Tạp chí khoa học
Journal of Science

CONJUGATE POLYMER PEDOT:PSS INCORPORATED WITH NANO-PARTICLES USED FOR GAS SENSING

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Abstract. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) incorporated with nanocrystalline TiO_2 (PEDOT:PSS+nc-TiO_2) and silver nanoparticles (PEDOT:PSS+AgNP) films were prepared by a spin-coating technique. AFM and FE-SEM surface morphologies, UV-Vis spectra and NH_3 gas sensing characteristic of the composite films were studied. The results showed that the PEDOT:PSS+nc-TiO_2 film with a content of 7.0 wt.% of TiO_2 is suitable for both the hole transport layer and the NH_3 sensing characteristic. The response time of the sensor made from this composite film reached a value as fast as 30 s. The rapid response to NH_3 gas could be attributed to the efficient movement of holes as the major charge carriers in the PEDOT:PSS+nc-TiO_2 composite films. Useful applications in the organic electronic devices like light emitting diodes and gas thin film sensors can be envisaged.

Keywords: *PEDOT:PSS+nc-TiO_2 and PEDOT:PSS+AgNP composites; UV-Vis spectra; Hole transport; NH_3 gas sensing.*

I. Introduction

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is a conjugate polymer that can be easily prepared in thin film form. The PEDOT:PSS films have a high conductivity of 80 S/cm and a high transmission in the visible region [1-3] that is why PEDOT:PSS is used as the hole transport layer in many optoelectronic devices such as organic light emitting diodes (OLED), organic solar cell (OSC), electrochromic windows, etc. [4-7]. The PEDOT:PSS possesses also a highly valuable property: when adsorbed by some typical gases, its electrical conductivity changes considerably. Thus the PEDOT:PSS can be used for the functional materials in the gases sensors [8]. Recently, Olenych et al. [12] used the hybrid composites based on PEDOT:PSS-porous silicon-CNT for preparation and characterization of humidity sensors. Various nanocomposite films consisting of conducting polymers mixed with carbon nanotubes (CNT) as an active materials have been prepared for application in gas thin film sensors for detecting the adsorption of gas molecules such as CO [9], NH_3 [10] and vapors of organic solvents or water [11, 12]. Xing et al [13] reported that the formation of a nanometer-scale chemically responsive junction (CRJ) within a silver nanowire (AgNW) strongly affected the sensing properties of nanocomposites. The proposed mechanism of the resistance response for a CRJ, supported by temperature-dependent measurements of the conductivity for CRJs and density functional theory calculations, is that semiconducting p-type Ag_xO is formed within the CRJ and the binding of molecules to this Ag_xO modulates its electrical resistance. We have shown by our experients that with embedding nanocrystalline TiO_2 (nc-TiO_2) particles in PEDOT:PSS, the performance parameters of some electronic devices like OLED and OSC were considerably improved [14].

This work presents our recent results on preparation and characterization the conjugate polymer PEDOT:PSS with embedding of nanocrystalline TiO_2 (nc-TiO_2) and silver nanoparticles (AgNPs) used for monitoring NH_3 gas.

II. Experimental

For preparing an initial solution of PEDOT:PSS, the pure PEDOT powder was dissolved in a largely diluted PSS with a volume ratio of PEDOT:PSS equals 1:10. To get the nanocomposite of PEDOT:PSS with nanocrystalline TiO_2 (nc-TiO_2), the commercial TiO_2 nanopowder with average size of 5 nm was embedded in PEDOT:PSS solution according to the TiO_2/PEDOT-PSS weight ratio of 0.07 (or 7.0 wt.%). To obtain a homogenous dispersion of nc-TiO_2 in the polymer, the solutions (called TPP) were mixed for more 8 hours by using magnetic stirrer.

To prepare AgNPs, we used ethylene glycol ($C_2H_6O_2$) abbreviated to EG as a catalyst agent for synthesizing AgNPs. Basing on the fact that ethylene glycol ($C_2H_6O_2$) produced from ethylene, via the intermediate ethylene oxide, ethylene oxide can react with H_2O to produce ethylene glycol according to the reaction:

$$C_2H_4O + H_2O \rightarrow HO–CH_2–CH_2–OH \quad (1)$$

20 ml of EG was filled in a glass, and magnetically stirred at 45°C for 15 min, then 17 mg of NaCl

was add to the EG solvent to get a NaCl+EG mixture. Heating the last to 100°C, 20 mg of $AgNO_3$ was put into the mixture. The reaction between NaCl and $AgNO_3$ gave a product of an AgCl opaque solution. While EG decomposed to its andehist and played a role of reducing agent for forming AgCl served as seeds for the Ag-nanoparticles growth. This process can be written by following reactions:

$$HO - CH_2 - CH_2 - HO \rightarrow CH_3CHO + H_2O$$

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$$

$$2HO - CH_2 - CH_2 - HO + O_2 \rightarrow 2HO - CH_2CHO + 2H_2O$$

$$2CH_3CHO + 2AgCl \rightarrow CH_3CO - COCH_3 + 2Ag + 2HCl \qquad (2)$$

The last solution is called EGH and kept at a maintained value of pH6. Next, the PEDOT:PSS solution was prepared by mixing 1 ml of PEDOT:PSS and 10 ml of distilled water, then stirred for 1.5 h by ultrasonic machine. The EGH was dropped into the PEDOT:PSS solutions according to a 5.0 wt.% and ultrasonically stirred for 1 h to get completely a homogenous PEDOT:PSS+EGH (called APP) solution.

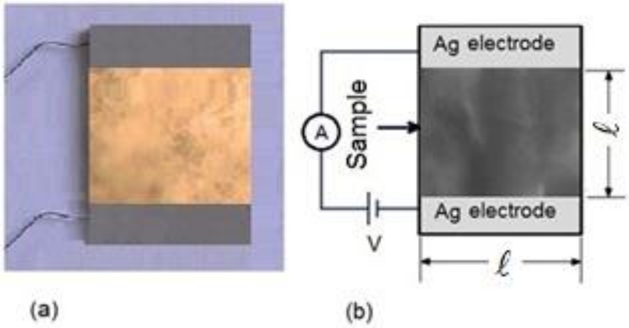

Fig.1. Image of the typical gas sensor based on PEACE film (a) and schematic configuration for measuring the film resistance change by using a constant DC-voltage applied betwen the two Ag electrodes (b).

To prepare the sensing films, the spin-coating technique was used. The two above mentioned solutions (namely TPP and APP) were deposited onto glass substrates integrated with two silver planar electrode arrays with a square of 5×5 mm^2 in size, as shown in Fig. 1. The two electrodes are separated each from other in a distance (ℓ) of 5 mm. The parameters of the spin-coating technique for preparing the composite films were chosen as: a delay time of 120 s, a rest time of 30 s, a spin speed of 1200 – 1500 rpm, an acceleration of 600 rpm, and finally a drying time of 5 min. To dry the films, the samples were immersed in a flow of dry nitrogen gas for 8 hours. For the solidification and completely eliminating the solvents, the film samples were annealed at 120°C for 8h in a “SPT-200” vacuum drier. The obtained TPP and APP composite films were abbreviated to TPPS and APPS, respectively. The thickness of both the TPPS and APPS films was controlled to obtain the values about 500 nm. All the samples were put in a vacuum box until the measurements were carried out.

Ultraviolet-Visible absorption spectra (UV-Vis) was carried-out by using a JASCO UV-VIS-NIR V570 spectrophotometer. The surface morphology of the samples was characterized by using a NT-MDT Atomic Force Microscope operating in a tunnel current mode (for TPPS). For gas-sensing measurement, the prepared sensors were put in a testing chamber of 10 dm^3 in volume. The gas concentrations can be fixed in a range from 100 to 1000 ppm by use of an "EPA-2TH" profilometer (USA). The adsorption process was controlled by insertion of measuring gas (NH_3 gas) and the desorption process was done by extraction of the NH_3 gas when inserted dry Ar gas.

III. Results and discussion

The surface of nanocomposite samples was examined by AFM technique. Fig. 2 shows AFM images of the pure PEDOT:PSS and the TPPS with an embedding of 7.0 wt.% nc-TiO_2. The PEDOT:PSS sample showed a highly porous surface with nanopores, whereas the TPPS composite sample indicated a uniform distribution of completely dispersive TiO_2 nanoparticles. Moreover, the nanopores were not observed in the TPPS composite film, instead of present of nc-TiO2 particles (as indicated at (1) and (2) postions in Fig. 2b). This behavior means that the PEDOT:PSS+nc-TiO_2 composite film was formed with numerous nano-heterojunctions between TiO_2 and PEDOT-PSS.

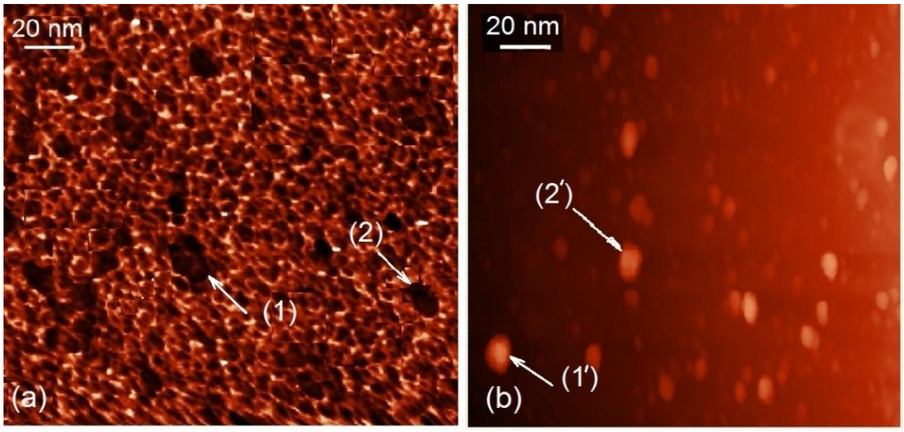

Fig. 2. AFM images of a pure PEDOT:PSS (a) and a PEDOT:PSS+nc-TiO_2 composite film (b).

Fig. 3 shows the optical transmittance spectra (UV-Vis) of the PEDOT:PSS and composite films. These UV-Vis data can be used to estimate the energy bandgap, E_g, of the samples by using the following expression [15]:

$$\alpha h\nu = A(h\nu - E_g)^n . \tag{3}$$

where h is Planck's constant, v is the frequency of the incident UV-Vis radiation, A is a constant and *n* is 1/2 for direct band semiconductors and 2 for indirect band gap semiconductors. As expected, the best fits were obtained for $n = 2$ (indirect band).

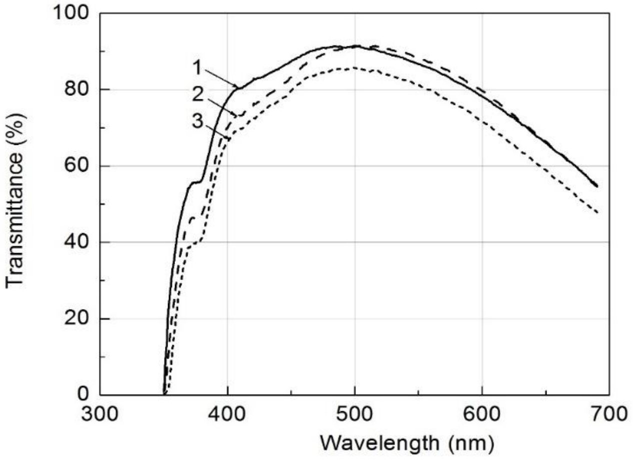

Fig. 3. UV-Vis transmittance spectra of the PEDOT:PSS film (curve “1”) and the films embedding with nc-TiO_2 (curve “2”) and AgNP (curve “3”).

In case the reflectance is ignored, the frequency dependence of $\alpha(\nu)$ can be calculated from the experimental transmittance spectra (T), using the relation [16]:

$$\alpha(\nu) = \frac{1}{d}\ln\left(\frac{1}{T}\right). \tag{4}$$

A graph is plotted between the square of $(\alpha h\nu)$ and $h\nu$ (as abscissa), and a straight line is obtained. From the extrapolation of the straight line to $(\alpha h\nu)^{1/2} = 0$ axis, one can determine the bandgap of the investigated sample (Fig. 4). Thus from our experiments, the energy gap (E_g) for the pure PEDOT:PSS was found to be of approximately 2.43 eV; for the APPS sample (namely PEDOT:PSS+AgNP) E_g = 2.57 eV and for TPPS sample (PEDOT:PSS+nc-TiO_2) E_g = 2.47 eV. The bandgap values of the nanocomposites are little larger than that of a pure PEDOT-PSS film prepared by electrochemical polymerization [17]. In addition, the effect of widening in the bandgap (or blue shift) of the PEDOT-PSS vs. the purity of AgNP and nc-TiO_2 was demonstrated and shown in Table 1. This is quite similar to the reported blue shifts that were observed for the MEH-PPV+nc-TiO_2 [18] or for the PPV+nc-SiO_2 [19], where the blue shift was explained by a reduction in the polymer conjugation chain length due to the presence of inorganic nanoparticles in polymers.

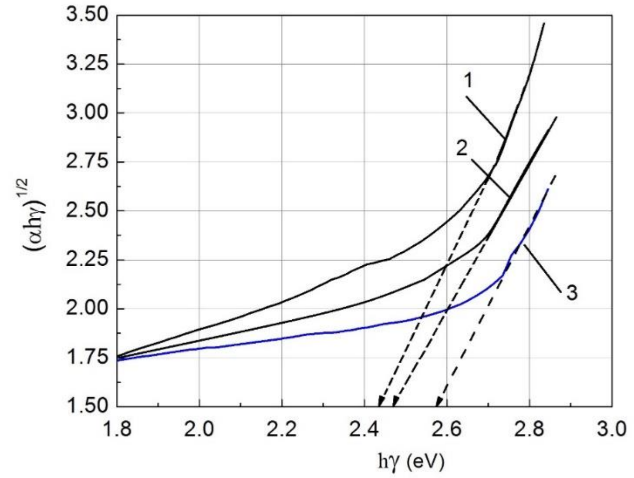

Fig. 4. Plots of $(\alpha h\nu)^{1/2}$ dependence on photon energy ($h\nu$) for determining E_g of the pure PEDOT:PSS (curve "1") and the films embedding with nc-TiO_2 (curve "2") and AgNP (curve "3").

Table 1: The widening in E_g of conjugate polymer (PEDOT:PSS) vs. AgNP and nc-TiO_2 particles

Samples	**Purity content (wt.%)**	**E_g (eV)**
PEDOT:PSS	0	2.42
PEDOT:PSS+AgNP	5.0	2.57
PEDOT:PSS+nc-TiO_2	7.0	2.47

It is known that a PEDOT:PSS can be seen as a p-type organic semiconductor, where holes play the role of major charge carriers. This is why the PEDOT:PSS thin film is often used as hole transport layer (HTL) in OLEDs [20-23]. Following, the effect of sensing through the resistance change of the composite films, when adsorb NH3 gas, is presented.

To test the gas response of the sensors made from above mentioned composites, the film samples were placed in a chamber and device electrodes were connected to electrical feedthroughs. For example, for sensing to NH_3 gas, the samples were put in a testing chamber of 10 dm^3 in volume. By using "EPA-2TH" profilometer (USA) a 100 ppm (in concentration) NH_3 gas value was chosen for monitoring. The adsorption process was controlled by insertion of measuring NH_3 gas and the desorption process was done by extraction of the gas followed by insertion of dry gaseous Ar.

To characterize the sensing performance of the composite films used for the sensors, a sensitivity (η) of the devices was introduced. It is determined by following equation:

$$\eta = \frac{R - R_0}{R_0}(\%) \tag{5}$$

where R_0 is the initial resistance of the sensor, and R - the resistance of the sensor after the NH_3 gas adsorption.

Typical NH_3 gas sensing data for the two sensors, namely APPS and TPPS are plotted in Fig. 5. From this figure, it is seen that with adsorption of NH_3 gas the resistance of the both composite films increased. The sensitivity of the sensors was evaluated equal to ca. 5% (for APPS) and 9% (for TPPS). The responding time of the NH_3 gas sensing was about from 30s. For two sensors, the device resistances quickly recovered to baseline when exposed to Ar gas (i.e. desorption of the NH_3 gas). Indeed, the recovery time of the sensor was estimated as 70s. The response is a little bit better than the one that was reported as 32s in Ref. [24] where the NH_3 gas sensors were made from Ag/polypyrrole nano-composites. This would imply that the electrons generated from the NH_3 adsorption process in the sensor surface eliminated a part of holes in PEDOT:PSS with results similar to those reported in [8]. The fast responding time of the sensor can be attributed to the efficient movement of the holes in the nanocomposite-based hole transport layer. The fact that the TPPS sensor showed a much better sensitivity than the one of the APPS sensor proves that a larger number of holes in the PEDOT:PSS+nc-TiO_2 in comparison with the PEDOT:PSS+AgNP were reached to the sensor surface. This is probably due to the more suitable energy gap structure of the heterojunctions of PEDOT:PSS/TiO_2 than PEDOT:PSS/Ag for the movement of holes, when a polarized electrical field was applied onto two electrodes of the sensor.

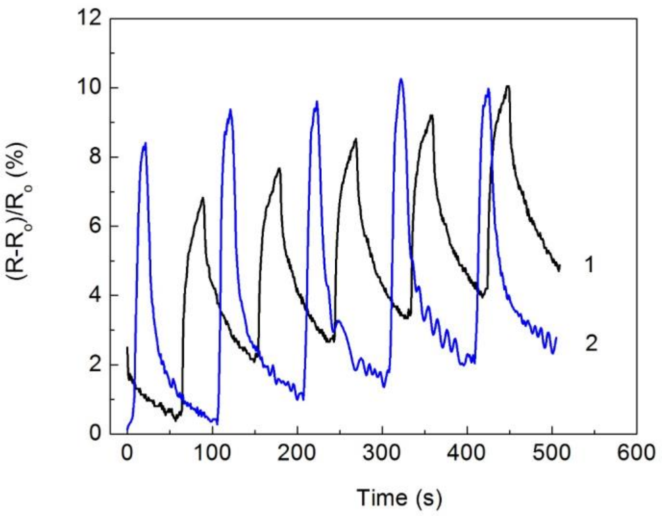

Fig. 5. The sensitivity of the APPS (curve “1”) and TPPS (curve “2”) sensors responding to NH_3 gas with a concentration of100 ppm.

IV. Conclusions

Using spin-coating technique, the PEDOT:PSS films embedded with nanocrystalline TiO_2 and Ag nanoparticles were prepared. The surface morphology, UV-Vis spectra and NH_3 gas sensing of the films were characterized. The results obtained showed that 7.0 wt.% of nc-TiO_2 and 5.0 wt.% of Ag-nanoparticles was the suitable concentrations embedded in the PEDOT:PSS for hole transport layer as well as for NH_3 sensing. The responding time of the sensor made from PEDOT:PSS+nc-TiO_2 possessed a value as fast as 30s that is much better than that of the sensor made from Ag/polypyrrole nano-composites. The rapid response to NH_3 gas was attributed to the efficient movement of the holes as major charge carriers in the PEDOT:PSS+nc-TiO_2 composite films. The obtained results could be suggested for useful applications in monitoring NH_3 gas with concentration range less than 100 ppm.

Acknowledgements

One of the authors (L. M. Long) expresses his sincere thanks to University of Engineering and Technology (VNU Hanoi) and University of Science, VNU Ho Chi Minh city for the support in sample fabrication and experimental measurements.

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VẬT LIỆU TỔ HỢP POLYMER DẪN PEDOT:PSS KẾT HỢP HẠT NANO DÙNG CHO CẢM BIẾN KHÍ

Tóm tắt. Màng poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDPT:PSS) trộn với hạt nano tinh thể TiO_2 (PEDOT:PSS+nc-TiO_2) và nano bạc (PEDOT:PSS+AgNP) được chế tạo bằng phương pháp quay phủ ly tâm. Các kỹ thuật AFM và FE-SEM, phổ hấp thụ UV-Vis và đo cảm biến khí NH_3 của màng tổ hợp được sử dụng để nghiên cứu cấu trúc và tính chất nhạy khí. Kết quả nhận được cho thấy tổ hợp PEDOT:PSS+nc-TiO_2 với 7,0% k.l. TiO_2 là thích hợp hơn cả cho lớp truyền lỗ trống và cảm biến khí. Thời gian đáp của cảm biến làm từ màng tổ hợp đạt giá trị nhanh đến 30 giây. Độ nhạy cao đối với khí NH_3 đạt được là do sự dịch chuyển nhanh của lỗ trống với vai trò hạt tải cơ bản trong màng tổ hợp PEDOT:PSS+nc-TiO_2. Điều này cho phép ứng dụng tổ hợp trên trong các linh kiện điện tử hữu cơ như điôt phát quang hữu cơ và cảm biến màng mỏng hữu cơ.

Từ khóa: *Tổ hợp PEDOT:PSS+nc-*TiO_2 *và PEDOT:PSS+AgNP; Phổ UV-Vis; Truyền lỗ trống; cảm biến khí* NH_3.