

Ag/PEPC/NiPc/ZnO/Ag thin film capacitive and resistive humidity sensors

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Abstract: A thin film of blended poly-N-epoxypropylcarbazole (PEPC) (25 wt.%), nickel phthalocyanine (NiPc) (50 wt.%) and ZnO nano-powder (25 wt.%) in benzene (5 wt.%) was spin-coated on a glass substrate with silver electrodes to produce a surface-type Ag/PEPC/NiPc/ZnO/Ag capacitive and resistive sensor. Sensors with two different PEPC/NiPc/ZnO film thicknesses (330 and 400 nm) were fabricated and compared. The effects of humidity on capacitance and resistance of the Ag/PEPC/NiPc/ZnO/Ag sensors were investigated at two frequencies of the applied voltage: 120 Hz and 1 kHz. It was observed that at 120 Hz under humidity of up to 95% RH the capacitance of the sensors increased by 540 times and resistance decreased by 450 times with respect to humidity conditions of 50% RH. It was found that the sensor with a thinner semiconducting film (330 nm) was more sensitive than the sensor with a thicker film (400 nm). The sensitivity was improved when the sensor was used at a lower frequency as compared with a high frequency. It is assumed that the humidity response of the sensors is associated with absorption of water vapors and doping of water molecules in the semiconductor blend layer. This had been proven by simulation of the capacitance–humidity relationship.

Key words: organic semiconductor; poly-N-epoxypropylcarbazole; nickel phthalocyanine; nano-powder; ZnO; sensor
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1. Introduction

In the last decade, organic semiconductor materials have attracted great attention in device fabrication because of their low cost, simplicity of device fabrication, and interesting electrical and optical properties. Organic semiconductors can be used for fabrication of different kinds of sensors for measurement of physical, chemical and biological parameters. Humidity sensors are important for assessment of environmental monitoring^[1–3] and for devices used in many industrial applications. Relative humidity measurements play a vital role in many industries. Some organic semiconductors are very sensitive to humidity^[4,5], temperature^[6,7], and different types of gases, such as ammonia^[8]. Therefore, organic semiconductor-based sensors under different conditions are a very promising field to be investigated.

Humidity sensors have several categories based on their measuring principles, which include capacitive, resistive, hydrometric, gravimetric, optical, and integrated types^[9–11]. Capacitive-type humidity sensors have various advantages, including low power consumption and large output signals. The performance of such sensors is therefore determined primarily by the properties of the hygroscopic material used to fabricate the sensing film and the design of the sensing electrode^[12]. To fabricate the sensors, different techniques and sensing materials have been reported. For capacitive-type humidity sensors, surface micromachining^[13] and bulk micromachining^[14] techniques are used in order to produce a porous silicon-based sensor. A thin-film surface micromachining technique, proposed

by Park *et al.*^[15], was used to manufacture humidity and temperature sensors. For the capacitive-type humidity sensor, cellulose acetate butyrate^[16,17] and polyimide^[18,19] are among the most often used sensing materials. A surface-type capacitive humidity sensor based on copper phthalocyanine (CuPc) was fabricated by Karimov *et al.*^[20]. The capacitance of the detector increased continuously by 200 times with an increase in humidity. The humidity-dependent capacitive and resistive response of a methyl-red thin film surface-type cell was studied in Ref. [21]. The resistance of the sensor decreased by 2 times and capacitance increased by 12 times with a change in humidity from 30% to 95% RH.

Complexes of poly-N-epoxypropylcarbazole (PEPC) are known as photosensitive organic semiconductors that are used for solar cells and photocapacitor fabrication^[22], while nickel phthalocyanine (NiPc) is an organic semiconductor that can be used to make a humidity sensor. Zinc oxide (ZnO) is an inorganic n-type semiconductor with a direct band gap of 3.3 eV. It has high chemical stability, non-toxicity^[23] and is used as a gas sensor^[24]. It would be reasonable to fabricate humidity sensors on the basis of complex blends and investigate them at different frequencies that may show higher performance and stability with respect to the described sensors^[20–23]. In this paper we have investigated the properties of capacitive and resistive sensors fabricated on the base of blended PEPC, NiPc and ZnO nano-powder.

2. Experimental

Figure 1 shows molecular structures of PEPC (here ‘*n*’ is

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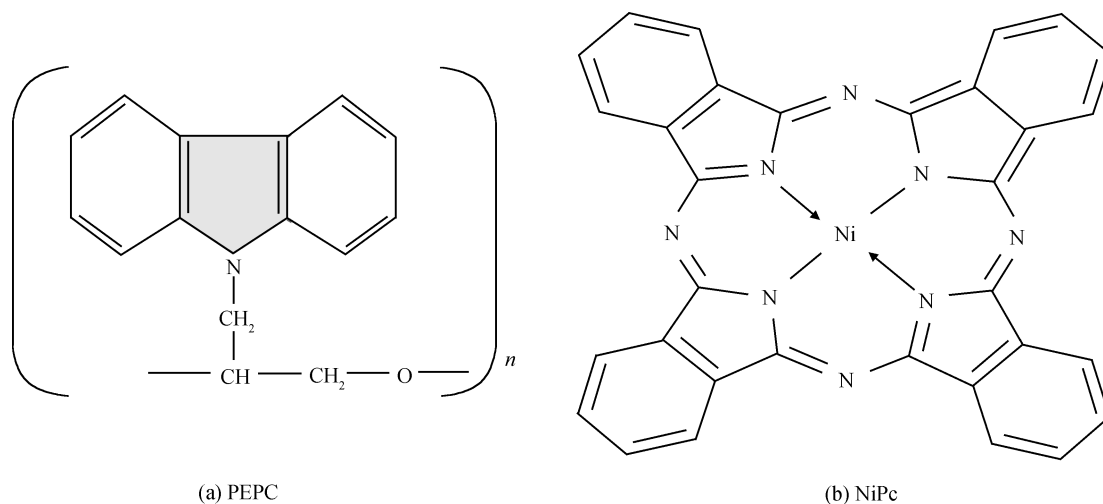


Fig. 1. Molecular structures of (a) poly-N-epoxypropylcarbazole (PEPC) and (b) nickel phthalocyanine (NiPc).

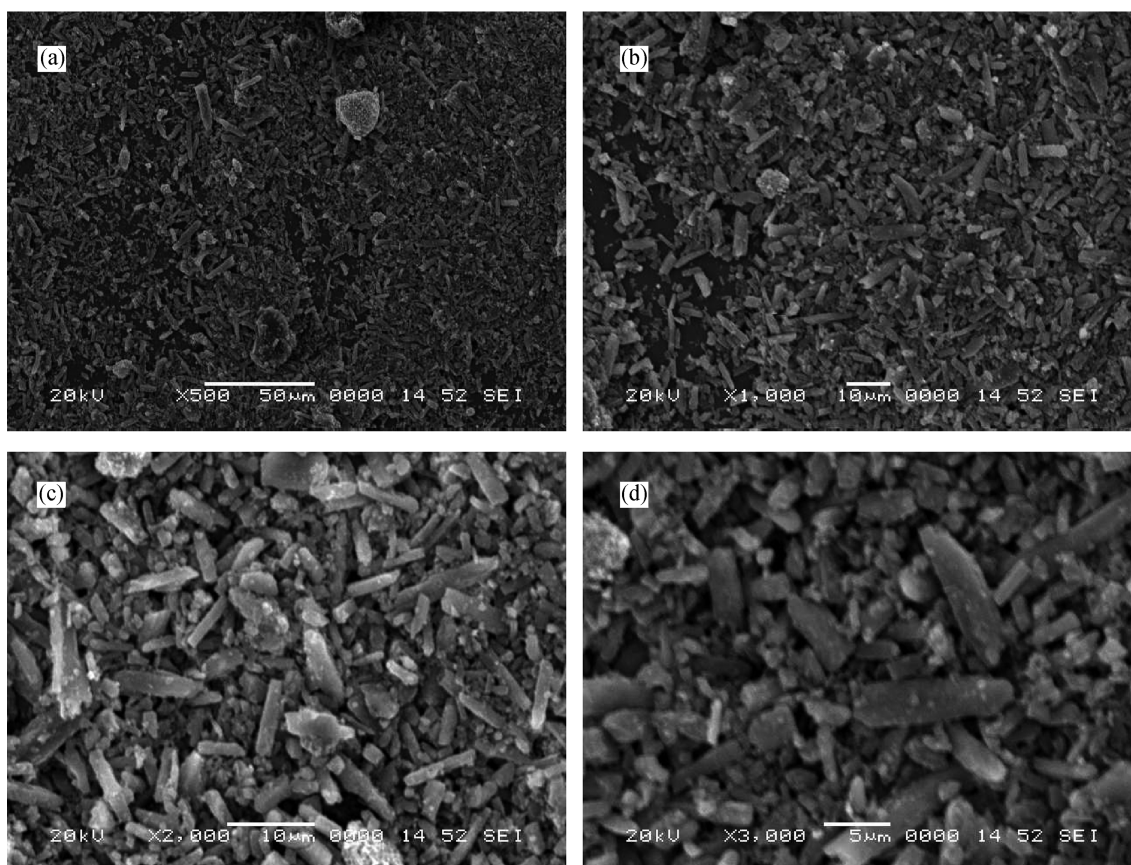


Fig. 2. SEM micrographs of the PEPC/NiPc/ZnO film.

about 4 to 6) and NiPc. The PEPC with a molecular weight of about 1200 atomic weight units was synthesized in the laboratory^[25] and NiPc (Sigma-Aldrich) was commercially purchased.

The ZnO nano-powder was synthesized via the sol-gel method. Zinc acetate dehydrates $Zn(Ac)_2$, 2-propanol and diethanolamine (DEA) were used as the source to produce a well controlled precursor. The Zn source originated from $Zn(Ac)_2$, while 2-propanol and DEA acted as a solvent and stabilizer, respectively. To produce the precursor, firstly, $Zn(Ac)_2$ was

mixed with 2-propanol and stirred for 30 min in an appropriate mole ratio. Subsequently, a reasonable and pre-determined amount of DEA was added to the solution followed by further stirring for 1 h. Then, the solution was filtered and dried in an oven at 100 °C for 30 min. The products were then calcinated at 800 °C for 30 min in air ambient and at atmosphere pressure.

The blend of poly-N-epoxypropylcarbazole (25 wt.%), nickel phthalocyanine (50 wt.%) and nano-powder of ZnO (25 wt.%) was prepared in a 5 wt.% benzene solution. On a glass substrate, two silver electrodes of 100 nm thickness

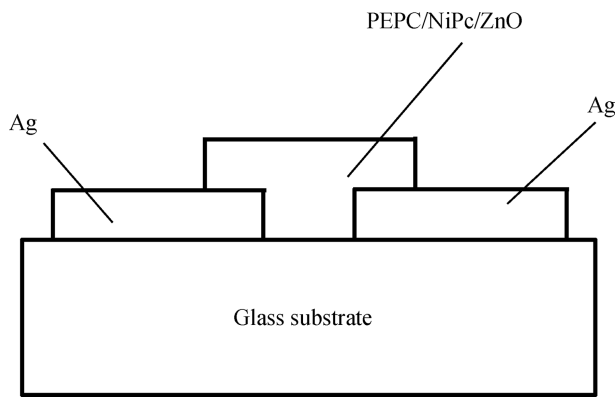


Fig. 3. Schematic diagram of the surface-type Ag/PEPC/NiPc/ZnO/Ag humidity capacitive and resistive sensors.

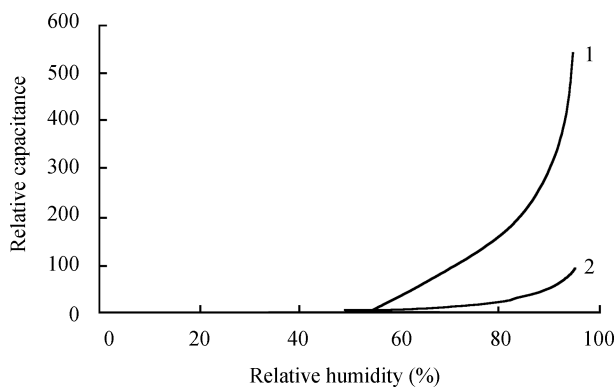


Fig. 4. Relative capacitance–relative humidity relationships for the surface-type Ag/PEPC/NiPc/ZnO/Ag sensor with a semiconductor blend film thickness of 330 nm measured at (1) 120 Hz and (2) 1 kHz of applied voltage.

were first deposited by a vacuum evaporator^[26]: the width of the electrodes and the gap between them were 20 mm and 40 μm, respectively. The spin coating method^[27, 28] was used to deposit the blended thin film using a P-6000 spin-coater with angular velocities of 700 RPM, 1000 RPM and 1200 RPM, which produced film thicknesses of 400 nm, 330 nm and 290 nm, respectively. The film thickness was estimated by an OSK 9763C ellipsometer. Figure 2 shows SEM micrographs of the PEPC/NiPc/ZnO film obtained by JEOL JSM-6460 at different magnifications. The structure of the fabricated Ag/PEPC/NiPc/ZnO/Ag capacitive and resistive surface-type sensor is shown in Fig. 3.

Room temperature measurements of capacitance and dissipation at different humidity levels were done by conventional instruments at a frequency of 120 Hz and 1 kHz in a special chamber. The resistance (*R*) of the samples was determined from values of dissipation (*D*) from the following expression^[29]:

$$R = 1/2\pi fCD, \tag{1}$$

where *f* is the frequency and *C* is the capacitance.

3. Results and discussion

Figure 4 shows the relative capacitance–relative humidity (*R_H*) relationships of the surface-type Ag/PEPC/NiPc/ZnO/Ag

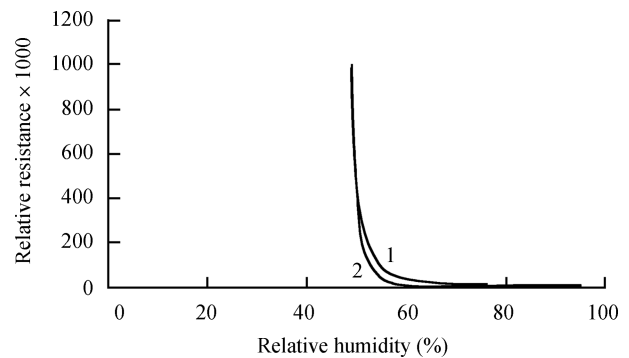


Fig. 5. Relative resistance–relative humidity relationships for the Ag/PEPC/NiPc/ZnO/Ag sensor with a semiconductor blend film thickness of 330 nm measured at (1) 120 Hz and (2) 1 kHz of applied voltage.

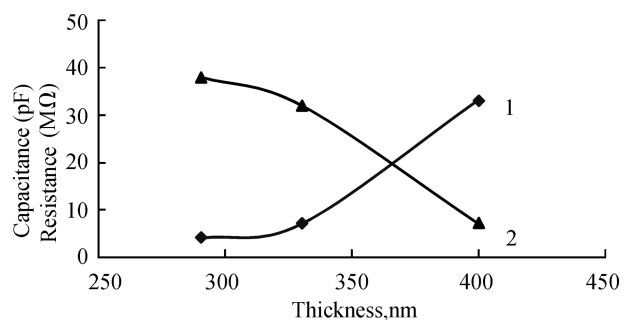


Fig. 6. (1) Capacitance–thickness and (2) resistance–thickness relationships for the Ag/PEPC/NiPc/ZnO/Ag sensors measured at a relative humidity of 50% and a frequency of 120 Hz.

sensor with a semiconductor blended film thickness of 330 nm measured at 120 Hz and 1 kHz of the applied voltage. It is seen from Fig. 4 that the capacitance of the sample increased at 120 Hz and 1 kHz by 540 and 90 times, respectively, when the humidity increased from 50% to 95% RH. Approximately the same results were obtained in the case of the PEPC/NiPc/ZnO film of 290 nm thickness. For the sensor made from a thicker blend film (400 nm), the increase of relative capacitance at the same conditions was equal to 160 and 70 times, respectively. Similar behavior has been demonstrated in capacitance as a function of temperature in polyimide films^[30].

The relative resistance–relative humidity relationships of the Ag/PEPC/NiPc/ZnO/Ag sensor with a 330-nm thick semiconductor blended film were measured at 120 Hz and 1 kHz and are shown in Fig. 5. It is seen from Fig. 5 that the resistance of the sample decreases at 120 Hz and 1 kHz by 450 and 550 times, respectively, with an increase of humidity in the interval of 50 to 95% RH. The same results were obtained in the case of the PEPC/NiPc/ZnO film of 290 nm thickness. For a sensor with a thicker blend film (400 nm), the decrease of relative resistance under the same conditions was 60 and 140 times, respectively. The increase of capacitance and decrease of resistance of the sensor might be caused by the absorption of water vapor in the semiconductor thin film, formation of charge transfer complexes and doping of the blend by H₂O. The data indicates that, most probably, a higher concentration of H₂O is being absorbed in thinner blend films.

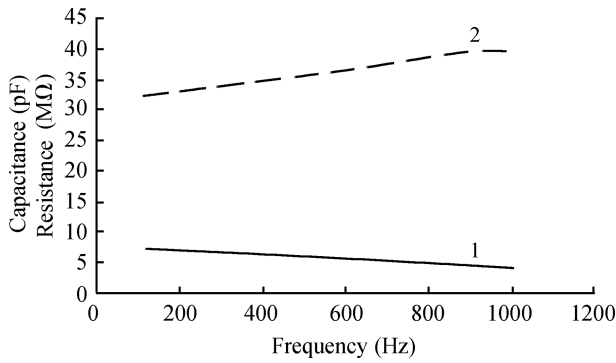


Fig. 7. (1) Capacitance–frequency and (2) resistance–frequency relationships for the Ag/PEPC/NiPc/ZnO/Ag sensor with a blend layer thickness of 330 nm measured at a relative humidity of 50%.

Figure 6 shows capacitance–thickness and resistance–thickness relationships of the Ag/PEPC/NiPc/ZnO/Ag sensors measured at a relative humidity of 50% and frequency of 120 Hz. It is seen that the relationships are non-linear; capacitance increases and resistance decreases with the increase of thickness. This might be due to increase of the cross-sectional area of the sample in the sensor with thicker blend films with respect to a thinner one. Figure 7 shows capacitance–frequency and resistance–frequency relationships for the Ag/PEPC/NiPc/ZnO/Ag sensor with a blend layer thickness of 330 nm measured at a relative humidity of 50%. It is seen that capacitance decreases and resistance increases with increase of frequency. The cause of these phenomena is probably a relatively longer (with respect to the period of applied AC voltage) relaxation time^[31] that may result in the decrease of displacement current due to orientation and deformation of H₂O molecules under the effect of electric field^[32].

The capacitance depends on a number of parameters such as capacitor plate area, distance between plates and relative dielectric constant of the materials between plates. The relative capacitance increase with increasing humidity can be explained by taking into account the different types of polarizabilities. As is known, the capacitance value depends on the polarizability of the material, and there are basically several sources of it such as dipolar α_{dip} , ionic α_i and electronic α_e polarizability^[31]. Electronic polarizability is the most universal and it arises due to the relative displacement of the orbital electrons. As there is a strong effect of humidity on the capacitance and resistance of the sensor, we assume that the absorption of H₂O increases dipolar polarizability (α_{dipH}) in the PEPC/NiPc/ZnO blend with respect to the dipolar polarizability (α_{dip}) due to PEPC and some uncontrolled impurities. As the NiPc may comprise an internal charge-transfer complex we can assume that ionic polarization takes place as well as in this semiconductor blend. The dipolar, ionic and electronic polarizabilities probably affect the capacitance at low frequency (100 Hz–1 kHz) measurements of capacitance whereas the electronic polarizability influences it at higher frequencies. In Refs. [33–35], it was reported that the polarizability was due to the transfer (α_n) of charge carriers as electrons and holes that were present under normal conditions. Therefore, we may write for the total polarizability under normal conditions (α_n),

$$\alpha_n = \alpha_{dip} + \alpha_i + \alpha_e + \alpha_n. \quad (2)$$

For the samples affected by humidity conditions the total polarizability (α_h) may be given by the following relationship:

$$\alpha_h = \alpha_{dipH} + \alpha_i + \alpha_e + \alpha_t, \quad (3)$$

where α_t is the polarizability due to the transfer of electrons/holes (charge carriers) produced under the effect of H₂O molecules, which play the role of dopants. Here we take into consideration that the concentration of H₂O molecules/charge carriers and total polarizability (α_h) are humidity-dependent.

In general form, the relationship between relative permittivity and molecular concentration, N , (or N_n as concentration of the electrons/holes under normal conditions) and polarizability of the molecule is determined by the Clausius–Mosotti relation^[31]:

$$(\varepsilon - 1)/(\varepsilon + 2) = N_n \alpha_n / 3\varepsilon_0, \quad (4)$$

where ε is the relative permittivity, and ε_0 is the permittivity of free space. Taking into account the fact that capacitance is proportional to permittivity, on the basis of Eq. (4), the following expression has been derived^[36]:

$$\frac{C_H}{C_n} = \frac{[1 + 2N_n \alpha_n (1 + k\Delta H)] / 3\varepsilon_0}{[1 - N_n \alpha_n (1 + k\Delta H)] / 3\varepsilon_0} \varepsilon, \quad (5)$$

where C_H and C_n are capacitances under the effect of humidity and under normal conditions (for example at relative humidity of 50%), k is the humidity capacitive factor and $\Delta H = H - H_0$ (initial relative humidity $H_0 = 50\%$) is the increment of relative humidity with respect to the initial level (H_0). Comparison of Eqs. (2–5) shows that actually $\alpha_h = \alpha_n(1 + kH)$. Assuming that the relative permittivity of the PEPC matrix is equal to 4^[36], we can obtain from Eq. (4) the value of ($N_n \alpha_n$) for the case of $C_H/C_n = 1$ and further we have found a value of k that is equal to 2.22 (1/%). So Equation (5) can be used for simulation of the capacitance–humidity relationships. Figure 8 shows the experimental and simulated relative capacitance–humidity relationship for the Ag/PEPC/NiPc/ZnO/Ag sensor at 120 Hz with a blend layer of 330 nm thickness. The simulation results match well with experimental results at lower (50% RH) and

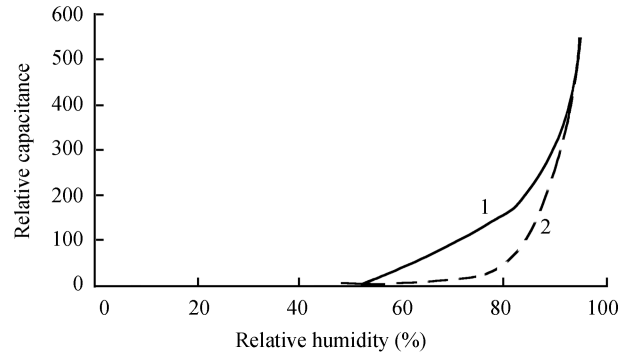


Fig. 8. (1) Experimental and (2) simulated relative capacitance–humidity relationships for Ag/PEPC/NiPc/ZnO/Ag sensor at 120 Hz with a blend layer thickness of 330 nm.

higher (95% RH) levels of humidity and show visible deviation at moderate humidity. Optimization of the simulation will be done in future work.

The obtained characteristics of the Ag/PEPC/NiPc/ZnO/Ag sensors and the discussion above help us to summarize some points relating to the mechanism of properties of the blend. The capacitive and resistive properties of the PEPC/NiPc/ZnO films depend on the presence and concentration of water molecules that are highly polarized. Secondly, the possible formation of charge-transfer complexes (that are a donor-acceptor system)^[4, 5, 33] by water molecules, from one side, and the blend's ingredients (PEPC^[25], NiPc and ZnO), from another side, will increase the hole concentration due to attraction of electrons by the positively charged hydrogen ions (of the water molecules) from the ingredients. Moreover, the presence of ZnO as nano-powder provides the developed surface area that definitely increases the rate of interaction at the molecular level between the environment and the blend's film.

4. Conclusion

Humidity Ag/PEPC/NiPc/ZnO/Ag capacitive and resistive sensors have been fabricated by using the spin-coating method from a solution of a blend of PEPC/NiPc/ZnO. Capacitance-humidity and resistance-humidity relationships were evaluated at different humidity conditions. It was observed that the capacitance increased and resistance decreased with increasing humidity level. It is assumed that in general the capacitive response of the sensor is associated with dipolar polarization of the absorbed H₂O molecules by the blend layer and polarization due to transfer of charge carriers. It is assumed that the decrease of resistance is due to the increase of H₂O molecule concentration and accordingly displacement current, and the concentration of charge carriers doped by water molecules.

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