Synthesis and Characterization of Nanocomposites of Tin Oxide-Graphene Doping Pd Using Polyol Method

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ABSTRACT

This paper report on polyol method for Pd doped tin oxide-graphene nanocomposite thin film. XRD result shows sharp peaks at certain 2θ value and match with tin oxide, graphene, and Pd database. FTIR result shows peak from alcohol chain for –OH strong bonded absorption (3444 cm^{-1}), also there are aldehyde and ketone which are indicated by C=O strong absorption (1751 cm^{-1}). Moreover, alkene is also formed for decreasing symmetry intensity C=C (1616 cm^{-1}), while alkyne is formed at strong deformation absorption at 646 and 613 cm^{-1}. SEM and TEM result show SnO_2 particles are attached uniformly on graphene surface layer. The composition for C, O, Sn, and Pd are 33.13, 25.58, 35.35 and 5.94%, respectively. This result indicated that the good composition is formed for Pd doped SnO_2-graphene nanocomposite. The nanocomposite is promising materials for toxic gas sensor application at low temperature.

Keywords: *tin dioxide-graphene; palladium; polyol method; composite; nanostructure*

ABSTRAK

Paper ini melaporkan metoda polyol untuk mensintesis lapisan nanokomposit tin oksida-grafena dengan doping Pd. Hasil XRD menunjukkan terdapat puncak yang tajam pada posisi 2θ yang sesuai dengan data base untuk puncak tin oksida, grafena dan Pd, yang menunjukkan telah terbentuknya struktur kristal komposit. Hasil FTIR menunjukkan terdapat puncak rantai alkohol untuk absorpsi ikatan kuat –OH dari H (3444 cm^{-1}), serta terdapat juga aldehid dan ketone yang menunjukkan absorpsi rantai kuat C=O (1751 cm^{-1}). Alkena juga muncul pada absorpsi untuk penurunan intensitas simetri C=C (1616 cm^{-1}), sedangkan alkyne muncul pada absorpsi deformasi yang kuat di 646 dan 613 cm^{-1}. Hasil SEM dan TEM menunjukkan bahwa partikel SnO_2 tersebar secara merata pada permukaan lapisan grafena. Komposisi yang terbentuk untuk C, O, Sn dan Pd secara berurutan adalah 33,13, 25,58, 35,35 dan 5,94%. Hasil ini menunjukkan komposisi masa yang baik terlah terjadi pada komposit SnO_2-grafena dengan doping Pd. Komposit yang hasilkan ini merupakan material yang sangat mejanjikan untuk dapat diaplikasikan sebagai sensor untuk dapat mendetekasi gas beracun yang dapat beroperasi pada temperatur rendah.

Kata Kunci: *tin dioksida-grafena; palladium; metoda poliol; komposit; struktur nano*

INTRODUCTION

Metal oxide semiconductor (MOS) is a type of material that is commonly used as a thin film in the various application including gas sensors. The MOS thin film shows microstructure and electrical tunability properties that can lead to the increase of the sensor performance. Various MOS materials such as SnO_2, ZnO, WO_3, CuO, Co_3O_4 and NiO have been used for gas sensor to detect NO_2, NH_3, CO, H_2 and C_2H_5OH [1-7]. Formation of MOS nanostructured has significantly enhanced the performance of the gas sensor [8-11]. Tin dioxide (SnO_2) as an n-type semiconductor has been extensively applied in various applications including the gas sensor. SnO_2 based nanomaterials have been widely investigated as a gas sensor because this kind of material has some advantages such as fast-response speed, chemical stability, and prominent selectivity. On the other hand, graphene as a two-dimensional (2D) monolayer comprising sp^2-

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bonded carbon atoms, has demonstrated a promising gas-sensing material, especially for the low-temperature region. The composite of SnO_2 and graphene with the doping addition of noble metal like Pd will be the novel materials for high sensor performance [1].

Some previous studies reported that the sensor performance of certain gases based on SnO_2 could be improved by Palladium (Pd) doped. The Pd doping helps to reduce the energy gap of SnO_2 [2,8,12,15]. However, SnO_2-Pd nanomaterial still shows some drawbacks when applied as gas sensors, such as high working temperature (350 °C) and high resistance (~100 MQ). On the other hand, graphene is also widely applied in gas sensors such as in NO_2 gas sensor [16-19], methane [11], alcohol [20-22] and vaporized water. Graphene shows some excellent performances such as ultrahigh sensitivity at extremely low concentrations, high specificity, fast response and recovery, low power consumption, room temperature operation and good reversibility [16]. The combination of the metal oxide-graphene in composite with the doping of noble metal is believed to yield high-performance sensor in the low region operating temperature. There are several strategies to incorporate graphene to the metal oxide, such as polyol, hydrothermal and spray pyrolysis [10,23-25]. In this study, polyol method has selected due to good thermal and mechanical stability, good solvent resistance and high flexibility for surface modification [23,26-27]. The main purpose of this study is to fabricate SnO_2 graphene composite nanostructure and doped with Palladium (Pd) for the potential application of the gas sensor. As far as our knowledge, there is no study has been done before that using this simple technique for the preparation of SnO_2-graphene nanostructure composite that is doped with Pd.

EXPERIMENTAL SECTION

Materials

$SnCl_2$•$2H_2O$, ethylene glycol (EG), palladium chloride ($PdCl_2$) were purchased from Merck, Graphene nanopowder with grain size up to 5 nm was purchased from Skyspring Nanomaterials Texas-USA. The materials were used without further purifications process.

Instrumentation

Transmission Electron Microscope (TEM) images were taken using HITACHI HT7700 and High Resolution (HR) TEM images was taken with HITACHI H9500. Scanning electron microscope (SEM) images were analyzed using JEOL-JSM-6510 LV and HITACHI SU3500. The crystal structure was identified using X-Ray Diffractometer (XRD) Rigaku Analytical X-Ray, Cu (A = 1.54060 A), 40 KV, 25 mA, angle 2θ = 20–90°, step resolution 0.02°/0.5 sec. Fourier-Transform Infrared Spectroscopy (FTIR) measurement was carried out using Prestige 21 Shimadzu Japan.

Procedure

The $SnCl_2$•$2H_2O$ precursor and graphene nanopowder were mixed into 200 mL EG and followed by sonication for 30 min to obtain a homogeneous solution. The solution was refluxed at 197 °C for 12 h and then undisturbed to solidified at least for 12 h. The sample was filtered and then washed using ethanol and DI water. Subsequently, the sample was dried at 100 °C in an oven. Subsequently, the sample was doped with 5% Pd by mixing tin oxide-graphene with $PdCl_2$ in some amount of isopropyl alcohol, stirring for 12 h and followed by drying process at 80 °C. Sample powder was then calcined at 550 °C for 2 h.

RESULT AND DISCUSSION

Fig. 1 shows XRD pattern of SnO_2-graphene doped by 5% Pd nanocomposite that clearly exhibits formation of face-centered cubic crystalline (fcc) orientation of SnO_2 powder according to JCPDS Card No. 710652. The XRD peak exhibited at 2θ = 26.78, 34.06, 38.18, 42.18, 52.06, 54.98, 58.24, 62.34, 65.94, 71.54, 81.56 and 84.02° in accordance with the (110), (101), (111), (210), (211), (220), (002), (310), (112), (202), (400) and (222), respectively. The characteristic XRD pattern of graphene indicated by peaks at 2θ = 26.64 and 42° associated to (002) and (100), respectively,

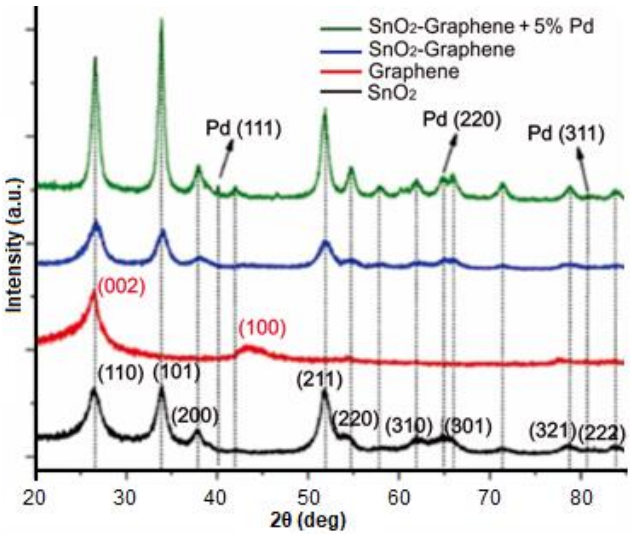

Fig 1. XRD spectra of pure SnO_2, pure graphene, SnO_2-graphene composite, and 5% Pd doped SnO_2-graphene composite

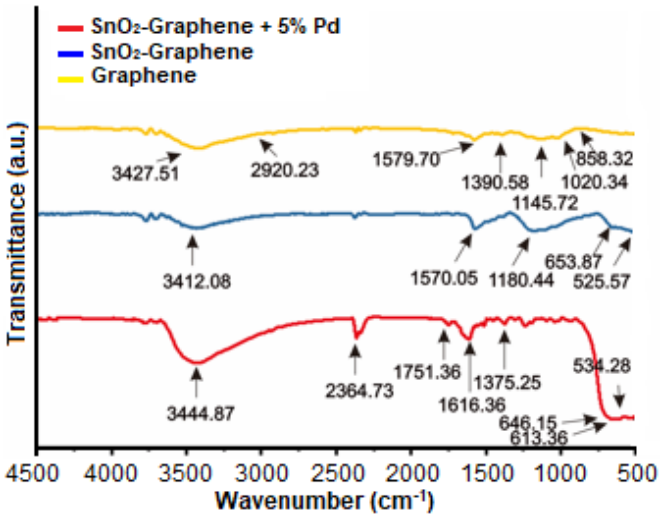

Fig 2. FTIR spectra of pure graphene, SnO_2-graphene composite, and 5% Pd doped SnO_2-graphene composite

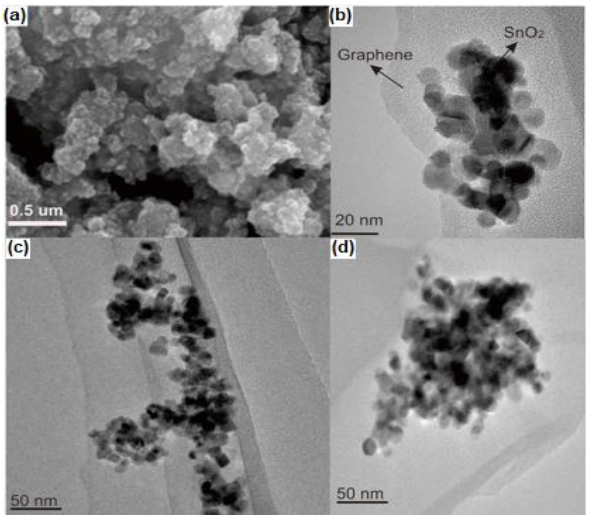

Fig 3. (a) SEM and (b), (c), (d) (TEM) images of 5% Pd doped SnO_2-graphene

Table 1. ZAF Method Standardless Quantitative Analysis of Pd doped SnO_2-graphene

Element	(keV)	Mass%	Error%	Atom%	K
C K	0.277	33.13	0.17	58.55	35.4762
O K	0.525	25.58	0.56	33.94	9.0270
Pd L	2.838	5.94	0.45	1.19	8.4136
Sn L	3.442	35.35	0.60	6.32	47.0833
Total		100		100	

according to the JCPDS Card No.01-0646.

The XRD peaks for palladium has exhibited at 2θ values of 40, 68 and 82° in accordance with the (111), (220), and (311), respectively (JCPDS Card No. 05-0681). The XRD pattern reveals that SnO_2-Pd-graphene has been successfully formed. From XRD pattern result, SnO_2 has tetragonal structure while graphene has one dominant peak that corresponds to (002) plane and well matches with (002) plane of graphite. In composite Graphene-SnO_2, the peak of graphene is not observed because the peak of (002) graphene is overlapped with a peak of (110) of SnO_2. Furthermore, the presence of graphene make the peaks of SnO_2 become weaken indicated that graphene could suppress the growth of SnO_2. From the patterns, adding Pd to the composite make the peaks become higher and sharper indicated that the presence of Pd could enhance the crystallinity of nanocomposite.

The Fourier Transform Infrared (FTIR) spectra of graphene, SnO_2-graphene, and Pd doped SnO_2-graphene are shown in Fig. 2. Graphene shows characteristic absorption peak at 1579 attributes to C=C aromatics vibration and 3427 attributes to OH stretching vibration. A small peak appears at 1751 indicates C=O stretching vibration 1579. Peaks at 1390 and 1020 are observed due to the presence of C-O carboxy and C-O alkoxy vibrations. SnO_2-Graphene shows peaks at 3412 (OH stretching vibration), 1570 (C=O stretching vibration), 1570 (C=C aromatics), 1180 (C-O vibration) and 653-526(O-Sn-O and Sn-O stretching vibrations). The FTIR transmission spectra of 5% Pd doped SnO_2-graphene indicated a carbon chain peaks as shown by a peak at 3444 cm^{-1} originating from stretching vibrations of –OH strong H-bonded. Similarly, aldehydes and ketones are assigned the absorption of C=O strong vibration (1751. cm^{-1}), the alkene is indicated by the absorption of C=C symmetric reduces intensity (1616 cm^{-1}). The alkane is clearly shown by the absorption of CH_2 and CH_3 med deformation (1375 cm^{-1}). The peaks at 646–534 cm^{-1} attribute to O-Sn-O and Sn-O stretching vibrations. Compared to SnO_2-graphene, 5% Pd doped SnO_2-graphene displays almost similar peaks with some shift due to the influence of Pd dopant.

The morphology of SnO_2-graphene was evaluated by Scanning Electron Microscope as showed in Fig. 3a. The SEM image shows that 5% Pd doped SnO_2-graphene particles form uniformly spherical morphologies that seem agglomerates each other with the particles size range between 0.1–0.5 nm. This phenomenon accordance with the XRD results in Fig. 1 shows that after addition of Pd on the SnO_2-graphene composite the peaks tend to be sharper than that of before addition of Pd. Transmission Electron Microscopy (TEM) was carried out to study Pd and

SnO_2 distributions on the graphene layer (Fig. 3b-d). Typical graphene is shown by a layered morphology with Pd and SnO_2 spherical particles distributed on it. The size distribution of Pd doped SnO_2 particles is in the range 5–8 nm.

Energy Dispersive Spectroscopy (EDS) result indicated the composition of SnO_2-graphene consist of C, O, Sn and Pd. Table 1 shows that the mass ratio of C, Sn, and Pd are 33.13, 35.35, and 5.94%, respectively. The mass ratio from EDS confirmed that the composition is proportional and succeed by using polyol method.

CONCLUSION

The one-pot polyol method has been chosen to synthesis CO gas sensor based on tin dioxide-graphene and Pd doped nanocomposite films to improve the sensors' sensing performance by designing novel nanostructures. X-ray diffraction (XRD) results indicated that SnO_2 peaks appeared at 2θ values of 26.78, 34.06° in accordance with (110), (101). The graphene peaks were shown at 2θ values of 26.64 and 42° in accordance with (002) and (100). Pd peaks were clearly exhibited at 2θ values of 40 and 68° in accordance with (111) and (220), respectively. FTIR results showed alcohol ring peak for absorption of -OH strong H-bonded (3444 cm^{-1}), while aldehydes and ketones were indicated absorption of C=O strong (1751 cm^{-1}). Moreover, alkenes were showed on the absorption of C=C symmetric reduces intensity (1616 cm^{-1}), while alkynes were showed absorption of C-H strong deformation at 646 and 613 cm^{-1}. The SEM and TEM results were exhibited that the SnO_2 particles were spread uniform on the surface of the graphene layer. The size distribution of agglomerate Pd doped SnO_2-graphene composite and SnO_2 particles are from 0.1–0.5 and 5–8 nm, respectively. Finally, the composition ratio of C, O, Sn and Pd are 33.13, 25.58, 35.35 and 5.94%, respectively. These results indicated good mass proportion in Pd doped SnO_2-graphene composite. The characterization results showed that the tin dioxide-graphene Pd doped nanocomposite films have been successfully fabricated using polyol method.

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