeno[1,2-b] thiophene (2): Under argon, (4-hexylphenyl)-magnesium bromide was prepared from 1 (4-bromophenyl)hexane (2.0 g, 8.29 mmol, 2.5 equiv) and magnesium (202 mg, 8.29 mmol, 2.5 equiv) in freshly distilled tetrahydrofuran (THF) (10 mL). This reaction mixture was stirred at reflux for 1 h. In a second flask, methyl 5-bromo-2-(thiophen-2-yl)-benzoate (1.0 g, 3.37 mmol, 1.0 equiv) was solubilized in THF (15 mL). Then the Grignard reagent was added dropwise and the solution was heated to reflux for 5 h. After cooling to room temperature, the crude mixture was poured into water. The organic layer was extracted twice with ethyl acetate and washed by water and brine, dried over sodium sulfate, filtered, and concentrated under vacuum overnight. The crude was







Figure 10. a) IPCE spectra, b) transient photovoltage data showing electron lifetimes versus electron density, and c) charge extraction data showing electron density as a function of induced voltage for DSSCs containing mesoporous 3D-IO (5 mol% SiO₂ removed) photoelectrodes, sensitized with N719 and YKP-88, respectively.

dissolved in glacial acetic acid (40 mL). After 30 min, concentrated HCL (4 mL) was added dropwise and was refluxed at 120 °C for 5 h. After back to room temperature, the acetic acid was removed by rotary evaporation, and the crude was extracted by pentane. The organic layer was washed several times by water and dried over sodium sulfate, filtered, and concentrated under vacuum. The crude was chromatographed on silica gel using *n*-hexane as eluent to afford colorless oil (1) (1.40 g, 73%).

¹H NMR (CDCl₃, 400 MHz): δ (ppm): 7.47 (d, J = 1.7 Hz, 1 H), 7.40 (dd, J = 8.0, 1.8 Hz, 1 H), 7.31 (d, J = 4.9 Hz, 1 H), 7.30 (d, J = 8.0 Hz, 1 H), 7.08 (d, J = 8.4 Hz, 4 H), 7.04 (d, J = 8.4 Hz, 4 H), 6.99 (d, J = 4.9 Hz, 1 H), 2.58–2.51 (m, 4 H), 1.62–1.52 (m, 4 H), 1.38–1.23 (m, 12 H), 0.92–0.84 (m, 6 H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm): 156.2, 155.5, 141.4, 414.0, 139.7, 136.1, 130.5, 129.3, 128.4, 128.2, 127.4, 122.9, 120.3, 118.9, 35.3, 31.5, 31.1, 28.9, 22.4, 13.9. High Resolution Mass Spectrometry (HRMS) (ESI): [M+H]^{+.} = 571.2033 (1 ppm) (calcd. for C₃₅H₃₉⁷⁹BrS: 571.2029).

Synthesis of the Dye YKP-88,4,4-Bis(4-hexylphenyl)-N,N-diphenyl-4Hindeno[1,2-b] thiophen-6-amine (3): Under argon, Pd2dba3 (4 mg, 4.37 µmol, 1 mol%) and tri-tert-butylphosphine tetrafluoroborate (3 mg, 8.75 µmol, 2 mol%) were dissolved with anhydrous toluene (5 mL). After stirred for 15 min, a solution of the compound (2) (250 mg, 437.3 μmol, 1.0 equiv) and diphenylamine (81.4 mg, 481.0 μmol, 1.1 eq.) in anhydrous toluene (10 mL) was added. Before refluxed for 48 h, potassium tert-butoxide was added (161.94 mg, 1.44 mmol, 3.3 eq.) and the resulting mixture was stirred for 30 min at room temperature. The crude was filtered through celite and poured into HCl aqueous solution (2 M). The organic phase was extracted with dichloromethane (DCM), washed with water, dried over Na₂SO₄ and concentrated. The crude oil was chromatographed on silica using n-hexane/DCM, 9:1 as eluent to afford pale yellow oil (3) (266 mg, 92%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm): 7.29 (d, J = 8.2 Hz, 1 H), 7.24–7.16 (m, 6 H), 7.13–7.02 (m, 8 H), 7.02-6.92 (m, 8 H), 2.57-2.49 (m, 4 H) 1.61-152 (m, 4 H), 1.37-1.24 (m, 12 H), 0.92–0.82 (m, 6 H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm): 155.0, 147.5, 145.4, 141.7, 141.0, 131.9, 128.9, 127.9, 127.5, 126.7, 123.7, 123.01, 122.95, 122.5, 119.6, 62.6, 35.3, 31.5, 31.2, 29.5, 28.9, 22.4, 13.9. HRMS (ESI): $[M]^{+}$ = 659.3579 (0 ppm) (calcd. for C₄₇H₄₉NS: 659.3580).

the Dye YKP-88,4-(7-(6-(Diphenylamino)-4,4-Synthesis of bis(4-hexylphenyl)-4H-indeno[1,2-b]thiophen-2-yl)-benzo[c][1,2,5]-thiadiazol-4-yl)benzaldehyde (5): Under argon, the compound (3) (240 mg, 364 µmol, 1.0 eq.) was dissolved in distilled THF (15 mL) then n-BuLi (279 $\mu\text{L},$ 418 $\mu\text{mol},$ 1.15 eq.) was added at –78 °C. The solution was stirred for an hour at -78 °C before adding *n*-hexane solution of Me₃SnCl (545 μ L, 545 μ mol, 1.5 eq.) at -78 °C. The solution was allowed to reach room temperature and stirred for 2 h. The reaction was quenched with a saturated solution of ammonium chloride and the organic phase was extracted with *n*-hexane, watches by water and dried on Na₂SO₄, filtered, and concentrated under vacuum. The resulting oil was engaged without any further purification in a Stille coupling with 4-bromo-7-(4formylbenzyl)-2,1,3-benzothiadiazole (93 mg, 291 µmmol, 0.8 eq.). This stannic product was put under argon with Pd_2dba_3 (6.7 mg, 7.27 μ mol, 2 mol%) and P(o-tolyl)3 (4.4 mg, 14.55 μ mol, 4 mol%). The products were dissolved in anhydrous toluene (20 mL) and refluxed for 24 h. The mixture was then poured into HCl aqueous solution (2 M). The organic phase was extracted with methylene chloride, washed with water, dried over Na₂SO₄, and concentrated. The crude solid was purified by chromatography on silica using methylene chloride/*n*-hexane, 6:4 as eluent to afford dark red solid (5) (195 mg, 75%).

¹H NMR (CD₂Cl₂, 400 MHz): δ (ppm): 10.09 (s, 1 H), 8.19 (d, J = 8.3 Hz, 2 H), 8.15 (s, 1 H), 8.02 (d, J = 8.5 Hz, 2 H), 7.97 (d, J = 7.6 Hz, 1 H), 7.81 (d, J = 7.6 Hz, 1 H), 7.42 (d, J = 8.2 Hz, 2 H), 7.30–6.94 (m, 21 H), 2.62–2.48 (m, 4 H), 1.68–1.45 (m, 4 H), 1.40–1.18 (m, 12 H), 0.94–0.79 (m, 6 H). ¹³C NMR (CD₂Cl₂, 100 MHz): δ (ppm): 192.0, 156.2, 155.6, 154.1, 152.7, 147.9, 146.9, 143.5, 143.4, 142.03, 141.95, 141.5, 136.1, 131.6, 130.7, 130.0, 129.5, 129.3, 128.6, 128.4, 128.0, 124.6, 124.3, 123.3, 123.1, 122.1, 120.6, 63.6, 35.8, 32.0, 31.8, 29.4, 22.9, 14.2. Anal. Calcd for C₆₀H₅₅N₃OS₂: C, 80.23; H, 6.17; N, 4.68; S, 7.14. Found: C, 80.19; H, 6.06; N, 4.59; S, 6.71.

Synthesis of the Dye YKP-88,2-Cyano-3-(4-(7-(6-(diphenylamino)-4,4bis(4-hexylphenyl)-4H-indeno[1,2-b]thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)phenyl)acrylic acid (YKP-88): Under argon, the compound (5) (180 mg, 200 μ mol, 1.0 equiv) and cyanoacetic acid (85 mg, 1 mmol, 5 eq.) were dissolved in a mixture of acetonitrile (9 mL) and chloroform (9 mL). A catalytic amount of piperidine was added and the solution was refluxed for 3 h. Solvent was removed under reduced pressure and the solid was dissolved in chloroform. The organic phase was washed with HCl aqueous solution (2 M), dried on Na₂SO₄, and concentrated. The crude solid was purified by chromatography on silica using methylene chloride first then methylene chloride/MeOH, 90:5 and then methylene chloride/MeOH/acetic acid, 90:5:5 as eluent to afford the corresponding dye YKP-88 a dark red solid (179 mg, 93%).

¹H NMR (THF-d8, 400 MHz): δ (ppm): 8.33 (s, 1 H), 8.31 (d, J = 8.3 Hz, 2 H), 8.27 (s, 1 H), 8.21 (d, J = 8.4 Hz, 2 H), 8.12–8.07 (m, 1 H), 8.00–7.95 (m, 1 H), 7.45 (d, J = 8.2 Hz, 1 H), 7.24–7.17 (m, 6 H), 7.15 (d, J = 8.2 Hz, 4 H), 7.08–7.01 (m, 8 H), 7.01–6.95 (m, 3 H), 2.59–2.52 (m, 4 H), 1.63–1.53 (m, 4 H), 1.38–1.27 (m, 12 H), 0.91–0.84 (m, 6 H).

¹³C NMR (THF-*d*8, 100 MHz): δ (ppm): 164.2, 157.4, 156.8, 155.0, 154.4, 153.8, 149.1, 147.9, 144.8, 143.3, 142.9, 142.5, 133.0, 132.3, 131.3, 130.9, 130.4, 130.1, 129.4, 129.2, 125.7, 125.5, 124.3, 124.2, 123.5, 121.5, 116.7, 105.1, 64.7, 36.8, 33.1, 33.0, 31.1, 30.5, 23.9, 14.8. HRMS (ESI): [M]+. = 964.3835 (0 ppm) (calcd. for C₆₃H₅₆N₄O₂S₂: 964.3839).

Fabrication of Different DSSC Devices: To prepare the photoanode containing the different 3D-IO TiO₂ nanostructures, pastes were first prepared according to published work.^[29] In a typical process, 0.5 g of the 3D-IO TiO₂ powder was first added into 2 mL of ethanol and stirred for 10 min, then the suspension was put into an ultrasonic bath for 3 s (repeated for five times) to make sure that the 3D-IO structures are well dispersed. In addition, for comparison pastes mixed with 25 wt% of TiO₂ NPs (P25) were also prepared by mixing 0.125 g P25 TiO₂ NPs with 0.375 g of the 3D-IO TiO₂ powders in 2 mL of ethanol. Then, 0.25 g of ethyl cellulose (10 wt%) was added and subsequently 17 μ L



of acetic acid, and 80 mg of terpineol. Finally, the mixture was stirred and concentrated on a hot plate until the desired viscosity was reached. Afterward, the paste was deposited on FTO-coated glass electrodes containing a 11 μ m thick layer of mesoporous TiO₂ (Solaronix), and the thickness of the 3D-IO TiO₂ film was controlled by the doctor-blade technique to a value of 5.0 μ m on a 0.6 cm \times 0.6 cm area. After drying at room temperature, the photoelectrodes were subsequently annealed at 500 °C for 30 min with a heating ramp of 12 °C min⁻¹ in air to improve the interconnection between the 3D-IO structures and its contact with the mesoporous TiO₂ layer on the substrate as well as to remove any residual solvents or organic compounds.

Before immersion into the dye solution, the 3D-IO porous TiO₂ photoanode was impregnated with a 0.2 м TiCl₄ aqueous solution at 70 °C for 30 min. Then, it was heated to 500 °C in air with a ramp of 20 °C min⁻¹ and kept at this temperature for 30 min before cooling down to room temperature. The as-prepared electrodes were immersed for 15 h at room temperature into a mixture of CH₃CN and *t*-BuOH (volume ratio = 1:1) containing 2 \times 10^{-3} $\,{}_{M}$ CDCA together with 0.2 \times 10^{-3} $\,{}_{M}$ of YKP-88 or containing 5×10^{-3} ${}_{M}$ CDCA together with 5×10^{-3} ${}_{M}$ of N719 dye, $Ru(dcbpy)_2(NCS)_2(N_3)$ (dcbpy = 2,2'-bipyridine-4,4'-dicarboxylic acid). The Pt counter electrodes were prepared by drop casting Platisol T onto washed FTO plates and sintering at 500 °C for 30 min under air. The electrolyte was composed of 0.1 M Lil, 0.03 M I2, 0.5 M, tertbutylpyridine, 0.5 м 1-butyl-3-methylimidazolium iodide, and 0.1 м guanidinium thiocyanate in acetonitrile. The sensitized photoanodes were rinsed with dichloromethane and dried under argon flow. Then they were assembled and sealed with the counter electrode using thermal adhesive films (16 µm thick) as a spacer to produce sandwich-type cells. The electrolyte solution was introduced through a hole drilled in the counter electrode. Finally, this hole was sealed with a hot-melt film and a cover glass. The active area of all cells is 0.36 cm².

Photovoltaic and Photoelectrical Measurements: Photovoltaic measurement of the DSSCs was recorded by applying an external potential bias to the cells while recording the change of generated current with a digital source meter (Keithley model 2400). The cells were measured under irradiation using 1000 W m⁻² air-mass (1.5) simulated solar light generated by an Oriel class AAA solar simulator. IPCE was measured as a function of wavelength from 300 to 800 nm. A 75 W xenon lamp was used as the light source for generating a monochromatic beam. Calibration was performed using an National Institute of Standards and Technology (NIST)-calibrated silicon photodiode as a standard. IPCE values were collected at low chopping speed.

Other Types of Characterization: The morphology of the samples was inspected using a ZEISS-ultra 55 field emission scanning electron microscope (SEM) with accelerating voltage of 5 kV. Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images were recorded on a JEM-3010 transmission electron microscope using a working voltage of 300 kV, equipped with a LaB6 gun and a Gatan Orius SC 200 2 k \times 2 k Charge Coupled Device (CCD) camera. The specific surface areas of the 3D-IO samples were investigated using the Brunauer–Emmett–Teller (BET) method (BEL Japan, Inc.).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

dye-sensitized solar cells, inverse opals, photoanodes, photovoltaics, ${\rm TiO}_2$

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