INTRODUCTION

Jaundice affects ~60% of infants worldwide, and only 6% get phototherapy to prevent high risk of brain damage. The surviving infants also prone to get long-term health disorders like cerebral palsy, hearing loss and intellectual difficulties (Greco et al., 2016; Olusanya, Osibanjo, & Slusher, 2015). The jaundice is induced by the presence of excess amount of total bilirubin (BR), a yellow product formed by the degradation of aged haemoglobin and combines with bile secreted from the live. The concentrations of free and total bilirubin in the circulating blood are 0.05 to 0.3 mg/dl (1–5 μM) and 1.46 mg/dl (25 μM). Hyperbilirubina, defined as total serum bilirubin (TSB) ≥2 mg/dl (34 μM), leads to permanent neurological sequelae and death. On the other hand, hyphobilirubin induces coronary artery diseases and anaemia. Therefore, development of analytical methods for accurate quantification of total BR concentration in blood becomes clinically very important. Methods such as ultraviolet–visible direct spectrophotometry (Harrison & Barlow, 1989), diazo reaction (Westwood, 1991) and fluorometric analysis (Senthilkumar & Asha, 2015) are reported for the BR quantification. However, while the spectrometric technique is not selective and diazo reaction is pH sensitive, the fluorescence method requires separation and labelling chemistry. Recently, electrochemical method is widely accepted as simple, direct, accurate, sensitive and easy technique to develop sensing devices for point of care applications such as glucometers for diabetes monitoring. Electrochemical sensors that use bilirubin oxidase enzyme have been reported by various groups (Andreu et al., 2002; Fortuney & Guibault, 1996; Guo & Dong, 1997; Kurosaka, Senba, Tsubota, & Kondo, 1998; Mullon & Langer, 1987; Shoham, Migron, Riklin, Willner, & Tartakovsky, 1995; Wang, Luo, & Farias, 1985; Wang & Ozsoz, 1990; Zeng, Liu, & Zhou, 1994). Even though enzymatic biosensors are highly specific, selective and sensitive, they are unstable and require special chemistry to improve the stability, temperature sensitive and expensive. In the context of development of non-enzymatic sensors development, metal (Mn–Cu, (Noh, Won, & Shim, 2014) Au), polymer-modified Au electrodes (Huang et al., 2007), graphite, single- and multi-walled carbon nanotubes, graphene, screen-printed electrodes and nanographite electrodes
Materials with different triboelectric polarities generate charge when they come into contact through mechanical force. In this category, a triboelectric nanosensor fabricated based on the poly(tetrafluoroethylene) (PTFE) polymer and Poly methyl metha acrylate (PMMA) polymers for dopamine detection (Jie et al., 2015). As the flexibility parameter is essential in several applications including wearable sensor development, an automatic, flexible and stretchable sensor is developed using thermoelectric properties of conducting polymer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) for stress sensing (Taroni et al., 2018). A piezoelectric nanogenerator is fabricated using ZnO nanowire arrays for gas sensing (Xu et al., 2010; Xue et al., 2013). In the field of biomedical diagnostic applications, the mechanical harvesting is quite inconvenient. Solar energy-dependent SPS devices based on ZnO p-n junctions, activated under UV light due to the large band gap of ZnO (3.37 eV), are familiar for gas sensing applications (Ozug, Hofstetter, & Morkoc, 2010). A solar diode SPS device Cds/n-ZnO @p-si (low band gap 2.4 eV) is utilized for the detection of oxidizing and reducing gases under visible light (Wang et al., 2012). Single-walled carbon nanotube is anchored on the gold micropatterned silicon surface to construct p-SWNT-n-Si photo-voltaic device for hydrogen sulphide gas sensing (Liu et al., 2017). A self-powered wearable non-invasive Cu$_2$O/ZnO p-n heterojunction is reported for the detection of oesophageal cancer cell by photo-electrochemical reactions (Wu et al., 2017). However, no non-enzymatic SPS is reported in the literature. Rather than the inorganic materials, the organic conducting polymer-based photo-voltaics are more cost-effective. Further, the organic polymer-metal oxide composite favours high electron mobility compared to the pure organic photo-voltaics, supported by the behaviour of poly[2-methoxy-5-(3,7, dimethyloctyloxy) 1,4 phenylvinalene]-ZnO. The highest band gap of the HOMO (5.3 eV) and LUMO (3.3 eV) along with the valence band (7.3 eV) and conduction band (4.4 eV) of the ZnO relative to the vacuum level indicates the photogeneration of electrons and holes at the polymer ZnO interface by the exciton dissociation (Beek, Wienk, & Janssen, 2004). Recently, a photovoltaic device based on the ZnO nanostructures/poly(3-hexylthiophene)](P3HT):TiO$_2$ nanorod hybrid is reported with higher photoconversion efficiency (Lin et al., 2007). The efficiency depends on the height and width of ZnO nanorods grown on the silicon substrate and thickness of the polymer. Although the polymer–zinc oxide hybrid solar cell has been extensively developed for high energy harvesting systems, no self-powered sensor is reported using polyaniline and zinc oxide nanocomposites. This is because of its poor stability and difficulty in processing. These properties can be modified by developing composites with other polymers and metal oxides. It has been shown that the poly(vinyl alcohol) (PVA) is used as an additive to enhance the mechanical stability and its conductivity is in the range of 10⁻² S/cm. Another interesting aspect of inorganic semiconducting materials is that the foreign doping with other metals increases the electronic and catalytic activities. Aluminium-doped ZnO system is reported for the improved conductivity and attributed to the reducing of the
band gap of ZnO. Polyaniline–ZnO blend is reported for biosensing (Sen, Mishra, Sonawane, & Shimpi, 2017). Similarly, a composite of PANi and PVA is reported for the biomedical and energy applications (Mohamoud, 2013). Combination of PANi with PVA and ZnO may enhance the photovoltaic effect. Hence, in this work, we report layer-by-layer fabrication of polyaniline–poly(vinyl alcohol)–Al-doped ZnO-based SPS for the selective non-enzymatic bilirubin quantification for the first time. In order to maximize the activity, along with the polyaniline–ZnO, a photoluminescent sodium zinc phosphate (NaZnPO₄) is placed between the anode and cathode to promote the hole–electron recombination processes and increase the lifetime of the device.

2 EXPERIMENTAL SECTION

2.1 Preparation of NZP

NaZnPO₄ was prepared from the solutions of NaH₂PO₄ and ZnCl₂ separately in the presence of 5% polyethylene glycol (PEG) as a capping agent. The 0.1 M NaH₂PO₄ solution was added drop wisely into the ZnCl₂ solution under continuous stirring (give rpm) for 30 min. A white colour precipitation was washed by double distilled water until the filtrate showed neutral pH and dried at 50°C for 12 hr in an hot air oven. It was further annealed at 450°C in the oxygen gas atmosphere for 3 hr to remove the capped PEG.

2.2 Preparation of AZO

Aluminium-doped zinc oxide was prepared by wet chemical method. Briefly, mixture of 0.099 M ZnCl₂ and 0.001 M AlCl₃ was prepared in 5% PEG. To this, 0.1 M NaOH was drop wisely added to form white colour precipitate and processes of drying and annealing were repeated as made for NZP. The AZO material was further annealed at 800°C in the nitrogen gas atmosphere to obtain a yellow-coloured AZO which indicates oxygen vacancy to enhance n-type conductivity (Wiberg & Holleman, 2001).

2.3 PVA/PAn preparation

Ten per cent PVA (4,000) and 0.5% glycerol were prepared in the double distilled water under constant stirring at 50°C to obtain dense gel. Polyaniline was prepared separately by chemical polymerization of aniline (0.1 M) monomer in the presence of potassium persulfate (0.15 M) in 1 M HCl medium (Khulbe & Mann, 1982). A dark green polyaniline product was washed in 1 M HCl for three times dried. The powdered PANi was mixed in the PVA solution and stirred for 12 hr. The gel like PVA/PAn is spin-coated at 1,000 rpm on glass substrate. The film thickness measured by screw gauge is 0.27 mm. The PVA film shows current in the order of pico ampere due to its insulating property.

2.4 Preparation of solar-powered flexible electrode

Solar-powered flexible electrode was fabricated by simple spin coating technique. On top of the PVA/PAn film on the glass substrate, the photocatalyst NZP and AZO materials, dissolved in 20% DMSO, were spin-coated in a sequential steps to form a layer-by-layer structured flexible sensor. In this structure, the PVA/PANI film acts as anode and the AZO film acts as negative terminals. Contact leads are pasted by silver conducting ink which is a simple and cost-effective technique.

2.5 Measurement

A solar power equaling light intensity was 45 mW/cm² supplied by 250 W halogen lamp in a closed chamber (El-Shaer, Tadros, & Khalifa, 2014). A Keithley 2000 was used for the measuring characteristics of the sensors. For the bilirubin potentiometric sensing, a simple MASTECH (MAS 830L) digital multimeter (voltmeter) was used (Scheme 1). The noise control in the sensing device (Scheme 1) is made using a simple resistance–capacitor (RC) filter and a load resistor (10 kΩ).
2.6 | Instruments

A conventional three-electrode cell consisting of Ag/AgCl reference electrode, Pt wire counter electrode and 2-mm-diameter Pt disc working electrode having 0.03 cm² geometric area was used for electrochemical measurements. The CV was recorded in the potential window −200 to +600 mV at a scan rate 50 mV/s. FTIR spectra were recorded using Perkin Elmer Nicolet IS10 in the frequency range 4,000–400 cm⁻¹. UV–visible spectra were recorded using Shimadzu UV2450 high-performance single monochromator instrument in the frequency range 400–700 nm. A PANalytical make Bruker D8-Advance powder diffractometer (PANalytical B.V.) which uses Cu–Ka1 radiation (2.2 kW max) was used for powder X-ray diffraction measurements. The PL spectra (Hitachi) are used to investigate material emission. Cross-sectional and morphological characterization was carried out with a SEM. Flexibility and shape retainable properties are tested by foldable ankle.

3 | RESULTS AND DISCUSSION

3.1 | Fabrication and characterization of PANi-AZnO p-n junction self-powered photodiode

Multi-layered SPS shown in Scheme 1 is constructed in three different sequential steps. In the first step, the anode layer consisting of PANi/PVA and glycerine elastomer composite is spin-coated (1,000 rpm) on a glass substrate (25 × 45 cm). The molar percentage of PANi is varied at constant while keeping the concentrations of PVA and glycerine constant. The film conductivity is measured using the four-probe method and the tensile strength by Burst Strain equipment, Figure 1a. Maximum conductivity is observed for the PANi/PVA blends prepared at the ratio 5:1, Figure 1a. Beyond this ratio, the film becomes brittle and poorly conductive. The photoluminescent (PL) emission spectra of PANi/PVA recorded in the 340–600 nm show a maxima at 396 nm due to the π-π transition in PANi (Rohom, Londhe, Mahapatra, Kulkarni, & Chaure, 2014) and no evidence for the PL property of the PVA is noticed, confirming the fact that PVA does not influence the conducting property of the PANi (Figure 1b, curve a). The FTIR spectra of freestanding PANi–PVA film exhibit characteristic peaks for the chemical interactions of PVA and PANi. The −OH peak appears at 3,432 and 3,465 cm⁻¹ for the pure PANi and PVA compounds, Figure 1c, curve a, and interaction between them is indicated by the appearance of OH stretching peak at 3,496 cm⁻¹. The peaks at 2,947–2,926 cm⁻¹ and 2,857–2,861 cm⁻¹ correspond to the N–H 2, C–H and C–H 2 stretchings, respectively, and absorption band at 1,600–1,560 cm⁻¹ is assigned to a quinoid and benzenoid C–C ring vibration. The XRD, Figure 1d, shows a broad peak at 20.2° along with a sharp peak at 29.7° due to the presence of amorphous PANi molecules. A small satellite peak with weak intensity appears at 32.08° indicates the formation of PANi/PVA composite (Figure 1d, curve a) (Bhadra, Madi, Al-Thani, & Al-Maadeed, 2014). The SEM shows nanorod-like morphological structure for the PANI–PVA at 200 nm magnification and smoothed and unwrinkled morphology at 1 µm magnification, Figure 2a. In the second step of the fabrication, the photocatalyst NaZnPO₄ (NZP) layer (25 µm) is spin-coated (1,000 rpm) as the second layer. The NZP XRD pattern shows hkl planes at 2θ 19.39° (100), 21.11°(002), 22.73°(101), 24.64°(211), 27.45°(141), 29.13°(102), 31.29°(202), 33.84°(142), 35.53°(023), 37.14°(061), 39.21°(133), 46.71°(262) and 48.22°(333) are assigned to the monoclinic orthorhombic crystal structure (JCPDS: 32-1211) with P2₁/a space group of orthorhombic phase and β phase (Figure 1d, curve b) (Elammari, Durand, Cot, & Elouadi, 1987). The FTIR (Figure 1c, Figure S2 and Table S1) shows the presence...
of Zn–O, Zn–P stretchings at 435 and 590 cm\(^{-1}\) and P–O stretching at 651 cm\(^{-1}\) and 1,000–1,200 cm\(^{-1}\) corresponding to multiple P–O stretching. C–OH frequencies for the residual PEG are observed in the region 2,800–3,000 cm\(^{-1}\). The PL emission spectrum of the photocatalyst NZP in the range of 340–600 nm is shown in Figure 1b, curve b. The emission peaks observed at 390, 494, 520 and 545 nm indicate the photocatalytic behaviour of the NZP. That is, photocatalytic activity is enhanced due to the creation of surface defects by annealing temperature. The PL spectra behaviour of NZP with peak maxima at 300 and 545 nm compared to the PANI-PVA (360 nm) confirms the high luminescent property of the NZP, which is in corroboration with the UV spectra that showed a maximum absorbance at 250 nm, Figure S1A, curve c. SEM shows a flower-like morphology for the NZP which provides large surface area and improved photocatalytic activity. Figure 2b. In the third step of device fabrication, the third layer consisting of aluminium-doped ZnO (AZO) is coated over the NZP to act as a cathodic junction. The prepared AZO material is characterized by XRD. For comparison, the characterizations of the undoped ZnO are also included, Figure 1 curve c and S1B curve b. The pristine ZnO shows the XRD (Figure S1B curve a) peaks at 2\(\theta\) 31.89°, 34.55°, 36.40°, 47.64°, 56.74°, 62.99°, 66.43°, 67.99°, 69.24° and 72.70° and 76.97°. These are assigned to (101), (100), (002), (102), (110), (103), (200), (112), (201), (004) and (202) planes corresponding to the hexagonal crystal structure (JCPDS: 89–7102) with crystal parameters \(a\) (3.248 Å), \(b\) (5.206 Å) and unit cell volume of 47.61 Å\(^3\) and space group P63mc. The aluminium doping in the ZnO lattice positively shifts the 2\(\theta\) values of the (100), (200) and (001) planes (Figure S1C curve b) and increased the crystallite size to 37.3 nm from 32.1 nm, observed for the undoped ZnO, due to the induced lattice strain or oxygen vacancies (Cho, Park, & Kwon, 2015).

Absorption peaks appear in the region from 1,000 to 4,000 cm\(^{-1}\) for different functional groups. A broadband at 3,445 cm\(^{-1}\) is assigned to the O–H stretching mode of hydroxyl group. Peaks between 2,830 and 3,000 cm\(^{-1}\) are due to C–OH stretching vibration of alkane groups. Conductivities of the AZO and NZP are 0.14 S/cm and 80.4 nS/cm, respectively.

The pristine ZnO showed a absorption maximum at 340 nm. The Al doping into the semiconductor ZnO (AZO, 363 nm) red shifted the absorption maxima by 23 nm due to high optical transference and increased amount of valence electrons (Chongsri & Pecharapa, 2014). This is similar to the copper-doped ZnO system which showed higher conduction than the pristine ZnO upon UV illumination due to increased trapping and detrapping of electrons by dopant (Ghosh et al., 2017). The calculated band gap using Tauc’s plot (Figure S3) for the AZO and ZnO is 3.21 and 3.28 eV. The decreased band gap of the AZO indicates the effective detrapping of electrons by Al in the ZnO. The detrapping effect can be effectively used for the self-powering of solar cells. The Al\(^{3+}\) doping replaces the Zn\(^{2+}\) and induces excess of e\(^{-}\). The number of charge carrier was further enhanced by annealing the oxide samples at 800°C under N\(_2\) atmosphere. As the number of electrons increases, the AZO acts as a n-type conductor (Rotella et al., 2017). Four main emission peaks at 393, 410, 438 and 490 nm are obtained for the ZnO and AZO, Figure S4 curve a and b. Al doping into the ZnO decreased the intensities of peaks at 393 and 410 nm, but increased intensities of peaks at 438 and 490 nm.
confirming the enhancement of direct transition of photoelectrons (Ding, Chen, & Ma, 2010).

SEM image of the SPS device is shown in Figure 2d. The cross-sectional view shows the total thickness of 300 µm (Figure 2e). While thickness of the anodic PVA/PANI polymer film is 269 µm (Figure 2e), the thicknesses of the NZP and AZO layers are 25 and 6 µm (Figure 2f), respectively. Smaller thickness of the AZO layer is essential for the effective penetration of the visible light towards the NZP photoactive material to produce photoelectricity. On the other hand, thicker anodic polymer layer is essential for mechanical stability of the whole device. The device fabrication is highly reproducible, required and easily disposable due to its biocompatible components which reduces the environmental pollution.

3.2 | Solar power signal

The electrical I–V characteristics (more importantly $P_{\text{max}}$) of a solar cell or panel are critical in determining the device's output performance and solar efficiency (Figure S5). Figure 3a shows the I–V characteristics obtained at 45 mW/cm² light intensity. The forward-bias a voltage applied at p-PANI/PVA anode clearly demonstrates rectifying behaviour above 0.4 V, Figure 3a, inset, due to the formation of built-in electric field at NZP/polyaniline interface. The device showed a short circuit current density of 240 µA/cm² and an open circuit voltage (OCP) of 0.425 V. The OCP remains constant for any number of cycles. The constant OCP is related to the presence of NZP layer between the p and n materials extending the lifetime of light-generated electrons and holes by promoting the electron–hole pair recombination. This is ascribed to the strong terrestrial solar photons flux which is a primary factor influencing the photoinduced carrier mechanism of a solar cell efficiency limiting. That is, low absorption of photons by the NZP/polyaniline solar cells is solved by increasing the absorption spectrum of polyaniline in the visible region using suitable dopants.

3.3 | Role of photocatalyst NZP on bilirubin oxidation

In the absence of NZP catalyst, the bilirubin shows maximum absorbance at 539 nm for the 1.46 mg/dl (25 µM) concentration and degraded under visible irradiation at $t_{1/2}$ of 6 hr period. On the other hand, the presence of NZP catalyst enhances the rate of bilirubin degradation and the $t_{1/2}$ is reduced by six times (55 min), Figure 4. Hence, the NZP photocatalyst is sandwiched between the p-type (PANI) and n-type (AZO) junction. Now the bilirubin oxidation is made using the solar cell under dark and light conditions. Under the dark conditions, there was no change in the OCP potential (0.427 V) observed in the presence of BR analyte on the sensor surface. On the other hand, under the illuminated condition, the OCP potential increased to 0.8 V in the presence of 58.4 mg/dl (1 mM) bilirubin. This behaviour indicates that the NZP promotes the electron–hole recombination processes and increases the OCP values (Figure 3b) in the presence of BR effectively.

When light illumination induces the voltage development, the anode receives the oxidative electrons from the BR and the reduction processes is induced at the cathode simultaneously. At this time, the blocking layer NZP maximizes the photo processes and enhances the oxidation by injecting the electrons concurrently in the
Manikandan et al. conduction band, which in turn increases the OCP potential. This potential is quite closer to oxygen evolution reaction of metal oxides and, hence, kinetically drives the reaction \( E_{\text{sp}} = 303[B\text{L}] + 0.452 \) (Imran, Manikandan, & Dharuman, 2015). That is, BR oxidation generates electrons which is biased to cathode (n-Al–ZnO), whereas the holes biased to p-PANI/PVA and sustains the detection voltage at 0.832 V. Activities of bilirubin reactions at the solar-powered sensor surfaces depend on the solution pH, and therefore, effect of solution pHs on the catalytic activity is examined, Figure 5a. From the slope \((0.125 \text{ V/pH})\) of pH versus peak potential plot and the Nernstian equation \( \Delta E_{p}/(0.058\Delta pH) = n \), the number of electrons involved in the oxidation reaction is calculated as two protons and two electrons (Manikandan & Dharuman, 2017; Moussa, Kanoute, Herrenknecht, Levillain, & Trivin, 1988). The selectivity of the sensor was examined in the presence of 58mg/dl (1 mM) concentrations of potential interferences like ascorbic acid, uric acid and dopamine (Figure 5b). The interferences do not show any change in the OCP.

The concentration effect of bilirubin is studied in the concentration range from 5.8 \( \mu \)g/dl to 175 mg/dl (0.01 \( \mu \)M–3 mM) (Figure 5c). The OCP versus concentration showed a linear range from 3 \( \mu \)g/dl to 87 mg/dl (0.05 \( \mu \)M–1.5 mM) with \( r^2 = 0.9981 \) and the lowest detection of \( 1.2 \pm 0.06 \mu \)g/dl. As the total thickness of the solar cell device affects the OCP voltage, effect of cell thickness on the open circuit voltage is measured using a commercial multimeter, Figure S6. For this, both NZP and AZO film thicknesses are maintained constant at 25 and 6 \( \mu \)m while the polymer blend thickness is varied by varying the number of coating. The total thickness of constructed solar cell is measured using a screw gauge and plotted against the OCP. It is noted that OCP increases with increasing thickness and reaches a maximum potential.

**FIGURE 4** (a) UV–vis spectra of the degradation of bilirubin at self-powered sensors device fabricated using NZP as a photocatalyst (curve a). Curves b and c represent the UV curves obtained after the degradation of BR at different \( t_{1/2} \). (6 hr (curve b) and 55 min (curve c)) and (B) Photodegradation of bilirubin in the absence (curve a) and presence of NZP (curve c) under dark and visible light of 45 mW/cm\(^2\) irradiation using 250 W halogen lamp.

**FIGURE 5** (a) Effect of pH on bilirubin oxidation potential at the self-powered sensors (SPS). (b) Selectivity of SPS towards bilirubin in the presence of ascorbic acid, uric acid and dopamine interferences. (c) Effect of bilirubin concentration on the open circuit potential of SPS.
TABLE 1 Clinical validation of solar-powered sensor using different blood and serum samples

| Sample   | Estimated bilirubin concentration µM (mg/dl), n = 3 | Clinical detection µM (mg/dl) |
|----------|-----------------------------------------------------|-------------------------------|
| Serum 1  | 26 (1.52 ± 0.06)§ | 27.4 (1.6)§ |
| Serum 2  | 12 (0.7 ± 0.03)   | Unknown                      |
| Serum 3  | 19 (1.1 ± 0.06)   | Unknown                      |
| Blood 1  | 24 (1.4 ± 0.06)   | 27.4 (1.6)                   |
| Blood 2  | 20 (0.7 ± 0.03)   | Unknown                      |
| Blood 3  | 19 (1.1 ± 0.06)   | Unknown                      |

§Represents the bilirubin concentration in mg/dl equivalent to concentrations in micromole.

3.4 | Real sample analysis

The human blood samples containing bilirubin are collected from nearby hospital following the ethical guidelines. Both serum and whole blood samples were used to evaluate the performance of the sensor (Table 1). The developed chips showed consistent data when different chips are used to measure the OCP potential for 0.58 mg/dl (10 µM) bilirubin. For each measurement, a fresh chip is used. No reproducibility is noticed when the premeasured chip is reused for measuring the same concentration of bilirubin second time. That is, similar to glucocectics, the self-powered solar cell-based sensor can be used as disposable chips for regular monitoring. The method is quite fast and simple to be handled by the common and unskilled person. Further, this sensor does not utilize the enzyme for bilirubin sensing and battery for sensing induction which are useful to reduce the cost per analysis.

4 | CONCLUSION

In summary, a self-powered sensor was fabricated using P-N photovoltaic solar cell by simple spin coating method for the direct detection of blood bilirubin without using any active electronics components. High flexibility and mechanical properties are further reinforced by the photo-electrochemical determination of bilirubin under the visible light irradiation. Linear range from 3 µg/dl to 87 mg/dl (0.05 µM–1.5 mM) with r² 0.9981 and the lowest detection of 1.2 ± 0.06 µg/dl observed is well within diagnostic range of jaundice detection in the human physiological system. This forms a basis for developing various non-enzymatic SPS with the integration of additional features for developing simple self-monitoring sensor devices.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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