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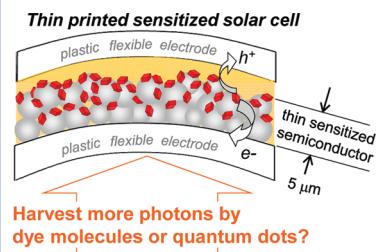
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Toward Printable Sensitized Mesoscopic Solar Cells: Light-Harvesting Management with Thin TiO₂ Films

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ABSTRACT Sensitized mesoscopic solar cells can exhibit high performance and processability by the use of a thin semiconductor layer in combination with a sensitizer of superior light-harvesting ability. This combination is an important key toward the realization of high-efficiency flexible solar cells using solution-based, rapid roll-to-roll printing processes. To this goal, preparation of a binder-free TiO₂ paste is presented as a key process to low-temperature plastic electrode fabrication. For the future challenges of printable sensitized solar cells, this Perspective is focused on the importance of sensitizer choice for thin TiO₂ films with regards to optimum light harvesting, showing photovoltaic behaviors of organic dye sensitizers and lead halide perovskite nanocrystals as inorganic sensitizers. Further, the author offers a comparison of the light-harvesting ability between organic dye sensitizers and inorganic quantum dot size sensitizers based on optical extinction coefficients and the surface density of the sensitizer.



Recent global-scale investments in new-generation solar cells are stimulating a large number of studies on dye-sensitized semiconductors, organic heterojunction films, and organic–inorganic hybrid structures as photovoltaic materials. These newcomers from the field of chemistry to the solar cell industry place their goals of R&D not only on the development of high device performance but also on technologies for cost reduction with a view to minimize the consumption of energy during manufacture. The study of dye-sensitized semiconductor electrodes dates back to the late 1960s when Gerischer and co-workers explored various combinations of organic sensitizers and semiconductors.^{1,2} After the discovery of water photolysis on TiO₂ by Fujishima and Honda,³ TiO₂ has been extensively employed as a highly stable n-type semiconductor in photoelectrochemistry. After the invention of mesoscopic dye-sensitized solar cell (DSSC) by the Grätzel group, the DSSC has reached a solar energy efficiency of 12%,⁴ surpassing the average efficiency of amorphous silicon solar cells. Recent advances of the high-efficiency DSSC have been reviewed by Grätzel.⁵ The principle advantage of DSSCs over silicon solar cells, however, is the ability to manufacture at a considerably lower cost due to device fabrication requiring only simple wet coating processes and chemical treatments in vacuum-free and ambient conditions.

Drastic cost reduction, essential to photovoltaic devices, is realized by high-speed printing of the entire cell structure.

Organic thin film photovoltaic cells (OPVs) are catching up to DSSCs, with the highest-efficiency OPV, comprised of solution-processed thin films of polymer photovoltaic materials obtained through nonvacuum processes, now approaching 8%.⁶ In this respect, the OPV and DSSC are members of the printable solar cell family. However, one major difference is the thickness of the power generation (active) layer, which is more than 100 times thinner in OPVs than that in DSSCs. This is a consequence of much shorter carrier diffusion lengths of < 100 nm. Thin-film manipulation and suitable machinery therefore are prerequisites for the development of OPVs. At present, the lifetimes of OPVs are shorter than those of DSSCs because of structural fragility and antiwater sensitivity of the organic layers. To overcome these matters, hybrid-type OPVs combining organic layers with protective metal oxide nanostructures (TiO₂, ZnO, etc.) have been employed^{7,8}. On the DSSC side, solidification of the cell structure has been an important subject to improve durability and obviate solvent leakage, issues that hinder the liquid electrolyte. The liquid electrolyte can be replaced by various hole conductors^{9,10} and polymer electrolytes^{11,12} in the solid or quasi-solid state, which are prepared by solution coating followed by solvent evaporation. Solvent-free coating methods are also applicable to the DSSC solidification, for example, by printing polymer/carbon composite materials, mixed with ionic liquids, on mesoporous TiO₂ as ion conductors.^{13,14} These situations show that the manufacture of a DSSC is more suited to low-cost printing processes.

The processes of the preparation of colloidal semiconductor nanoparticles, wet coating, and dye sensitization in DSSC

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resemble those used in color photographic materials (dye-sensitized silver halide particles), the latter being manufactured on the high-speed roll-to-roll line. It is assumed that the cost and speed of DSSC manufacturing can reach the level of photographic materials given that the electrode substrate is replaced by low-cost flexible conductive substrates. In the solar panel industry today, mass production of polycrystalline silicon solar cells (efficiencies of around 15%) boasts the lowest cost, which is less than 200 USD in terms of factory cost per square meters. Such figures set the cost target of any type of next-generation solar cell to be less than 100 USD if the efficiency and lifetime do not surpass the silicon cell. For DSSCs with lower efficiency and life, we understand that the target should be around 50 USD. To realize such a low cost level, a potential solution is to establish a full-printing high-speed process for manufacture, similar to that established in the photographic industry. There is, however, another perspective of the cost target to consider. In the market of consumer electronics, secondary batteries, such as lithium ion types, are heavily consumed, leading to increased energy consumption and CO₂ emission. One solution is to replace a part of the battery power with a photovoltaic cell. For this “low-power” application, organic solar cells are particularly suitable because of their excellent sensitivity to low-intensity light or indoor light. This is especially true in the case of DSSCs, where the output voltage, fixed by an electrochemical potential gap, is kept virtually constant in a wide range of incident intensities. Low reflection index of the active layer (mesoporous film) helps to enhance responsivity to weak diffused light that illuminates the cell at a high (shallow) incident angle. While efforts are continuously being made by industry to reduce energy consumption, changing human behavior and lifestyle is difficult. In this respect, replacing secondary batteries with photovoltaics is a particularly painless lifestyle change with measurable benefits.

To truly realize cost-effective solar cells, electrode fabrication should be changed drastically in respects of minimal material consumption, simplified manufacturing equipment, and high-speed production. Among the solar cell industries, the DSSC stands out as the candidate with the most potential of realizing this change. With this in mind, our research efforts have focused on the design of rapidly made, printable DSSC electrodes compatible with thin flexible substrates required for roll-to-roll manufacturing.

DSSCs on Flexible Substrates with Thin Semiconductor Films. DSSCs of the highest performance have been made on glass substrates bearing transparent conductive oxide (TCO) layers such as F-doped SnO₂. The choice of glass as a substrate material enables the high-temperature sintering (> 450 °C) of TiO₂ paste in order to form a mesoporous film. An important determinant in the enhancement of photocurrent–voltage (*I*–*V*) performance in TiO₂ is the electron diffusion length.¹⁵ In the mesoporous TiO₂, the electron diffusion length is of a sufficiently large range exceeding 20 μm¹⁶ with a considerably long electron lifetime (> ms); such properties allow a thick active layer to be employed, subsequently improving light harvesting. High photoelectric conversion efficiencies of 10–12%^{5,17–19} have been obtained with a family of Ru

complex dyes sensitizing TiO₂ films of thicknesses exceeding 10 μm.

Sinterless printing of dye-sensitized TiO₂ yields 6% efficiency, leaving room for improving photon collection.

In contrast, challenges to prepare TiO₂ electrodes without the sintering process have been made for the purpose of utilizing flexible plastic films as electrode substrates. A special coating material (paste) that is able to form a mesoporous film with good semiconductor characteristics at low temperature (< 150 °C) is crucial to flexible solar cell technology. Important to the design of such a paste is to exclude binder materials (polymers) as coating additives; any binder material left in the nonsintered film will increase the resistance against electron diffusion.

Binder-free mesoporous films of TiO₂ can be prepared without high-temperature sintering by chemical treatments of TiO₂ colloidal solutions.²⁰ On the other hand, a binder-free paste of TiO₂ with sufficiently high viscosity directly applicable to screen printing and/or doctor blade coating can be prepared by a mesoscopic dispersion technology. Homogeneously dispersing nanocrystalline TiO₂ in a water–alcohol mixture in the presence of a TiO_x aqueous sol generates a hydrogen-bonding network of TiO₂ particles exhibiting a sufficient viscosity for coating. A thin layer of this paste coated on an electrode substrate is treated by a dehydration condensation reaction at 120–130 °C for around 10 min. These processes yield a mesoporous TiO₂ film of high porosity (> 50%).²¹ A film of ITO-coated polyethylene naphthalate (PEN) has been employed as a flexible substrate. This simple method produces a TiO₂-coated plastic film electrode with high adhesion strength.^{21,22}

Spectral sensitization of the TiO₂ layer with various kinds of dyes has been examined, including a Ru complex dye, N719. It was found that the nonsintered TiO₂ exhibits a low electron diffusivity because of weak interparticle connection compared to that of the sintered TiO₂ network. Electron diffusivity (*D*) (cm²s) and electron lifetime (*τ*) were highly affected by external electric conditions (photocurrent density and voltage applied), and the different electrolyte compositions have been investigated elsewhere.^{15,23} The electron diffusion length (*L*), defined as $L = (D\tau)^{1/2}$, of the above N719-sensitized TiO₂ layer was as high as 13–15 μm. The result agrees with observations that the photocurrent tends to saturate at a thickness of around 12 μm for electrodes sensitized by N719, and the best efficiency under 1 sun occurs at a thickness of around 8 μm.²²

To realize a high-efficiency DSSC without sintering, a strategy for cell fabrication is now clear. The semiconductor layer should be as thin as possible to minimize wasteful energy dissipation to heat, the sensitizer should be of high

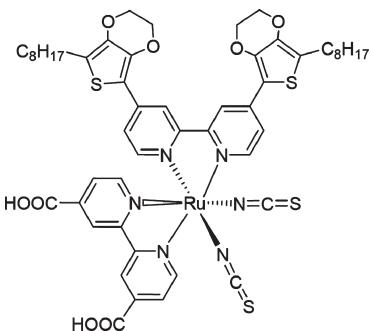


Figure 1. An amphiphilic ruthenium sensitizer, SJW-E1.

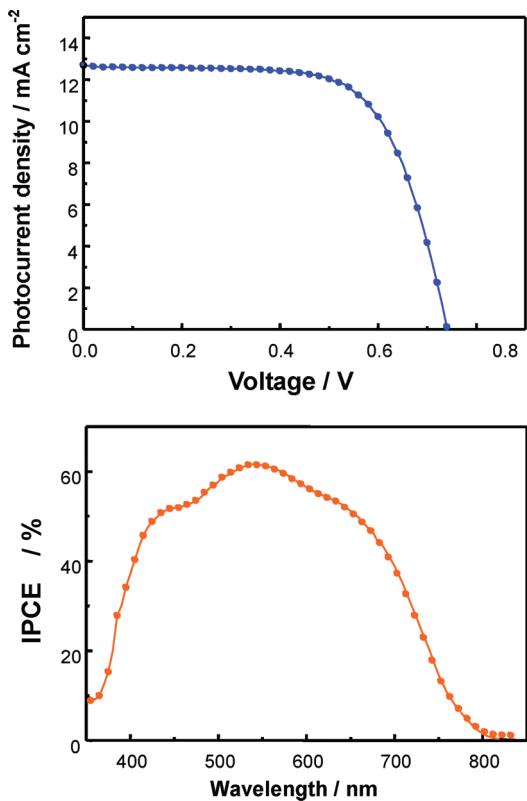


Figure 2. $I-V$ characteristics (top) and an IPCE action spectrum (bottom) for a SJW-E1-sensitized $7\text{ }\mu\text{m}$ thick TiO_2 photoelectrode made on an ITO-PEN substrate with a conversion efficiency of 6.31%. $I-V$ curves are measured under AM 1.5 100 mW cm^{-2} irradiation.

optical extinction, or it should possess a panchromatic window of spectral sensitivity. As an alternative to N719, an amphiphilic Ru complex sensitizer, SJW-E1 (Figure 1), has a molar extinction coefficient of $18\,700\text{ M}^{-1}\text{ cm}^{-1}$, higher than that of N719 ($\sim 13\,500\text{ M}^{-1}\text{ cm}^{-1}$). The hydrophobicity of the dye also improves the stability against desorption at the TiO_2 -electrolyte interface. With a thick sintered TiO_2 layer on a glass substrate, the conversion efficiency of the dye is as high as 9.02%,²⁴ which is lower than the best level of N719 (> 11%). However, with a nonsintered TiO_2 film prepared under the above thickness limitation, the order in performance can be reversed. As for N719, on the basis of the

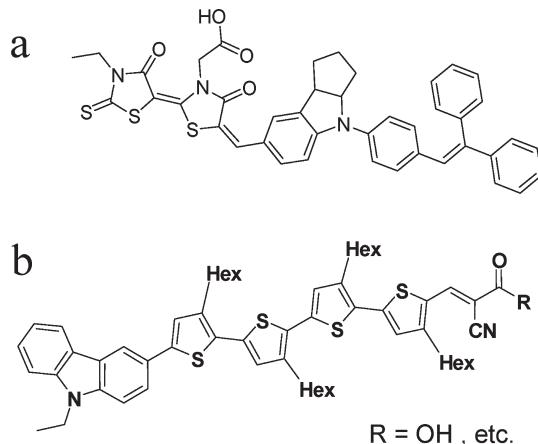


Figure 3. Structures of an indoline-type dye, D149 (a), and carbazole-type dyes (b).

extinction coefficient and an average amount of dye molecules loaded on TiO_2 ($5 \times 10^{-5}\text{ mol/g}$), absorption of incident photons is guaranteed to be 90% with a $10\text{ }\mu\text{m}$ thick TiO_2 film (or $16\text{ g TiO}_2/\text{m}^2$) at the peak absorption wavelength, while it decreases to 70% with a $5\text{ }\mu\text{m}$ thick film. Sensitizers of higher extinction coefficients are thus capable of harvesting photons with thin TiO_2 films ($< 8\text{ }\mu\text{m}$). Use of SJW-E1, however, needs an additional compound, a coadsorber, employed in the dye adsorption because such a bulky sensitizer often undergoes molecular aggregation, which causes quenching of excitation energy. Use of cholic acid, for example, as the coabsorbent suppresses such aggregation and remarkably improves the quantum efficiency of sensitization. In contrast, it gives little effect on N719, which does not easily aggregate. The use of coadsorbent, however, reduces the dye surface density and light-harvesting ability. With a nonsintered TiO_2 layer, SJW-E1 mixed with cholic acid shows an optimum thickness for the photocurrent density at $7\text{ }\mu\text{m}$, which is thinner than that observed with N719. With this thickness, this dye yields a conversion efficiency of 6.31% with a V_{oc} of 0.73 V and a fill factor of 0.67 at 1 sun of intensity.²⁵ This efficiency is the highest achieved for plastic film electrodes prepared by the low-temperature method and higher than the efficiencies obtained with N719 (5.80²²–6.20%²⁵). Figure 2 shows $I-V$ characteristics and the action spectrum of incident-photons-to-current conversion efficiency (IPCE). The IPCE maximum is 63%. On the basis of the transmittance of ITO-PEN being 75%, internal overall efficiency of photon collection and current generation is around 84%, indicating that there is still a loss in harvesting photons.

Besides new Ru complex dyes, porphyrin dyes²⁶ and organic dyes with much larger extinction coefficients are assumed to be more suitable for sensitizing a thin semiconductor film. In this respect, our group has examined various indoline-type dyes, such as D102, D149,^{27,28} and D205²⁹ (Figure 3). These organic dyes are little affected by the addition of coadsorbents in the IPCE and photocurrent performance, indicating that the aggregation does not matter. This allows increasing of the dye surface density on TiO_2 . In our experiments, D149 ($\epsilon = 68\,000\text{ M}^{-1}\text{ cm}^{-1}$, 530 nm) yielded

3.7 % as a conversion efficiency with a 7 μm thick TiO_2 film.³⁰ With D205, the efficiency was improved to 5.2 % with a TiO_2 thickness half of that of D149 (3.5 μm). A family of carbazole-type dye ($\epsilon = \sim 36\,000\text{ M}^{-1}\text{ cm}^{-1}$)³¹ also works as an excellent sensitizer to a thin TiO_2 film. Absorbing in a wavelength region of 350–800 nm, the dye yields high IPCEs exceeding 60 % and a conversion efficiency close to 5 % with a 6 μm thick TiO_2 film. Despite the high extinction coefficients, their light-harvesting abilities are not reaching those of the aforementioned Ru complex sensitizers. This situation mainly reflects a narrower window of spectral sensitivity (< 750 nm).

At present, a core problem in the low-temperature TiO_2 coating is the relatively low level of IPCE. In order to increase IPCE, some fundamental improvements of the semiconductor electrode are necessary, one of which is to increase the electron diffusion length within the mesoporous TiO_2 ; the other is to modify the ITO surface for better electron rectification. The former may concern abandoned electron-trapping sites residing at TiO_2 – TiO_2 interfaces as a result of nonsinter preparation. Minimizing such traps may require use of non-spherical TiO_2 -like nanotubes. The modification of ITO is assumed to be best made by coating a nonporous highly crystalline TiO_2 film as the blocking layer. Development of a low-temperature method for this coating is an important subject.

Inorganic Sensitizers and Quantum Dots (QDs). There are, however, fundamental drawbacks in the application of organic dyes as a sensitizer and light absorber. The stability of organic dyes against light (particular UV) and heat limits the range of practical applications. A sufficiently long time is required to achieve loading of the sensitizer through chemical adsorption. For thin film applications, the optical characteristics of organic dyes are often not ideal due to their photon-collecting ability being confined to molecular excitation with narrow absorption bands. The use of coabsorbents against molecular aggregation further reduces light absorption. A solution to these issues can be use of inorganic materials as sensitizers. Typical inorganic sensitizers are nanosized, or quantum dot (QD) size, crystalline semiconductors which pump electrons by the intense band gap light absorption. Optical absorption coefficients, α , of solid-state crystalline semiconductors are generally in the range of 10^4 – 10^5 cm^{-1} . In terms of extinction coefficient per mole of particles, ϵ , QDs such as CdS and CdSe give coefficients of 10^5 – $10^6\text{ L(mol particles)}^{-1}\text{ cm}^{-1}$, depending on the particle size, which varies in the range of 2–6 nm.³² In addition to this intense optical absorption, inorganic compounds generally have high stability to light and heat. On the basis of this strategy, various QD sensitizers have so far been examined, which are compound-type semiconductors such as CdS,^{33,34} CdSe,^{35–37} PbS,³⁸ InP,³⁹ and InAs.⁴⁰ These inorganic sensitizers strongly absorb visible light, showing their spectral sensitivity to be tunable by changing the particle size. To expand the spectral window, attempts have also been made to use a combination of QD and dye on TiO_2 .³⁴

For the design of a thin and flexible photovoltaic cell, the type of sensitizer is of particular importance to ensure light-harvesting performance. Mechanically, thinner photoactive

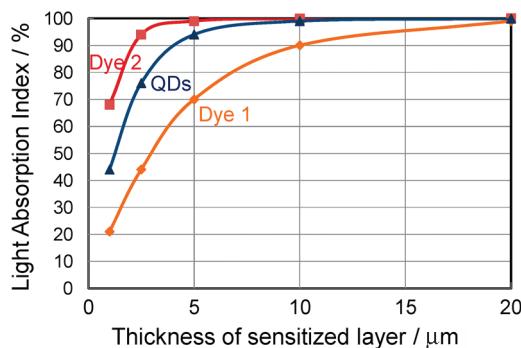


Figure 4. Relationship between the calculated light absorption index and the thickness of the sensitized TiO_2 layer for two organic sensitizers and a group of QDs. Dyes 1 and 2 have low and high extinction coefficients, respectively. QDs are typically CdS or CdSe with a particle size range of 2–4 nm. See text for detailed conditions set for the calculation.

layers are more stable and durable on flexible substrates. In modification of the cell structure, such as solidification, thin layers favor use of organic charge-transport layers (hole conductors,^{9,10} etc.) having short carrier diffusion lengths (< 100 nm). In order to understand the effect of the extinction coefficient of the sensitizer on the light-harvesting ability, Figure 4 plots the light absorption index (%) against the thickness of sensitized mesoporous semiconductors. Three kinds of sensitizers as models are compared here. There are two organic sensitizers possessing high and low extinction coefficients, $13\,000$ and $65\,000\text{ M}^{-1}\text{ cm}^{-1}$; the former corresponds to N719, and the latter is an example of a metal-free organic dye. The other is a QD, typically CdS or CdSe, which exhibits an extinction coefficient of $10^5\text{ L (mol particles)}^{-1}\text{ cm}^{-1}$ with a particle size of 2 nm.³² The calculation of the light absorption index was based on our experimental measurements (for dyes) and reported data (for QDs).³² A target mesoporous TiO_2 layer for sensitization has a porosity of 60 %, giving an approximate roughness factor of 600 at a thickness of 10 μm . The amount of N719 dye adsorbed on TiO_2 is measured to be $5 \times 10^{-5}\text{ mol g}^{-1}$ or $8 \times 10^{-8}\text{ mol}$ per unit projected area (cm^2) of the TiO_2 layer. This indicates that the average area of TiO_2 occupied by single N719 molecule is 2 nm^2 , which is twice the molecular size of N719 ($\sim 1\text{ nm}^2$). On the other hand, the minimum size of the QD is assumed to be 2 nm in diameter ($\sim 3\text{ nm}^2$ in the projected area), which is more than twice larger than the organic sensitizer. It is reasonable to assume that the area occupied by the QD on TiO_2 is more than three times that of N719. This difference should be taken into account when the loading amount (surface density) of sensitizers is estimated. In Figure 4, the absorption index (A) was calculated at a peak absorption wavelength, based on the optical density (D), by the equation $A = (1 - 10 \exp D)$, where no optical scattering effect to enhance photon absorption was taken into account. This calculation also teaches that a QD with a larger size of 4 nm ($\epsilon = 4 \times 10^5$) gives the same absorption index as the 2 nm QD as a result of lower surface density.

The results of Figure 4 demonstrate that light absorption of the QD sensitizers at the absorption peak is not necessarily

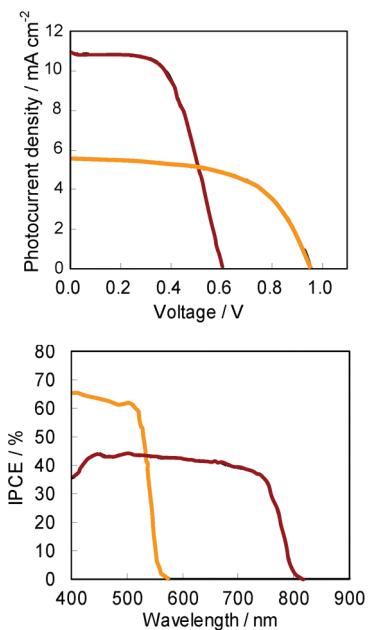


Figure 5. I – V characteristics (top) and IPCE action spectra (bottom) for cells sensitized with $\text{CH}_3\text{NH}_3\text{PbBr}_3/\text{TiO}_2$ (yellow line) and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ (brown line). I – V curves are measured under AM 1.5 100 mW cm⁻² irradiation.

more intense than that of the group of organic dyes. Light absorption of QDs competes with that of organic dyes; it must be surpassed by dyes of high extinction coefficients. This comparison, however, does not reflect photon harvesting by the effect of spectral distribution. By absorbing light by band gap excitation, a QD maintains its strong absorption up to its longer edge wavelength, where the molecular sensitizer undergoes tailing of absorption. This effect may improve substantially the harvesting ability of QDs by surpassing that of organic sensitizers. Further, coloading of the dye sensitizer and QD can benefit by the highest effect of light harvesting.

Organic dyes of high extinction coefficients are superior light harvesters to QDs; they expand the spectral window by hybrid use with QDs.

In electrode fabrication, some inorganic sensitizers can be quickly loaded on the semiconductor surface by a simple deposition method. This aspect is quite different from dye sensitizers. We have employed a unique kind of nanocrystalline sensitizer that is synthesized on TiO₂ by a quick self-organization. Absorbing in the visible region (< 800 nm), the sensitizer is an organic–inorganic hybrid compound represented by the structure $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X = \text{Br}, \text{I}$), which is characterized as the perovskite crystal structure.⁴¹ To deposit

the compound into the mesoporous interior of TiO₂, a precursor solution, containing stoichiometric amounts of $\text{CH}_3\text{NH}_3\text{X}$ and PbX_2 dissolved in an organic solvent (*N,N*-dimethylformamide, γ -butyrolactone, etc.), is spin-coated on a thin film of TiO₂ (8–12 μm). In a short time after coating (< 0.5 min), precursor films on TiO₂ are stained yellow ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) or black ($\text{CH}_3\text{NH}_3\text{PbI}_3$), indicating formation of the nanocrystals. Scanning electron microscopy (SEM) revealed the existence of quantum size particles (2 nm) on the TiO₂ surfaces. The photovoltaic cell was fabricated by using a F-doped SnO₂ (FTO)-coated glass as the substrate of the sensitized photoelectrode in combination with a Pt counter electrode. The kind of redox electrolyte was optimized. $\text{CH}_3\text{NH}_3\text{PbBr}_3$ was coupled with 0.4 M LiBr and 0.04 M Br₂ dissolved in acetonitrile, while $\text{CH}_3\text{NH}_3\text{PbI}_3$ was coupled with 0.15 M LiI and 0.075 M I₂ dissolved in methoxyacetonitrile. Figure 5 shows IPCE spectra for the two perovskites. IPCEs exhibit sharp rises at wavelengths corresponding to the band gap absorption of the perovskites. The iodide, $\text{CH}_3\text{NH}_3\text{PbI}_3$, gives a lower IPCE maximum (45%) but shows an extended spectral responsivity to 800 nm, exhibiting a black color absorbing the entire visible light.

On the basis of work function analysis of the valence band by photoelectron spectroscopy and band gap energy measurements, the conduction band (CB) levels versus the vacuum level of these perovskites, $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (3.36 eV) and $\text{CH}_3\text{NH}_3\text{PbI}_3$ (4.0 eV), are situated higher than or close to that of TiO₂ (~4.0 eV). Despite the estimated small difference between the CB levels of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and TiO₂, the short-circuit photocurrent density (J_{sc}) measured is much larger for $\text{CH}_3\text{NH}_3\text{PbI}_3$, most likely being influenced by its wider spectral window of photon collection. In contrast, a higher open-circuit voltage (V_{oc}), 0.96 V, can be obtained with the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ sensitization which employs Br[−] as a donor of electrochemical potential (5.1–5.6 eV), which is more positive than that of I[−] (4.5–5.0 eV). The power conversion efficiency was 3.81% for $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 3.13% for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ ⁴¹ with the former owed to its larger photon-collecting density leading to a higher efficiency. While the 3.8% efficiency is among the highest values ever obtained by the QD sensitization, a maximum efficiency for the perovskite/TiO₂ system is expected to reach 12% if the IPCE is improved to a level comparable to that of dye sensitization of around 80% while maintaining a high voltage, > 0.9 V. In the real case, the accompaniment of back electron transfer at the semiconductor–electrolyte interface is the predominant cause of low quantum conversion efficiency (IPCE). To solve this problem, a recent report shows that coating the absorber with blocking layers such as SiO₂⁴² or Al₂O₃⁴³ significantly improves IPCE.

Toward the Design of a Fully Printable DSSC Module. Regardless of the sensitizer, organic or inorganic, photoelectrochemical cells have a unique advantage in collecting energy of low-intensity light (diffused light, indoor illumination, etc.) without lowering voltage; furthermore, photoelectrochemical cells possess a small temperature dependence in power generation.^{44,45} The property of mechanically flexibility allows a large-area module to be set on a round surface which is exposed to diffused light with multiple incident angles. Figure 6



Figure 6. A flexible film-type DSSC made on a belt-shaped plastic ITO-PEN. Exposure of the cell to indoor illumination generates a DC voltage exceeding 0.7 V.

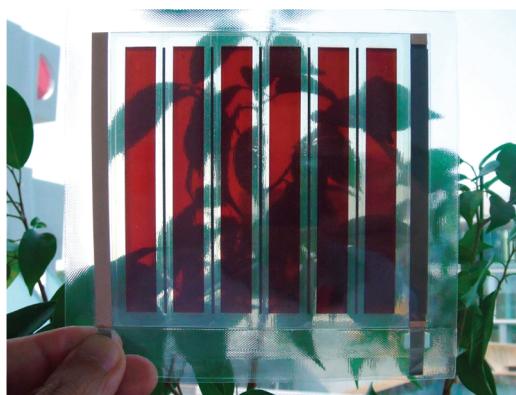


Figure 7. A film-type bifacial module of a DSSC comprised of a series connection of six unit cells. The output DC voltage is 4.2 V. Total thickness of the module including substrates is 0.5 mm.

demonstrates an example of a large belt-shaped cell made on ITO-PEN films, in which the photocurrent is collected by metal films at the edges of the cell; the high voltage of the cell, > 0.7 V, is maintained under exposure to indoor illumination.

A smart and cost-effective configuration of the DSSC, based on the aforementioned discussions, is to use a semiconductor layer of the lowest possible thickness, a sensitizer of the highest extinction, and the thinnest possible electrolyte to minimize internal resistance caused by ionic diffusion. Such architectures are simple to devise using plastic film substrates. These configurations ultimately lead to the production of a cell that boasts bifacial power generation in which incident light at the both sides (working and counter electrode) produces an equal power. At this stage, the design of the counter electrode is of high importance for the bifacial cell. While the use of Pt as a cathode catalyst has demonstrated high performance, Pt is expensive and requires high-temperature processes. We have invented low-temperature, non-Pt printable materials for counter electrodes based on a polymer-based composite film.^{46–48} An example of the bifacial-type full-plastic DSSC module is exhibited in Figure 7, in which sensitizers are high-extinction organic dyes. To generate a high DC voltage, unit

cells or submodules are processed to compose a series electrical connection. Typically, the device of six-cell connection (Figure 7) generates a DC output of more than 4.2 V, which corresponds to a charging maximum voltage of lithium ion batteries.

The future of DSSC fabrication will see the liquid electrolyte hole transporter being replaced by solid- or quasi-solid-type ionic conductors for the purpose of improving the cell life. This will also be the case expected for flexible plastic modules. Further, the methods of electrochemistry-based DSSCs and solid-physics-based OPVs will be unified in the form of a hybrid organic–inorganic solar cell. A trial in this direction is under way in our group.

Summary: Future Direction to Printable Photovoltaics. Future success of sensitized photovoltaic devices largely depends on the feasibility of drastic cost reduction, which needs innovation of rapid production processes free of vacuum, high temperature, and other time-consuming processes. To this goal, the cell structure should be improved so that all elements constituting the layered structure meet solution-processable methods. A roll-to-roll electrode manufacturing process requires use of flexible substrates such as plastic films and metal foils. Here, mechanical stability of a solid-state (ceramic) layer on the flexible substrate can be guaranteed by coating a thinnest possible layer durable against transformation. In this situation, the light-harvesting ability should be ensured by designing a sensitizer system yielding high extinction coefficients. Polymethine-type organic dye molecules can be excellent in the light-harvesting power even compared to inorganic QDs, as exhibited in Figure 4. However, they permit light transmission at wavelengths where coefficients shrink. In this respect, a promising candidate for the sensitizer system is a combination of QDs and organic sensitizers. Here, an organic dye is employed not only as the sensitizer to the base semiconductor but also to act as an antenna dye to QDs that works via electron or energy transfer, so that the light absorption of QDs is reinforced. A challenge of this method was currently demonstrated by the Grätzel group using CdSe QDs.³⁶ At the pinnacle of sensitizer research where the spectral window of sensitization is expanded up to 1000 nm, the conversion efficiency of solar energy is expected to reach 15%, given that the cell maintains an IPCE value of 85%, a photovoltage of 0.8 V, and a fill factor of 0.7.

Biographies

Tsutomo Miyasaka received a Ph.D in 1981 from The University of Tokyo. He was a researcher in 1981–2000 at Fuji Photo Film, Co. In 2000, he moved to Toin University of Yokohama as a Professor in the Graduate School of Engineering. In 2004, he established Peccell Technologies, Inc. In 2009, he was awarded a Ministry-of-Education prize on the achievements of green sustainable chemistry. His research is focused on sensitized semiconductor and organic–inorganic hybrid photovoltaic cells.

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