



Fabrication and characterization of perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) solar cells

Amrit Kumar Mishra¹ · R. K. Shukla¹Received: 24 October 2019 / Accepted: 15 January 2020 / Published online: 3 February 2020
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Abstract

Perovskite material has emerged as an attractive strategy to efficiently convert light into electricity. We are using organic–inorganic–halide $\text{CH}_3\text{NH}_3\text{PbI}_3$ as a heart of solar cells with the device structure: FTO/compact TiO_2 /mesoporous TiO_2 /perovskite/spiro-MeOTAD/Au. The 1.51 eV energy bandgap is in the perovskite material which is great for power conversion efficiency. We are studying the degradation of perovskite solar cell device in the presence of UV light and white light, for a clear understanding of degradation we are measuring I–V characteristics and dielectric properties under various conditions. The schematic energy level diagram shows that electron–hole transport in the tuneable energy band of the intermediate layer of the device. Due to high light absorption, photovoltaic and diffusion length properties of perovskite is the most appropriate material for solar cell application.

Keywords Perovskite solar cell · Humidity · Degradation · Stability · I–V · C–V · C–f · Photovoltaic

1 Introduction

Organometallic perovskite solar cells have shown great promising for next-generation thin-film solar cells [1–4]. Solar cell devices made of organometallic halide perovskite material have reached an efficiency of more than 21% [5]. Perovskite materials are the most appropriate for energy harvesting technology; we are using perovskite materials as the heart of solar cells because perovskite material has good photovoltaic properties. The absorption of light and diffusion length is also a major factor to select material for energy harvesting. The direct bandgap of the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ material is 1.55 eV which is good for the power conversion efficiency of the solar cells.

Perovskite material has a high absorption coefficient, high mobility of electron ($7.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and holes ($12.5\text{--}65 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), long carrier diffusion length (100 nm to 1 μm) [6] and large grain size. Due to the large grain size of the perovskite material hysteresis effect reduces [7–11]. In this work, we are analyzing a complete perovskite solar

cell with the device structure: FTO/c- TiO_2 /mesoporous TiO_2 /perovskite/spiroMeOTAD/Au. Where FTO stands for fluorine-doped tin oxide, c- TiO_2 stands for compact TiO_2 (work as a hole blocking layer), mesoporous TiO_2 (size of the grain 5–40 μm), perovskite works as a heart of the solar cells, spiroMeOTAD works as a hole transporting layer and finally Au is used for the electrode of the typical solar cell's [12–15].

The major problem to make the perovskite solar cell as commercially is their stability [16–22]. Perovskite material degrades due to humidity, temperature, UV light, and oxygen. To analyze the effect of humidity on the perovskite solar cell we have to minimize the other degradation factor (O_2 , temperature, light) as well as we need to keep the solar cell at a particular humidity to analyze its degradation with time. Controlling the humidity in an open environment is very difficult, so we made a chamber to control each factor precisely. Humidity is an important factor in the degradation so we first start analyzing the degradation

✉ R. K. Shukla, rajeshkumarshukla_100@yahoo.co.in | ¹Department of Physics, University of Lucknow, Lucknow 226007, India.



of perovskite solar cells under different humidity conditions. In the chamber, we can control humidity precisely.

In this paper, I am going to analyzing how the perovskite solar cell parameters open-circuit voltage, photocurrent, and capacitance are going to change in different humidity conditions and how perovskite solar cell parameters change with degradation in high humidity condition.

2 Materials and methods

2.1 Device fabrication

The solar cell fabrication technique is done by a spin coating method. We are using patterned fluorine-doped tin oxide substrates (FTO) etched by Zn metal powder and dilute hydrochloric acid. The cleaning of etched FTO done by sequential sonication technique into the soap solution, deionized water, and isopropanol for 15 min each. And next, coat TiO_2 (hole blocking layer) on it by using spin coating method with 5000 rpm for 45 s and heated at 450 °C for 25 min, which is prepared by the mixture of 0.5 ml Ti(IV) isopropoxide (Sigma Aldrich), 7.25 ml of ethanol and 75 microlitre of concentrated HCl. A TiO_2 mesoporous layer is made by using a dilute solution of Dyesol 18N-RT paste (1:3.5 w/w in ethanol) at 4000 rpm for 30 s and heated at 500 °C for 30 min and the film thickness to be formed 360 nm.

2.1.1 Preparation of perovskite

For the perovskite deposition, TiO_2 films were transformed into the glove box. The perovskite layer was deposited [6].

2.1.2 TiCl_4 treatment

First, we take 2 M TiCl_4 (1 ml) in 100 ml D.I. water and put TiO_2 film's into the solution and heat at 80 °C in the oven. After that, the film is wash by water, ethanol and dry Ar gas, and then heated at 500 °C at 30 min and again we take 1 M PbI_2 (462 mg) solution in DMF (1 ml) and steering at 40 °C up-to dissolve, after that spin-coated at 6000 rpm for 5 s. Heated for 25 min at 70 °C on a hot plate, drop into MAI (8 mg/ml) in isopropanol after that dip the PbI_2 film into the above solution for 15 min, and then washed with isopropanol and then heated at 70 °C for 15 min.

2.1.3 Spiro-MeOTAD layer deposition

First, we take 100 ml of Spiro-MeOTAD in 1 ml chlorobenzene 28.5 μl of TBP (Tursary butyl pyridine) + Li salt solution (17.5 μl) using spin coater at 4000 rpm for 30 s and finally gold deposition on Spiro-MeOTAD layer by the thermal evaporator. The Schematic diagram of typical perovskite solar cells is shown in Fig. 1 and the energy level diagram of the perovskite solar cell is shown in Fig. 2.

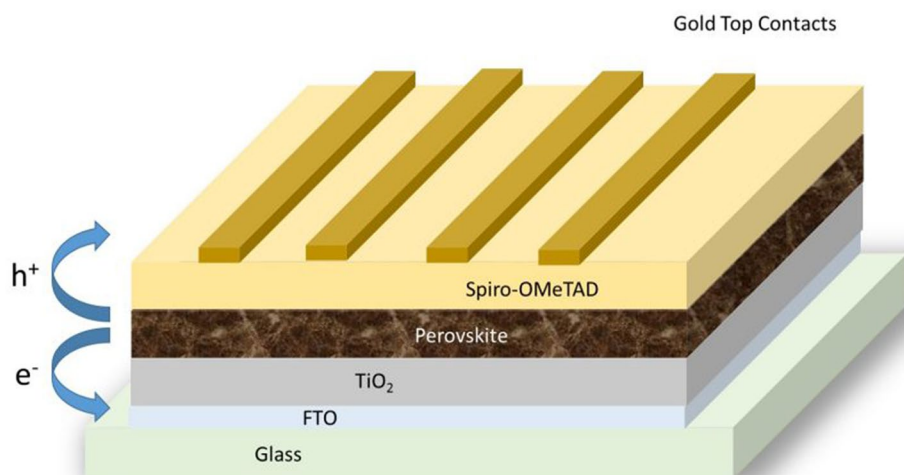
2.1.4 Solar cell parameter in different humidity condition

We have done the quick measurements to avoid the degradation quick change the humidity from RH 50 to RH 6% and then again RH 50% condition. In this condition, the I–V curve shows overlapping in nature. It is confirmed that the solar cell will not degrade quickly.

2.2 I–V curve

In every photovoltaic device, open-circuit voltage (for which the total current in the external circuit is zero)

Fig. 1 Schematic diagram of a typical perovskite solar cell



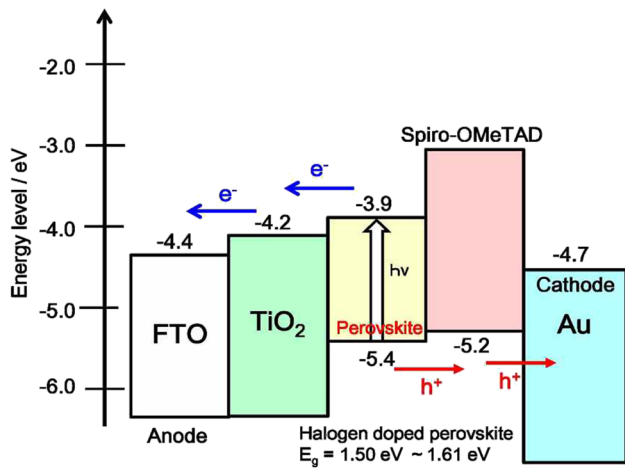


Fig. 2 Energy level diagram of perovskite solar cell

or short circuit current (current in the external circuit for which applied voltage is zero) is two key factors which decide the photovoltaic device performance. So we measure how the I–V curve is changing in different humidity conditions without degradation (quick measurement and the humidity condition was at 50% RH as shown in Fig. 3).

First I–V curve of red was taken at room temperature and humidity at 50% RH, then humidity was decreased with the flow of dry N₂ and I–V curve of green color was taken at low humidity condition at 6% then again humid N₂ gas was flown through the chamber and I–V curve of blue was at 50% RH condition. A solar cell in this humidity condition doesn’t degrade because all the measurement at 50% RH was quick. Perovskite solar cells

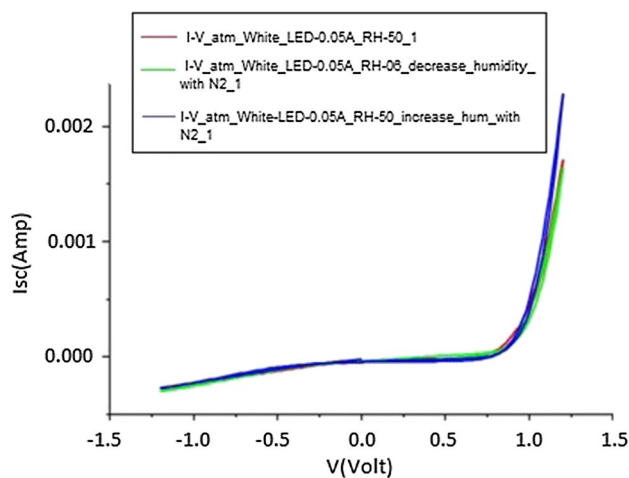


Fig. 3 I–V characteristics of a perovskite solar cell at various humidity conditions

degrade quickly in humidity more than 80% (Fig. 1) so the changes in Voc were small.

2.3 Perovskite solar cell parameters (without degradation)

We use LED of white color for measurements and its intensity was very small (around 4–5 mW/cm²).

| Relative humidity (%) | Open circuit voltage (V) | Short circuit current I _{sc} (A) |
|---|--------------------------|---|
| Humidity at 50% RH | 0.7451 | 4.537E–5 |
| Humidity 06% RH with dry N ₂ | 0.6508 | 4.003E–5 |
| Humidity 50% RH with humid N ₂ | 0.7789 | 4.186E–5 |

2.4 C–f and C–V measurement in different humidity condition

The C–f and C–V data were taken in different humidity conditions to analyze the solar cell performance and defect distribution [4] in different humidity conditions. All the C–f and C–V data were taken in dark conditions to avoid the photo-generated charge carrier’s contribution to capacitance.

From Fig. 4, we can see that with the changing humidity, capacitance increases. From the C–f data, we can see that the value of capacitance at lower and higher frequency remains the same both humidity conditions there is an increase in capacitance at middle frequencies and maximum changes have seen around 10–1000 Hz freq.

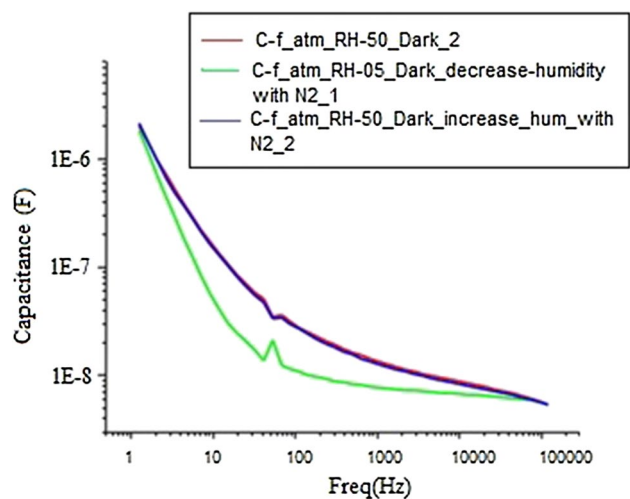


Fig. 4 C–f characteristic with various humidity (humidity changing with N₂ flow in the control rate)

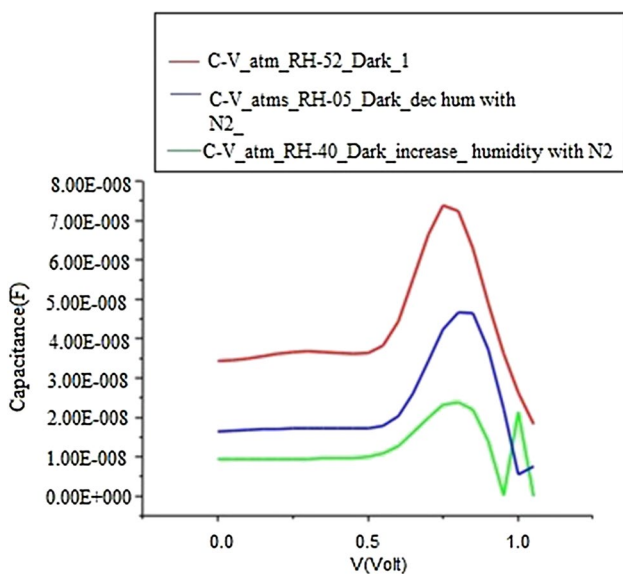


Fig. 5 C–V characteristics with various humidity (humidity changing with N₂ flow in the control rate)

In Fig. 5 shows the variation of C–V, we have taken the value in dark condition and at the particular Frequency 217 Hz. When the humidity increases, the value of capacitance increase but the curve remain same and there is an increase in capacitance value after 0.4 V which is related to ion migration in perovskite solar cells (Fig. 5).

2.5 Change in the parameter of the solar cell with degradation at high humidity

2.5.1 I–V curve

First, the sample was exposed to humidity condition (30% RH) and the I–V curve of red color was taken at that point and then humidity was increased to 80% RH and quickly measure I–V value was taken so there is only small degradation because just after the exposing we took the measurements. After that, the sample was kept at 80% RH for 2 h and I–V data was taken after the 2 h degradation in this environment, this time there is huge degradation in the solar cell because we kept it in high humidity for a long time and it shows by curve of blue color in Fig. 6. This time I–V and noise data were taken under UV light (intensity of UV light is very small around 2–3 mW/cm², to avoid the degradation from UV light we keep the intensity low).

2.5.2 Perovskite solar cell parameter with degradation

| Relative humidity (%) | Open circuit voltage (V) | Short circuit current (A) |
|---|--------------------------|---------------------------|
| Humidity at 30% RH | 0.1025 | 1.18E–5 |
| Humidity 80% RH just after the exposer | 0.0687 | 1.274E–5 |
| Humidity 80% RH (keep for 2 h to degrade) | 6.552E–4 | 0.697E–6 |

After 2 h in high humidity condition i.e. 80% RH solar cells almost degrade. Both open circuit voltage (V) and *I*_{sc} (A) decrease and diode behavior of the solar cell was disappeared as shown in Fig. 6.

2.5.3 The measurement of C–f and C–V with the degradation of a solar cell in high humidity condition

As the value of humidity increases the solar cell start to degrade and capacitance increase due to more ionic contribution (hydrated ion present in perovskite solar cell). In dark condition difference between capacitance value is high in the middle frequency range (10–1000 Hz) which is shown in Fig. 7.

C–V data were also taken in dark condition and as the solar cell degrades the value of capacitance increases but the nature of curve changes, the increase in capacitance behavior after 0.4 V due to ionic movement [23] is

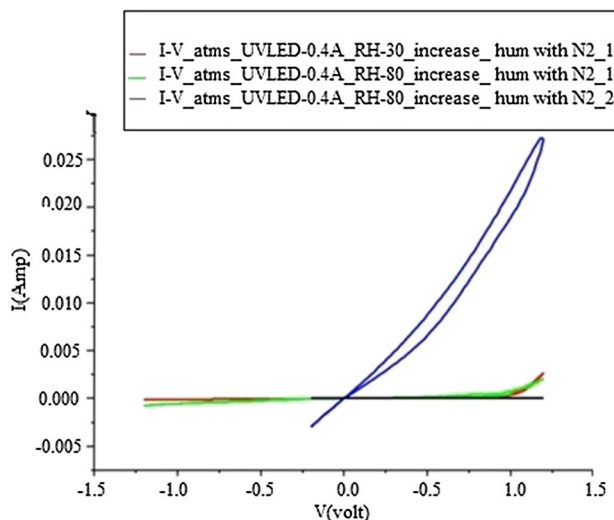


Fig. 6 I–V characteristics with UV light at various humidity conditions without degraded and degraded solar cells

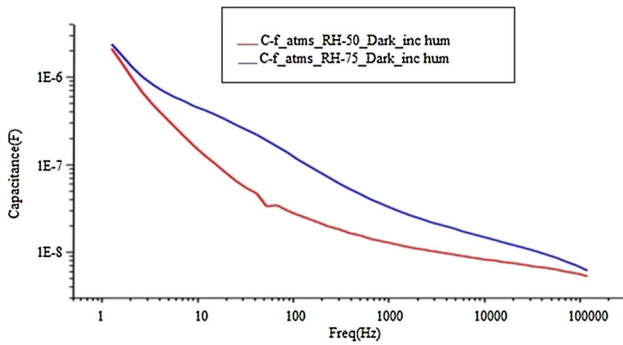


Fig. 7 C-f at various humidity conditions (humidity controlled by N₂ flow)

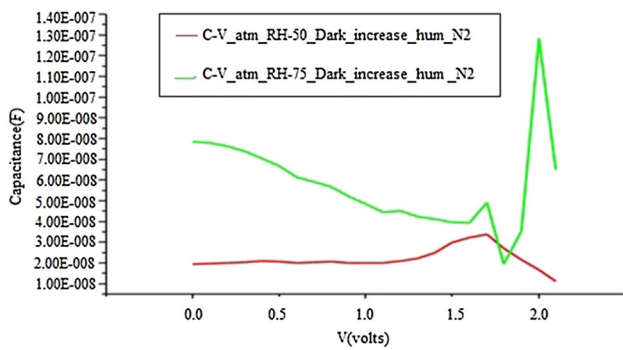


Fig. 8 C-V characteristics at various humidity conditions

lost and the value of capacitance starts to decrease with voltage (Fig. 8).

2.6 Comparison between perovskite solar cell parameter of degraded and without degraded

Now we will compare parameters of a without degraded solar cell (diode behavior and high open-circuit voltage) and degraded (lost diode behavior and low open-circuit voltage) solar cell.

2.6.1 I-V curve

In Fig. 9, the I-V curve of red color is without a degraded sample when we initially load the sample at room humidity and the I-V curve of blue color is for the degraded solar cell. I-V curve was taken with a white LED at a very low intensity (around 4–5 mW/cm²). V_{oc} (open circuit voltage) of the degraded solar cell is very small compared to the without degraded sample but the photocurrent difference is not that much so we still have photocurrent in the degraded solar cell but the diode behavior will disappear.

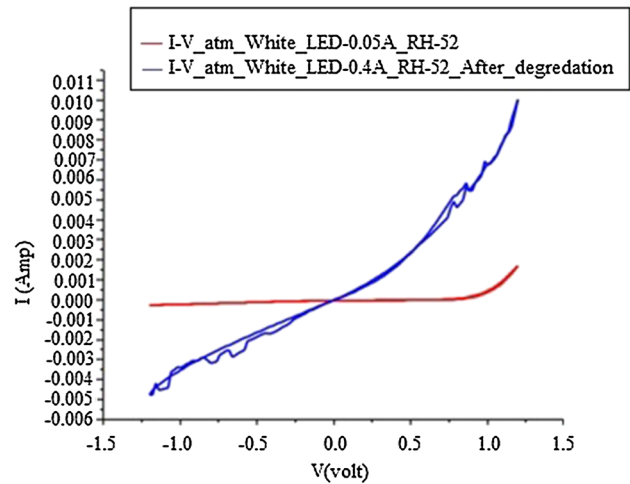


Fig. 9 I-V characteristics of without degraded and with degraded perovskite solar cell at fixed humidity condition

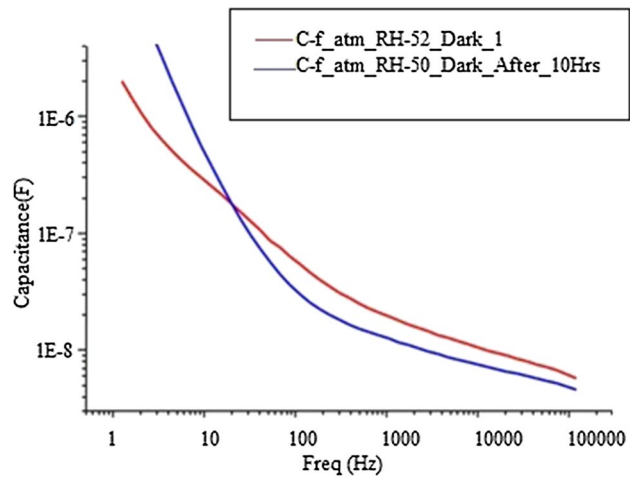


Fig. 10 C-f characteristics of degraded and without a degraded solar cell

2.6.2 Without degraded and degraded solar cell parameters

| Humidity 52% RH | Open circuit voltage (V) | Short circuit current I _{sc} (A) |
|-----------------|--------------------------|---|
| Without sample | 0.7458 | 4.537E-5 |
| Degraded sample | 0.0030 | 1.217E-5 |

2.6.3 The nature of C-f and C-V of without degraded and degraded solar cells at fixed humidity kept for 10 h

We measure the C-f and C-V of the without degraded and degraded solar cells in dark conditions at (52–50% RH) to

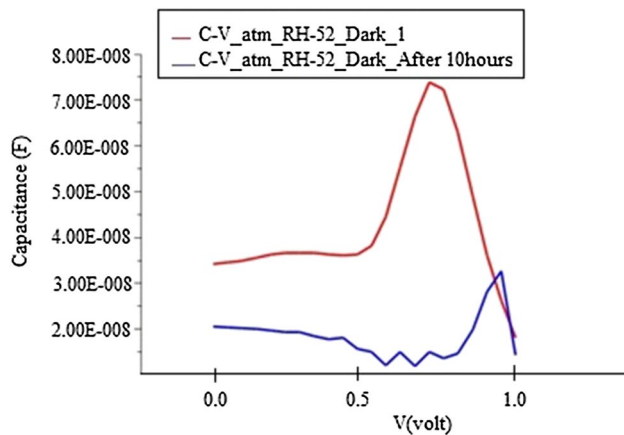


Fig. 11 C–V characteristics of without degraded and degraded solar cells at fixed humidity

see how they are varying for the degraded perovskite solar cell. This is shown in Figs. 10 and 11 respectively.

After degrading the sample in high humidity condition we put it in the vacuum for almost more than 15 h so all the water molecules at interfaces and from the hydrated ions (present in perovskite layer) removed from the solar cell but it's almost degraded because water molecule further degrade the methylammonium lead iodide into PbI_2 ions after making hydrated ions with it and it also degrades the hole transporting layer (Spiro MeOTAD), which decrease V_{oc} very much and the solar cell lost its diode behavior.

From the C–f data we can clearly see that capacitance of the degraded solar cell decreases and from the C–V measurement there is very small increase in capacitance with applied voltage at high applied voltage (around 0.8 V), in the Fresh sample capacitance started to increase at lower applied voltage (around 0.4 V) due to ionic movement [24]. So capacitance of degraded solar cell comparative to fresh one decrease and degraded solar cell also don't show the C–V curve behavior (increase in capacitance with applied voltage due to ionic movement) [25, 26].

3 Conclusion

We have found that degradation in the perovskite solar cell occurs due to variation of humidity, at high humidity condition water molecules traps in the perovskite layer which is used as a heart of solar cell in the device, due to this in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ decomposes in the $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 . So typical perovskite solar cell device degraded at various humidity conditions. We found

that current–voltage, capacitance–frequency, capacitance–voltage characteristics become changes and the efficiency of the solar cell also decreases. Our finding will help to understand the effect of white light, UV light with humidity in determining the various properties and stability of the perovskite solar cell.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

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