



Full paper

## A solar cell that breathes in moisture for energy generation

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### ABSTRACT

Aiming at energy issues, alternative energy sources to fossil fuels such as solar energy, wind energy and wave energy have been well studied. However, ubiquitous atmospheric moisture as a possible alternative has not been seriously explored. Comprising of nearly 13 trillion kiloliters of water, atmospheric moisture can be best exploited as a sustainable energy resource and an abundant hydrogen source. In our present study, we have exploited moisture absorption from the air and ensuing conversion into electricity. To effectuate moisture absorption and energy conversion, a hybrid solar device was constructed by integrating tailored hygroscopic materials with photosystems stimulated by metal free organic dyes. The hygroscopic materials absorb water from humid atmospheres, serving as the source of neutral water for the photoelectrochemical reaction, thereby transducing atmospheric humidity directly into electricity and hydrogen, in the presence of light. We have also reported a significant drop in the humidity levels of a confined space from 80% to 40%. This hybrid system, when in operation, effectuates simultaneous dehumidification and a photocurrent generation of  $240\mu\text{A}/\text{cm}^2$  under ambient indoor light.

### 1. Introduction

Harvesting solar energy has been one of the major areas which is of paramount importance to material scientists throughout the globe. Direct conversion of solar energy into electricity is accomplished through different types of photovoltaic systems whilst transduction of solar energy to chemical energy is achieved by photoelectrochemical water splitting for production of hydrogen gas [1–3] and photocatalytic conversion of carbon dioxide to liquid fuels [4]. Simple yet powerful, nature has been unparalleled in designing and optimizing intricate structures that harvest solar energy with almost unit photon conversion efficiency [5–7]. This process which triggered the onset of biological activity on a massive scale which led to the prospering and diversification of the living organisms on planet earth is commonly known as ‘photosynthesis’. The core reaction of this process is the splitting of water in the presence of natural sunlight. The absorption of photons triggers the generation of spatially separated electron-hole pairs which aid the oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) [8–11].

Research on artificial photosynthetic mechanisms has garnered tremendous attention over the past decade to develop novel technologies that aid in the sustainable production of energy and clean fuels from

photo-electrochemical (PEC) reactions [12,13]. The development of dye sensitized photoelectrochemical cells (DS-PECs) [14–16] is one such example wherein the operation of the device is analogous to that of a leaf. The surface of the dye sensitized semiconductor offers a lower energy level for the OER and the counter electrode (often Pt) serves as an excellent catalyst for HER [17]. In conventional DS-PECs the electrodes are immersed directly into water and a small bias needs to be applied between the electrodes to achieve efficient water splitting.

In the past few decades, much attention has been focused on the development of inexpensive metal-based catalysts and/or their integration into solid state devices that operate in aqueous media. Research works on the development of novel mesoporous electrodes [18,19] for achieving higher efficiencies of water splitting [1,20], drug delivery, [21] several electronic and optoelectronic applications [22] have found immense applicability in the development of DS-PECs. A major drawback associated with this approach is that the photocatalytic materials are designed to work in aqueous environments, thus demanding for large quantities of aqueous media. This poses severe constraints in scaling up the process for sustainable energy/fuel generation [23]. As an alternative to the use of aqueous media, atmospheric moisture in the form of humidity can be explored as a potential energy resource for sustainable energy generation and hydrogen production. Earth’s

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atmosphere contains a massive 13 million kiloliters of water at any point of time owing to natural water cycle [24]. Humidity in the air is usually considered a redundant resource that requires additional expense of energy to maintain at comfortable levels for human habitation. Relative humidity (RH) levels of above 60% (at any temperature) is often known to create thermal discomforts and it affects the way in which we perceive temperature.

Nature has witnessed numerous episodes of plants and insects that harvest atmospheric humidity to fuel their survival [25,26]. Some of the classic examples are cacti, Namib desert beetles and agamid lizards [27]. The techniques adapted by these species to utilize moisture from air provides a great insight to scavenge humidity in the air for practical purposes. Several artificial water harvesters have been developed recently, inspired from the mechanisms found in the beetles and cacti [28]. Though, water harvesting from various humid sources like mist [29], fog, dew [30] and arid air [31] have been in place for efficient moisture capture and conversion to potable water, scavenging atmospheric moisture for direct device realizations is relatively sparse. Previous attempts for utilizing air moisture for applications other than water harvesting was primarily focused on water-oil separation and biomedical applications [32,33]. In this work, we report a novel solar device architecture that concurrently performs dehumidification, sustainable energy generation and hydrogen production. This hybrid system combines a tailored super-hygroscopic hydrogel that effectively captures water from humid atmospheres and serves as the source of water and a dye-sensitized wide band-gap semiconducting layer which acts as a photocatalyst for water splitting to generate energy and produce hydrogen.

It is well known that hydrogen is becoming an increasingly important source of renewable energy as the global energy demand is escalating [34]. Hydrogen Evolution Reaction (HER) is a fundamental process in photo-electrocatalysis and plays a major role in the development of hydrogen based energy storage devices [35]. This reaction, however, is thermodynamically arduous requiring special conditions and catalysts to help reduce the energy barrier and increase the reaction rate [36,37]. To date, Platinum (Pt) group metals are best suited for HER reactions to take place at a near-zero overpotentials in acidic medium [38]. Scarcity of raw materials and the expense associated with recovery of these noble metals hinder their application in commercial devices. In this context, it becomes pivotal to identify alternative low-cost materials that can reduce the overpotential of HER and achieve the same performance as compared to Pt. Highly studied earth-abundant alternative materials and architectures include 3d transition metals [37], transition metal dichalcogenides [34] and dye-sensitized photoelectrochemical cells [39].

In this work, we have conceived a DS-PEC system that integrates tailored hygroscopic components with a dye-sensitized semiconductor. Fig. 1a shows the schematic of the device. Titanium dioxide ( $\text{TiO}_2$ ) was chosen as the wide band-gap semiconductor. For a semiconductor to perform water splitting, the minimum required bandgap is about 2eV, to harvest visible light and to compensate for the overpotentials required for slow kinetics of the processes. However, unmodified semiconductors do not effectively exhibit the charge separation and transfer. To overcome this drawback, the  $\text{TiO}_2$  layer was kept immersed in a metal free organic dye SK3 (Fig. 1b). Owing to the expensive raw materials and environmental concerns associated with Ruthenium based dyes, we have used a metal free organic donor- $\pi$ -acceptor (D- $\pi$ -A conjugated) carbazole dye (SK3) for sensitizing the  $\text{TiO}_2$  layer. The synthesis and characterization of the dye is reported in our earlier work [40,41]. This dye sensitized semiconducting layer is responsible for breaking down the absorbed water molecules. Additionally, the photocatalyst must be integrated with a hygroscopic material that can absorb large quantities of water from humid atmospheres at a faster rate. We have developed a zinc-based super hygroscopic hydrogel capable of absorbing more than 420% of its own weight with water [24]. This hydrogel is a non-stoichiometric oxide of Zinc, synthesized from its acetate salt

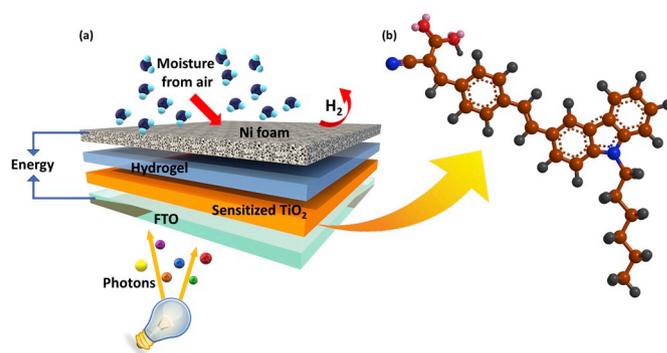


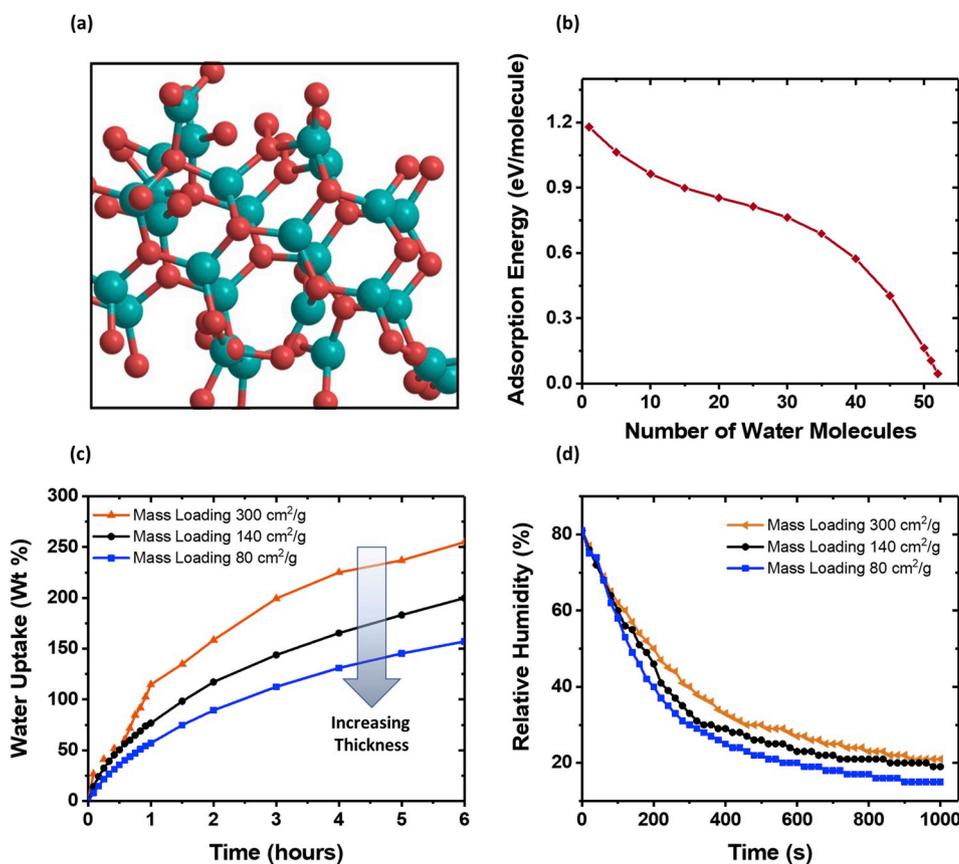
Fig. 1. Schematic diagram showing the construction of the hybrid device for simultaneous dehumidification and energy/hydrogen generation. (b) Structure of the SK3 dye used for sensitizing the  $\text{TiO}_2$  layer (Brown balls: Carbon atom; Blue balls: Nitrogen atom; Black balls: Hydrogen atom; Red balls: Oxygen atom; Pink balls: Oxygen lone pair).

blended with glycol ether, an amino-alcohol and water. This hydrogel exists in two distinct states namely hydrated (H) and dehydrated (DH) depending on the ambient humidity. This super hygroscopic hydrogel serves as the source of neutral water for the DS-PEC to operate. A highly porous Nickel (Ni) foam sputtered with minimal Pt was used as the counter electrode. The Ni foam offers a high specific area for electron collection and catalytic activity. The high porosity of the Ni foam permits transfer of moisture to the hydrogel and evolution of hydrogen after the PEC reaction.

In case of natural photosynthesis, the roots bring up the required water to the leaves. The pores in the leaf absorb carbon dioxide from the atmosphere and the pigment chlorophyll absorbs the photons. This results in excitation of the pigments leading to charge separation and eventual water splitting. The generated oxygen is let out into the atmosphere and the carbon dioxide reacts with the evolved hydrogen to form sugar (stored energy). Akin to this working mechanism, in our hybrid device, the super-hygroscopic hydrogel is responsible for providing atmospheric water to the dye-sensitized semiconducting layer where the charge separation takes place triggering water splitting reaction. The highly porous Ni foam enables inhalation (absorption) of moisture by the hydrogel and transferring it to the semiconducting layer for water splitting to take place and exhalation (evolution) of hydrogen, analogous to breathing in human beings.

The synthesized super-hygroscopic hydrogel is a non-stoichiometric oxide of Zinc (Fig. 2a). The synthesis, structure and characterization of the hydrogel is reported in our earlier work [27]. This amorphous hydrogel made of Zn and O atoms in a unique 1:1.1 ratio has a strong tendency to absorb moisture from humid air. Transmission Electron Microscopy (TEM) characterization of the hydrogel (Supplementary Fig. S1) was carried out to confirm the amorphous nature of the synthesized material. Density Function Theory was used to calculate the binding energy of water molecules with the hydrogel (Fig. 2b). It can be seen that as the number of water molecules increase, its binding energy with the hydrogel decreases. A logarithmic plot was used to fit the data and it can be projected that when the number of water molecules adhered to the hydrogel increases beyond 120, the binding energy becomes zero. This indicates that the adsorbed/adsorbed water molecules are only physically adsorbed and not chemically bound. This unique nature of the hydrogel enables easy water transfer to the semiconducting layer.

The absorption characteristics of the hydrogel was studied by varying the mass loading of the hydrogel and exposing it to humid atmospheres. Moisture absorption rate plays a crucial role in intensifying the dehumidifying effect of the hybrid device. The faster the hydrogel absorbs moisture from humid air, the rapid is the dehumidification effect. Several factors affect the rate of moisture absorption by the hydrogel



**Fig. 2.** (a) Simulated structure of the hydrogel with Zn:O ratio of 1:1.1 which was used as the hygroscopic material. This hydrogel serves as the source of neutral water for the photoelectrochemical reactions to take place at the photoanode. (Green balls: Zinc atoms, Red balls: Oxygen atoms). (b) The binding energy of water molecules with the hydrogel. (c) Moisture capture rates of the hydrogel when exposed to 80% RH. (d) The consequent decrease in RH of an enclosed space as a result of moisture absorption by the hydrogel.

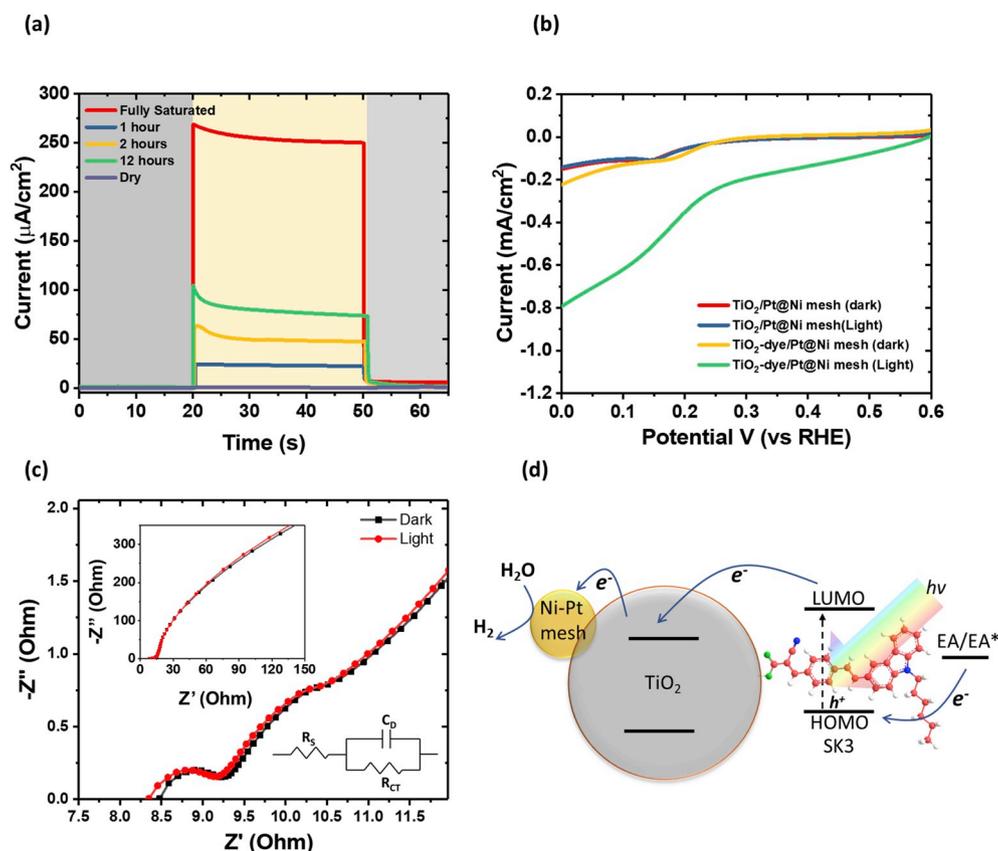
with thickness having the most profound effect. The absorption characteristics of the hydrogel is shown in Fig. 2c. The area of hydrogel coating was kept constant at 26 cm<sup>2</sup>. The amount of hydrogel loaded onto the fixed area was increased gradually and the absorption rate was studied. Loading of 0.09 g of the hydrogel yielded a mass loading ratio (Surface area/Weight of hydrogel) of about 300 cm<sup>2</sup>/g and this was the thinnest coating. The mass loading was then increased to about 0.19 g and 0.33 g to yield mass loading ratios of 140 cm<sup>2</sup>/g and 80 cm<sup>2</sup>/g respectively and eventually a thicker coating of the hydrogel. It can be seen from the figure that thinner the thickness of the coating, faster is the moisture absorption rate. This is evident from the fact that, thinner the coating, more surface is exposed for moisture capture. As the thickness of the hydrogel coating increases, there is a reduction in the absorption rate owing to the fact that diffusion of water molecules to the bottom layer is a slower process when compared to moisture absorption. As the hydrogel absorbs water, there is a consequent reduction in the RH of a confined space. Fig. 2d shows the effect of moisture absorption by the hydrogel on the RH of a confined space. It can be seen that, more the mass loading of the hydrogel, more is the amount of moisture absorbed and drier the confined volume. Though the thinnest coating absorbs moisture faster, the thicker layer can absorb and contain much more water (weight basis) and hence lead to a drier space.

Optical transmittance of the photoanode (dye-sensitized TiO<sub>2</sub> layer) controls the number of photons that are available for absorption by the dye. Supplementary Fig. S2 shows the UV-Visible absorption spectrum of the SK3 dye and the optical transmittance of the dye-sensitized TiO<sub>2</sub> film. The dye shows a peak absorption at  $\approx$ 435 nm. A strong red shift and broadening of the absorption band was observed in case of dye adsorption on TiO<sub>2</sub> surface due to the interactions of the anchoring group with the titanium ion. This confirms a stronger electron accepting tendency of the dye, which is of paramount importance for electron transfer reactions.

PEC measurements (Fig. 3a) were done on the assembled device at an

applied bias of 0 V vs RHE and at a pH of about 7. A LED lamp of light intensity 10 mW/cm<sup>2</sup> (0.1 sun) was used for illumination of the device. The emission spectrum of the LED used is shown in Supplementary Fig. S3. From the emission spectrum, there is no radiation emitted in the infrared region and hence there is no heating of the device, which in turn reflects that the generated photocurrent is only because of the PEC water splitting reactions. The device was assembled, and the hydrogel was initially in DH state. Without any water available for PEC reactions to take place, the device did not show any photoresponse in the DH state of the hydrogel. The device was then exposed to 70% RH for about 1 h, 2 h and 12 h to effectuate moisture absorption by the hydrogel and the PEC measurement was repeated and stable photocurrents of about 25  $\mu$ A/cm<sup>2</sup>, 50  $\mu$ A/cm<sup>2</sup> and about 80  $\mu$ A/cm<sup>2</sup> respectively were observed. The device was then exposed to 70% RH for about 24 h so that the hydrogel reaches a water saturated state. In this condition, a maximum photocurrent of about 270  $\mu$ A/cm<sup>2</sup> was observed, which stabilized at about 250  $\mu$ A/cm<sup>2</sup>. This clearly shows that, more the amount of water available for breaking down, higher is the photocurrent generated in the device. The effect of the mass loading of the hydrogel on the device performance was studied (Supplementary Fig. S4) and it was found to have almost nil effect to the photocurrent when the hydrogel is in water saturated state. The thickness effect and the mass loading of the hydrogel affected the dehumidification performance of the device only.

Fig. 3b shows the Linear Sweep Voltammetry plot for the dye-sensitized TiO<sub>2</sub> electrode in a KPI buffer (pH 7). Water reduction results suggest that the sensitization of TiO<sub>2</sub> with dye yields the maximum photocurrent (at 0 V vs RHE). Further to this, EIS spectra (Fig. 3c) of the photoanode was studied to understand the reaction kinetics and the photoelectrode-electrolyte interface resistance. The solution resistance for the electrode has a slightly decreased value under light illumination owing to the excess carriers generated by dye excitation. However, there is not much difference in the electrode-electrolyte interfacial interaction in dark and light conditions as the arc of the Nyquist plots are almost



**Fig. 3.** (a) PEC measurements for the fabricated device. When the hydrogel is fully saturated with water, a maximum photocurrent of about  $270\mu\text{A}/\text{cm}^2$  is generated. When the hydrogel is in dry state, there is no photocurrent which is indicative of the fact that it is the photocatalytic water splitting that generates the current. (b) LSV plot for water reduction reactions under light and dark conditions for pristine  $\text{TiO}_2$  and  $\text{TiO}_2\text{-SK3}$ . (c) EIS studies for the electrodes. The inset image shown the equivalent circuit used for fitting the EIS data (d) Working principle of the device.

identical (inset image). The working principle of the device is explained in Fig. 3d. The hydrogel inherently contains trace amounts of ethanolamine that was added during the synthesis. Additionally, to serve as the electron donor [42] to regenerate the dye, two drops of ethanolamine was added to the synthesized hydrogel during the assembly of the device. The reactions happening at the photocathode and photoanode can be summarized as follows:

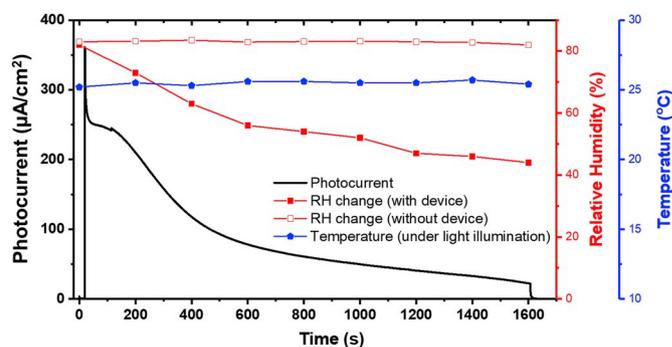
Photoanode:  $\text{TiO}_2\text{-SK3} + h\nu \rightarrow \text{TiO}_2\text{-SK3}^* \rightarrow \text{TiO}_2(e^-)\text{-SK3}^+ + \text{EA} \rightarrow \text{TiO}_2\text{-SK3} + \text{EA}^*$

Photocathode:  $\text{TiO}_2(e^-)\text{-SK3}^+ + \text{Pt} \rightarrow \text{TiO}_2\text{-SK3} + \text{Pt}(e^-) + \text{H}^+ \rightarrow \text{Pt} + \frac{1}{2} \text{H}_2$

Mott-Schottky analysis (Supplementary Fig. S5) was carried out to study the shift in the flat-band potential ( $E_{fb}$ ) and charge carrier density ( $N_c$ ) in the pristine  $\text{TiO}_2$  and SK3 sensitized  $\text{TiO}_2$  photoanode when in contact with the KPi solution (0.5 M  $\text{K}_2\text{HPO}_4$  and 0.5 M  $\text{KH}_2\text{PO}_4$  in DI water, pH7). A three-electrode system with  $\text{TiO}_2$  or  $\text{TiO}_2\text{-SK3}$  as the working electrode, aqueous  $\text{Ag}/\text{AgCl}$  electrode as a reference and a Pt wire as the counter electrode was used to perform the Mott-Schottky analysis with a bias from 0 to -1 V vs RHE without and with light illumination. Both electrodes had a positive slope, which indicates that  $\text{TiO}_2$  is a n-type semiconductor. The  $E_{fb}$  of the  $\text{TiO}_2\text{-SK3}$  (8eV) is slightly shifted, due to the interaction of the acidic proton ( $-\text{COOH}$ ) with  $\text{TiO}_2$  which led to positive charging of the  $\text{TiO}_2$  semiconductor, resulting in the shift of  $E_{fb}$ . The charge carrier concentration was calculated based on the known dielectric constant of  $\text{TiO}_2$  and permittivity of vacuum and it was found to be  $3.60 \times 10^{19} \text{ cm}^{-3}$  and  $4.50 \times 10^{20} \text{ cm}^{-3}$  for pristine  $\text{TiO}_2$  and  $\text{TiO}_2\text{-SK3}$  electrode, respectively. The 12.5 times high charge carrier density of  $\text{TiO}_2\text{-SK3}$  is indicative of effective photon-electron conversion by the adsorbed dye molecules.

To conclusively prove the effect of simultaneous dehumidification and energy/hydrogel generation by the device, an experiment was conducted wherein the device was placed in a controlled chamber that

was maintained at an RH of about 80% and was exposed to a LED lamp. The temperature and RH of the chamber was continuously monitored. The absorption of moisture by the hydrogel resulted in a continuous drop in RH of the chamber from 80% to about 45% in about 30 min. A plot showing the reduction in RH of the chamber with the device and the concurrent photocurrent generation is shown in Fig. 4. Since temperature has a profound effect on the levels of RH, the temperature of the chamber was also continuously monitored under light illumination. It was observed that the LED illumination did not increase the temperature of the chamber. Another study was conducted as a control measure wherein the RH and temperature of the chamber was monitored without the device and the results are shown in Fig. 4. The RH of the chamber remained constant at 80% in the absence of the device. This also proved that there is no dehumidification effect just by illumination of the LED light source. These experiments conclusively prove that the reduction of



**Fig. 4.** Control experiment showing the simultaneous dehumidification and energy generation by the device. The LED lamp used for illumination does not increase the temperature of the chamber. In the presence of the device, there is a RH drop in the chamber from 80% to 45% in under 30 min.

the RH inside the chamber is only due to moisture absorption by the device. Furthermore, long term studies were conducted to corroborate the proposed working mechanism of simultaneous moisture absorption and photoelectrochemical splitting of the absorbed moisture (Supplementary Fig. S6). A longer duration of the photocurrent in humid condition shows that the process of water absorption and water splitting happens in tandem which substantiates our working principle. In case of the dry chamber, there is not much moisture available for the hydrogel to absorb and hence the photocurrent decays at a much faster time.

To summarize, we have demonstrated a novel device architecture that can 'breathe-in' atmospheric humidity for energy generation thus serving as an effective smart dehumidifier which generates electricity. This has been achieved by integrating tailored hygroscopic materials into DS-PEC's to serve as the source of water for the photoelectrochemical reactions to take place. With continuous regeneration of the hygroscopic materials on the surfaces of the electrodes, we have shown that it is possible to generate photocurrents for a prolonged period when the cell is placed in a humid atmosphere.

### Data availability

The raw/processed data required to reproduce these findings can be shared under request.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.nanoen.2019.104263>.

### References

- Z. Zou, J. Ye, K. Sayama, H. Arakawa, Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst, *Nature* 414 (6864) (2001) 625–627.
- C.N. Rao, S.R. Lingampalli, Generation of hydrogen by visible light-induced water splitting with the use of semiconductors and dyes, *Small* 12 (1) (2016) 16–23.
- J.V. Vaghiasya, D.K. Nandakumar, Z. Yaoxin, S.C. Tan, Low toxicity environmentally friendly single component aqueous organic ionic conductors for high efficiency photoelectrochemical solar cells, *J. Mater. Chem.* 6 (3) (2018) 1009–1016.
- B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum, C.P. Kubiak, Photochemical and photoelectrochemical reduction of CO<sub>2</sub>, *Annu. Rev. Phys. Chem.* 63 (1) (2012) 541–569.
- S.K. Ravi, S.C. Tan, Progress and perspectives in exploiting photosynthetic biomolecules for solar energy harnessing, *Energy Environ. Sci.* 8 (9) (2015) 2551–2573.
- R.E. Blankenship, D.M. Tiede, J. Barber, G.W. Brudvig, G. Fleming, M. Ghirardi, et al., Comparing photosynthetic and photovoltaic efficiencies and recognizing the potential for improvement, *Science* 332 (6031) (2011) 805.
- M. Kamran, J.D. Delgado, V. Friebe, T.J. Aartsma, R.N. Frese, Photosynthetic protein complexes as bio-photovoltaic building blocks retaining a high internal quantum efficiency, *Biomacromolecules* 15 (8) (2014) 2833–2838.
- S.Y. Reece, J.A. Hamel, K. Sung, T.D. Jarvi, A.J. Esswein, J.J.H. Pijpers, et al., Wireless solar water splitting using silicon-based semiconductors and earth-abundant catalysts, *Science* 334 (6056) (2011) 645.
- T.R. Cook, D.K. Dogutan, S.Y. Reece, Y. Surendranath, T.S. Teets, D.G. Nocera, Solar energy supply and storage for the legacy and nonlegacy worlds, *Chem. Rev.* 110 (11) (2010) 6474–6502.
- I. McConnell, G. Li, G.W. Brudvig, Energy conversion in natural and artificial photosynthesis, *Chem. Biol.* 17 (5) (2010) 434–447.
- O.P. Judson, *The Energy Expansions of Evolution* 1, 2017, 0138.
- S. Chen, T. Takata, K. Domen, Particulate photocatalysts for overall water splitting, *Nat. Rev. Mater.* 2 (2017) 17050.
- C.-T. Dinh, T. Burdyny, M.G. Kibria, A. Seifitokaldani, C.M. Gabardo, F.P. García de Arquer, et al., CO<sub>2</sub> electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface, *Science* 360 (6390) (2018) 783.
- Z. Yu, F. Li, L. Sun, Recent advances in dye-sensitized photoelectrochemical cells for solar hydrogen production based on molecular components, *Energy Environ. Sci.* 8 (3) (2015) 760–775.
- N.S. Lewis, Light work with water, *Nature* 414 (6864) (2001) 589–590.
- J.R. Swierk, K.P. Regan, J. Jiang, G.W. Brudvig, C.A. Schmuttenmaer, Rutile TiO<sub>2</sub> as an anode material for water-splitting dye-sensitized photoelectrochemical cells, *ACS Energy Lett.* 1 (3) (2016) 603–606.
- K.S. Joya, Y.F. Joya, K. Ocakoglu, R. van de Krol, Water-splitting catalysis and solar fuel devices: artificial leaves on the move, *Angew. Chem. Int. Ed. Engl.* 52 (40) (2013) 10426–10437.
- B. Kong, J. Tang, Z. Wu, J. Wei, H. Wu, Y. Wang, et al., Ultralight mesoporous magnetic frameworks by interfacial assembly of Prussian Blue nanocubes, *Angew. Chem. Int. Ed.* 53 (11) (2014) 2888–2892.
- B. Kong, J. Tang, Y. Zhang, T. Jiang, X. Gong, C. Peng, et al., Incorporation of well-dispersed sub-5-nm graphitic pencil nanodots into ordered mesoporous frameworks, *Nat. Chem.* 8 (2015) 171.
- J. Brillet, J.-H. Yum, M. Cornuz, T. Hisatomi, R. Solarska, J. Augustynski, et al., Highly efficient water splitting by a dual-absorber tandem cell, *Nat. Photonics* 6 (12) (2012) 824–828.
- J. Tang, B. Kong, H. Wu, M. Xu, Y. Wang, Y. Wang, et al., Carbon nanodots featuring efficient FRET for real-time monitoring of drug delivery and two-photon imaging, *Adv. Mater.* 25 (45) (2013) 6569–6574.
- B. Kong, J. Tang, Y. Zhang, C. Selomulya, X. Gong, Y. Liu, et al., Branched artificial nanofinger arrays by mesoporous interfacial atomic rearrangement, *J. Am. Chem. Soc.* 137 (12) (2015) 4260–4266.
- K.E. Dalle, J. Warnan, J.J. Leung, B. Reuillard, I.S. Karmel, E. Reisner, Electro- and solar-driven fuel synthesis with first row transition metal complexes, *Chem. Rev.* 119 (4) (2019) 2752–2875.
- D.K. Nandakumar, Y. Zhang, S.K. Ravi, N. Guo, C. Zhang, S.C. Tan, Solar energy triggered clean water harvesting from humid air existing above sea surface enabled by a hydrogel with ultrahigh hygroscopicity, *Adv. Mater.* 31 (10) (2019) 1806730.
- Z. Pan, W.G. Pitt, Y. Zhang, N. Wu, Y. Tao, T.T. Truscott, The upside-down water collection system of *Syntrichia caninervis*, *Nat. Plants* 2 (2016) 16076.
- K.F. Kaseke, L. Wang, M.K. Seely, Nonrainfall water origins and formation mechanisms, *Sci. Adv.* 3 (3) (2017).
- D.K. Nandakumar, S.K. Ravi, Y. Zhang, N. Guo, C. Zhang, S.C. Tan, A super hygroscopic hydrogel for harnessing ambient humidity for energy conservation and harvesting, *Energy Environ. Sci.* 11 (8) (2018) 2179–2187.
- K.-C. Park, P. Kim, A. Grinthal, N. He, D. Fox, J.C. Weaver, et al., Condensation on slippery asymmetric bumps, *Nature* 531 (2016) 78.
- S.C. Thickett, C. Neto, A.T. Harris, Biomimetic surface coatings for atmospheric water capture prepared by dewetting of polymer films, *Adv. Mater.* 23 (32) (2011) 3718–3722.
- A. Lee, M.-W. Moon, H. Lim, W.-D. Kim, H.-Y. Kim, Water harvest via dewing, *Langmuir* 28 (27) (2012) 10183–10191.
- H. Kim, S.R. Rao, E.A. Kapustin, L. Zhao, S. Yang, O.M. Yaghi, et al., Adsorption-based atmospheric water harvesting device for arid climates, *Nat. Commun.* 9 (1) (2018) 1191.
- P. Li, Y.F. Poon, W. Li, H.-Y. Zhu, S.H. Yeap, Y. Cao, et al., A polycationic antimicrobial and biocompatible hydrogel with microbe membrane suctioning ability, *Nat. Mater.* 10 (2010) 149.
- J. Li, J. Xie, L. Gao, C.M. Li, Au nanoparticles–3d graphene hydrogel nanocomposite to boost synergistically in situ detection sensitivity toward cell-released nitric oxide, *ACS Appl. Mater. Interfaces* 7 (4) (2015) 2726–2734.
- D. Er, H. Ye, N.C. Frey, H. Kumar, J. Lou, V.B. Shenoy, Prediction of enhanced catalytic activity for hydrogen evolution reaction in janus transition metal dichalcogenides, *Nano Lett.* 18 (6) (2018) 3943–3949.
- Y. Zheng, Y. Jiao, A. Vasileff, S.-Z. Qiao, The hydrogen evolution reaction in alkaline solution: from theory, single crystal models, to practical electrocatalysts, *Angew. Chem. Int. Ed.* 57 (26) (2018) 7568–7579.
- K. Qu, Y. Zheng, X. Zhang, K. Davey, S. Dai, S.Z. Qiao, Promotion of electrocatalytic hydrogen evolution reaction on nitrogen-doped carbon nanosheets with secondary heteroatoms, *ACS Nano* 11 (7) (2017) 7293–7300.
- Z. Chen, R. Wu, Y. Liu, Y. Ha, Y. Guo, D. Sun, et al., Ultrafine Co nanoparticles encapsulated in carbon-nanotubes-grafted graphene sheets as advanced electrocatalysts for the hydrogen evolution reaction, *Adv. Mater.* 30 (30) (2018) 1802011.
- S. Bai, C. Wang, M. Deng, M. Gong, Y. Bai, J. Jiang, et al., Surface polarization matters: enhancing the hydrogen-evolution reaction by shrinking Pt shells in Pt–Pd-graphene stack structures, *Angew. Chem. Int. Ed.* 53 (45) (2014) 12120–12124.
- J.R. Swierk, T.E. Mallouk, Design and development of photoanodes for water-splitting dye-sensitized photoelectrochemical cells, *Chem. Soc. Rev.* 42 (6) (2013) 2357–2387.
- S.S. Soni, K.B. Fadadu, J.V. Vaghiasya, B.G. Solanki, K.K. Sonigara, A. Singh, et al., Improved molecular architecture of D-[small pi]-A carbazole dyes: 9% PCE with a

cobalt redox shuttle in dye sensitized solar cells, *J. Mater. Chem.* 3 (43) (2015) 21664–21671.

- [41] J.V. Vaghasiya, K.K. Sonigara, L. Suresh, M. Panahandeh-Fard, S.S. Soni, S.C. Tan, Efficient power generating devices utilizing low intensity indoor lights via non-radiative energy transfer mechanism from organic ionic redox couples, *Nano Energy* 60 (2019) 457–466.
- [42] K. Meyer, M. Ranocchiari, J.A. van Bokhoven, Metal organic frameworks for photocatalytic water splitting, *Energy Environ. Sci.* 8 (7) (2015) 1923–1937.



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