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Structural and Morphological Study of Sulfonated Graphene Oxide Prepared with Different Precursors

(Kajian Struktur dan Morfologi Grafin Oksida Bersulfonat yang Disediakan dengan Pelopor Berbeza)

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ABSTRACT

In this study, graphene oxide (GO) as nano sized filler to improve the properties of polymer electrolyte membrane was synthesized via the modified Hummers method. Hummers is the most common method used to synthesize GO. The GO is produced by exfoliation of graphite oxide under sonication method. Dispersion by sonication method shows mechanical disruption that breaks apart the graphite flakes which is then sterically stabilized in the base solution. The as-synthesized GO will be sulfonated using different precursors, namely (3-mercaptopropyl) trimethoxysilane (MPTMS), butane sultone (BS) and sulfanilic acid (SA). The structure and morphology of GO and sulfonated GO (SGO) were investigated in details by using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). FTIR analysis confirmed the presence of several functional groups such as hydroxyl, epoxy, carbonyl, carboxyl and sulfonic acid group. The obtained SEM and TEM images indicated, that the morphology of GO dispersion is folded, multilayered and crumpled with some wrinkles. The morphology of SGO showed a folded, thicker and overlap surface compared with GO sheets. Based on TEM image, the addition of sulfonic acid group into the GO network reveals the black spot on the sheets surface. This SGO will act as a potential base material for the application of solid acid catalyst, water purification as well as a composite in membrane fabrication.

Keywords: Graphene oxide; Hummers method; Polymer electrolyte membrane; Sulfonated graphene oxide

ABSTRAK

Dalam kajian ini, grafin oksida (GO) sebagai pengisi bersaiz nano untuk meningkatkan sifat-sifat membran elektrolit polimer telah disintesis melalui kaedah pengubahsuaian Hummers. Kaedah Hummers adalah kaedah yang sering digunakan unutuk mensintesis GO. GO telah dihasilkan melalui pengelupasan kimia grafit oksida melalui kaedah sonikasi. Penyerakan oleh kaedah sonikasi menunjukkan gangguan mekanikal yang dapat memecahkan serpihan grafit dan kemudiannya distabilkan secara sterik dalam larutan bes. GO yang disintesis disulfonat dengan menggunakan pelopor yang berbeza iaitu (3-merkaptopropil) trimetoksilan (MPTMS), butana sulton (BS) dan asid sulfanilik (SA). Sktruktur dan morfologi bagi GO dan GO bersulfonat (SGO) dikaji secara terperinci menggunakan spektroskopi infra merah jelmaan Fourier (FTIR), mikroskopi imbasan elektron (SEM) dan mikroskopi transmisi elektron (TEM). Analisis FTIR mengesahkan kehadiran beberapa kumpulan berfungsi seperti kumpulan hidrosil, epoksi, karbonil, karbosil dan kumpulan asid sulfonik. Imej SEM dan TEM yang diperoleh menunjukkan, morfologi bagi serakan GO adalah berlipat, berbilang lapis dan renyuk dengan beberapa kedut. Morfologi bagi SGO menunjukkan permukaan yang berlipat, lebih tebal dan bertindih berbanding kepingan GO. Berdasarkan imej TEM, penambahan kumpulan asid sulfonik ke dalam rangkaian GO menunjukkan tompokan berwarna hitam di atas permukaan kepingan. SGO ini akan bertindak sebagai bahan asas yang berpotensi untuk aplikasi pemangkin asid pepejal, penulenan air serta komposit dalam fabrikasi membran.

Kata kunci: Grafin oksida; Kaedah hummers; Membran elektrolit polimer; Grafin oksida bersulfonat

INTRODUCTION

The development of graphene material in terms of functionality, different structure and size has gained great interest among the researchers to be applied in different application especially polymer composite application. Graphitic oxide, sometimes known as graphite oxide has been investigated for a long time. Theoretically, graphite oxide is a compound consists of carbon, hydrogen and oxygen molecules (Shulga et al. 2015). Graphite oxide is synthesized by treating the graphite with strong acids such as sulphuric acid, nitric acid or phosphoric acid. These acids were used to remove an electron in the chemical reaction. The first graphite oxide was synthesized in 1859 (Brodie 1859) and since then the method was improved by the researchers in order to reduce the time-consuming and the hazardous of chemicals used (Hummers Jr & Offeman 1958). The Hummers method was found as the best way to overcome the problems. Recently, many studies on the modification of Hummers method have been done to produce the higher oxidation level of graphite oxide by increasing the quantities of potassium permanganate ($KMnO_4$) and adding the mixture of phosphoric acid (H_3PO_4) and sulphuric acid (H_2SO_4) to replace sodium nitrate ($NaNO_3$) (Nakajima & Matsuo 1994; Botas et al. 2013; Shahriary & Athawale 2014)

Graphite oxide and graphene oxide (GO) are really similar chemically but they are really different in structure (Dž et al. 2015). Graphite oxide can be known as multilayered of GO (Zaaba et al. 2017). The main difference between graphite oxide and GO is the distance between adjacent from the individual atomic layers of the compounds that produced by water intercalation. GO exhibits a unique feature where it is easy to disperse in base solution or in organic solvents due to the presence of oxygen functionalities. The common source used to produce GO are graphite flake and graphite powder which are purified to remove contamination (Marcano et al. 2010). GO synthesized from graphite flake or graphite powder can be directly dispersed in water or organic solvents and used for a large scale application such as large graphitic films fabrication.

GO also possesses a hydrophilic properties and its special structure has attracted many attentions for polymer composite membranes as an inorganic filler due to its high ionic conductivity, high mechanical strength and electrically insulating property (Yasmin & Daniel 2004; Jung et al. 2008; Kumar et al. 2014). GO is often known as electrical insulator because of the disturbance of its sp^2 bonding (Huang et al. 2013; Paulchamy et al. 2015). The level of oxidation in GO compound and the method of synthesis influence the ability of GO to conduct electrons (Paulchamy et al. 2015). GO has been used as a potential filler in inorganic membrane in order to improve the properties of membranes (in terms of proton conductivity, water uptake and etc.), as inorganic membrane has better thermal and chemical stability compared to organic membrane (Kamaruddin et al. 2007; Jiang et al. 2013). Kumar et al. 2012 studied about the effects of GO sheets on the proton conductivity of Nafion membrane. The proton conductivities of Nafion/GO, recast Nafion and Nafion 212 were 0.078, 0.043 and 0.068 S cm^{-1} respectively, showed that the presence of GO improve the value of proton conductivity (Kumar et al. 2012). In order to achieve high performance in polymer electrolyte membrane fuel cell (PEMFC), the membrane must have fulfilled the common properties such as high proton conductivity as well as good chemical and mechanical stability. However, the performance of PEMFC also could be limited by polarization factor (Kamaruddin et al. 2007).

The properties of GO could be further improved by the modification or functionalized process. The GO could be functionalized by grafting of sulfonic acid ($-SO_3H$) group to become more usable in various of application especially in incorporation of polymer membrane. In this work, GO was functionalized with MPTMS, BS and SA precursors to produce SGO. The presence of ($-SO_3H$) group is more efficient to dissociate the proton for ionic conductivity compared with the oxygenated group (Hou et al. 2015). Therefore, the ($-SO_3H$) group is expected to hold more water content as well as improve the conductivity, thermal and mechanical stabilities of the polymer electrolyte membrane.

METHODOLOGY

CHEMICALS REQUIRED

Sulphuric acid, H_2SO_4, 98%, hydrochloric acid (HCl, 37%), hydrogen peroxide (H_2O_2, 30%), graphite (Gt) powder, sodium nitrate ($NaNO_3$), $KMnO_4$, (3-Mercaptopropyl)trim ethoxysilane (MPTMS), sulfanilic acid (SA), butane sultone (BS), tetrahydrofuran (THF) and sodium hydride (NaH) were purchased and used as received without further purification.

PREPARATION OF GRAPHENE OXIDE

GO was prepared using modification of Hummers method. In a typical preparation, 3.0 g of Gt powders, 1.5 g of $NaNO_3$ and 100 ml of H_2SO_4 were added into a beaker and kept in ice bath (5 with continuous stirring. After 1 h, 12 g of $KMnO_4$ was added slowly and maintaining the temperature at below than 5. The mixture was stirred for 24 h. After that, deionized water (150 ml) was added slowly into the dark brown slurry and stirred for another night. The H_2O_2 (30%) was added to terminate the oxidation reaction. An appearance of yellow colour indicated a successful oxidation of graphite oxide. The yellow slurry was washed with 5% HCl and followed by deionized water for purification purposes. The brown dispersion was dried in the oven at 70 for 24 h (Wang et al. 2013).

PREPARATION OF SULFONATED GRAPHENE OXIDE

The as-prepared GO (0.2 g) was added to 250 ml deionized water and sonicated for 2 h until the solution was homogenized. The NaH (1.5 g) was added slowly to the GO/deionized water dispersion at 60 for 6 h in order to replace the terminated Na with H in GO (Heo et al. 2013). Then, 12.28 mmol of the precursor (MPTMS, SA or BS) was added dropwise into the mixture and stirred for 24 h at 80 . After the deprotonation reaction, the filtered reactant was immersed in HCl/deionized water (1:1) for 12 h and then washed with ethanol for several times to remove the reactant residue. The product was dried in oven at 80 for 24 h (Heo et al. 2013). Figure 1 gives a schematic diagram of the sulfonation process of SGO.

SAMPLE CHARACTERIZATIONS

The Fourier transform infrared (FTIR) analysis was performed to determine the functional groups of GO and SGO using a Nicolet 6700 spectrometer in the range of 4000-400 cm^{-1}. The overall morphology of GO and SGO were observed using scanning electron microscopy (SEM, Zeiss EVO MA 10, Germany) and transmission electron microscopy (TEM CM12, Philip) with operating voltage of 10 kV and 100 kV, respectively. A common fundamental step in sample

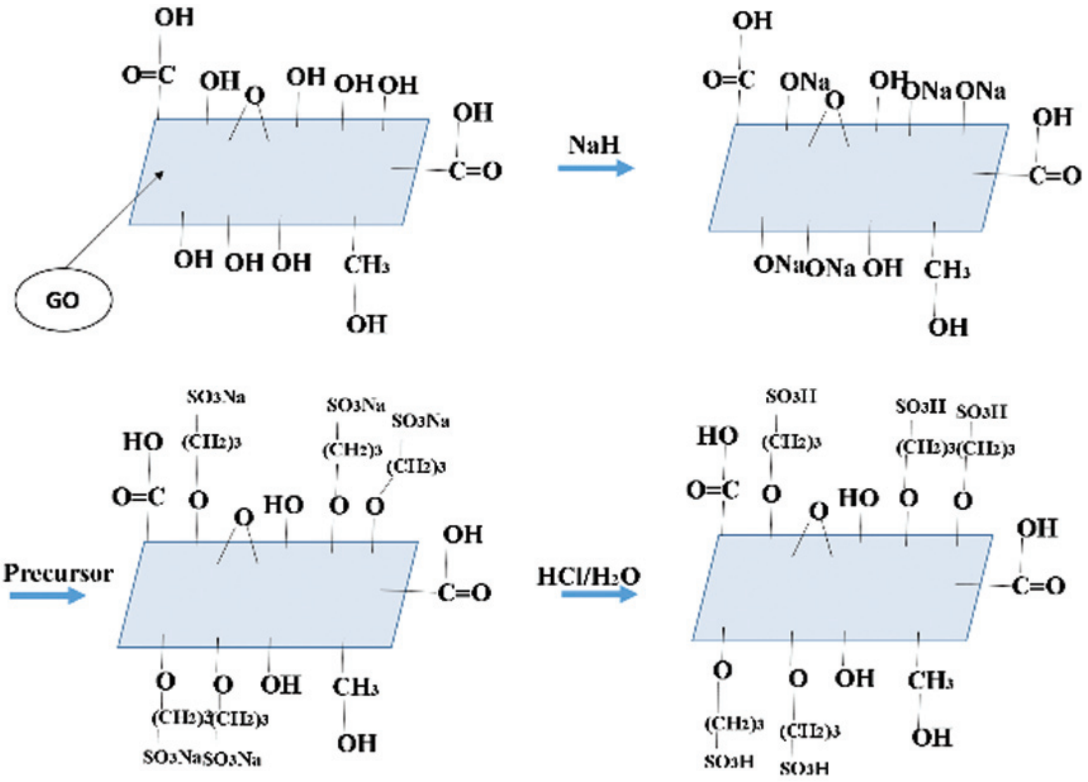

FIGURE 1. Preparation of sulfonated graphene oxide

preparation for SEM is by placing the powder sample on the sample holder using a double sided tape. The GO and SGO were then coated with gold and the SEM images of the samples were taken for further analysis. For TEM analyses, the sample was prepared by diluting the GO and SGO samples into ethanol solution. A drop of the suspension was placed onto a copper grid and then dried at room temperature before being transferred to the analysis room.

RESULT AND DISCUSSIONS

Figure 2 shows the images of synthesized GO solution and SGO powder. In this study, graphite oxide was dispersed in deionized water and sonicated for 2 h in order to form GO dispersion. Based on the literature, graphite oxide can form GO dispersion with long-term stability in deionized water compared with several organic solvents (DMF, NMP, THF) and mostly used in the preparation of graphene-based materials (Paredes et al. 2008). There are a few methods to exfoliate the GO from graphite oxide (Paredes et al. 2008). The most common techniques are by using sonication, stirring or a combination of sonication and stirring (Zhao et al. 2015). Sonication technique can be a very successful approach for exfoliating graphite oxide. However, sonication technique can also damage the graphene flakes by reducing the surface size from micronmeters to nanometers. Potts et al. 2011 reported the sonication technique reduce the lateral dimensions of GO down to a few hundred nanometers. The reduced size of GO from the sonication method is found by atomic force microscopy (AFM) (Potts et al. 2011). Mechanical stirring is also used to produce graphene oxide, but it takes longer time to accomplish.

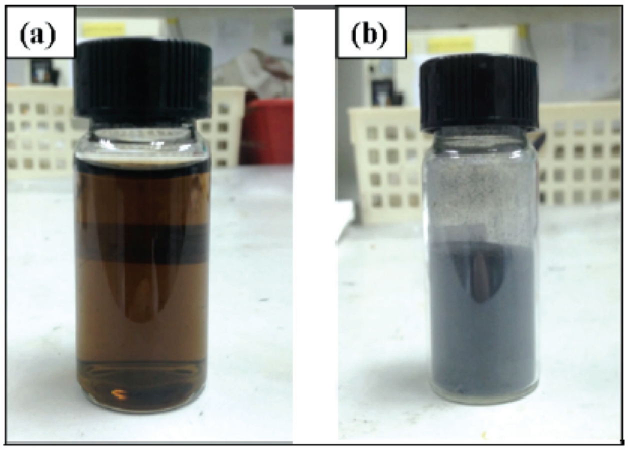

FIGURE 2. Images of (a) synthesized GO solution and (b) SGO powder

Figure 3 shows the morphology and micro-structure of graphite, GO and SGO in SEM images. Figure 3a revealed the SEM image of commercial graphite powder. It is clearly showed that the graphite sheets are stacked together (Paulchamy et al. 2015). The graphite powder was observed at the magnification of 5,000 and provided the sheet size of micronmetres. The morphology of GO in Figure 3b and SGO from different precursors (Figure 3c to 3e) were also viewed at the magnification of 5,000. Figure 3b showed a flat and exfoliated structure of GO. Theoretically, GO has larger surface area with micrometer edges size. The SEM image of GO resembles a thinner curtain sheet compared with commercial graphite. This morphology indicate that graphite was well exfoliated during the oxidation process (Sobon et al. 2012). The surface morphology of SGO-MPTMS (Figure 3c) showed a folded and wrinkled curtain sheet while SGO-BS (Figure 3d) showed the thick and overlapping sheet. The morphology of SGO-SA (Figure 3e) showed a clump of sheets. This might be due to the low solubility of SA precursor in GO/deionized water solution. The solubility of SA in deionized water or selected solvents increased with increasing temperature and time. The folded on the SGO morphology will greatly influenced the membrane's property such as proton conductivities, mechanical properties, water uptake, and so on. This is due to the interfacial hydrogen bond formed between oxygen-related functional group in SGO and polymer that could further facilitate the diffusion of proton (Vinothkannan et al. 2018).

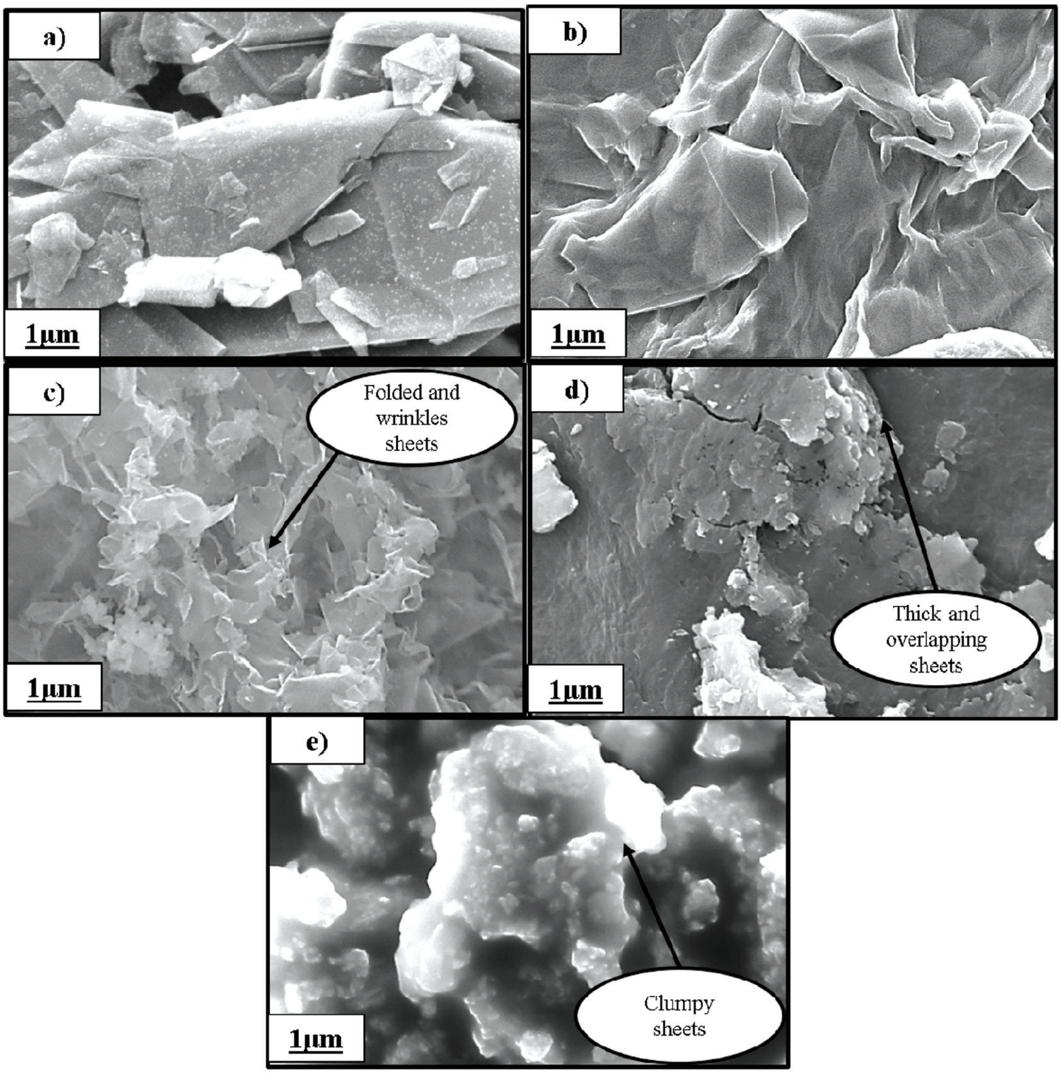

FIGURE 3. SEM images for a) graphite, b) GO, c) SGO-MPTMS, d) SGO-BS, e) SGO-SA at the magnification of 5000X

From the TEM images Figure 4, the morphology of typical graphite powder and GO dispersion are mostly multilayered, crumpled, wrinkled and overlapping graphene sheets (Ahmad et al. 2013). The GO sheet edges tend to fold slightly. The lack of any individual monolayer or thinner layer of graphene sheet showed that the graphite oxide is not fully exfoliated. Therefore, in order to achieve thinner layered of GO, graphite oxide needs to be re-exfoliated by sonicating for longer time before centrifuged to get a uniform distributed layers (Hernandez et al. 2008; Dhakate et al. 2011). For the SGO-MPTMS, SGO-BS and SGO-SA (images Figure 4c to Figure 4 e), the black spots on the surface might be attributed to the presence of -SO_3H groups. The presence of –SO_3H group can be further confirm through scanning transmission electron microscopy (STEM) (Pandey et al. 2014).

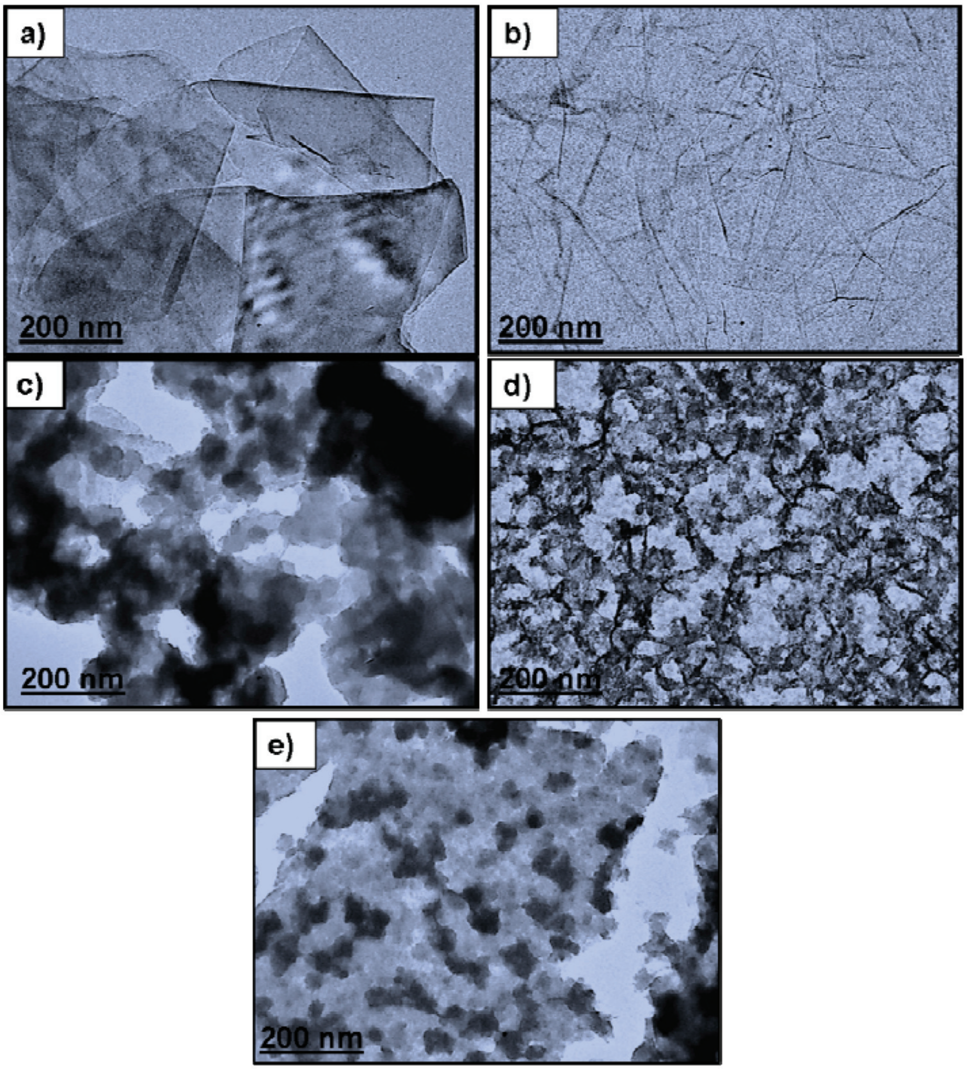

FIGURE 4. TEM images for a) multi-layered commercial graphite, b) overlapping GO in distilled water, c) SGO-MPTMS, d) SGO-BS, e) SGO-SA at the magnification of 17000K

The presence of oxygenated group (such as hydroxyl, carboxyl, carbonyl and oxygen epoxide) of GO was confirmed by the FTIR spectrum presented in Figure 5a. The absorption peak at 3210, 1709, 1012 cm^{-1} were observed due to O-H stretching, C=O stretching and C-O stretching vibrations, respectively (Jiang et al. 2013). For the SGO spectra (MPTMS, SA, BS) in Figure 5b, the peak around 1260-1036 cm^{-1} were observed due to the presence symmetric and asymmetric stretch of –SO$_3$H group (Pandey et al. 2014)

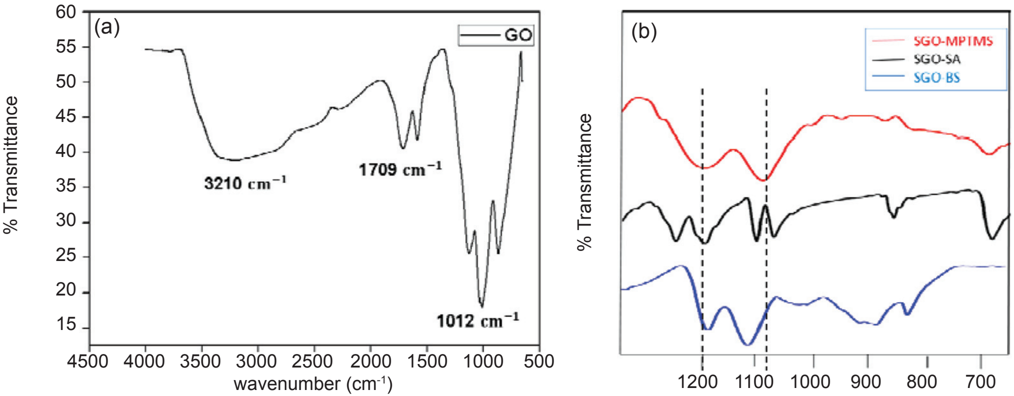

FIGURE 5. FTIR spectra for (a) GO and (b) SGO from different precursors

CONCLUSIONS

In summary, graphite oxide was successfully synthesized by using modified Hummers method and the as-prepared graphite oxide was dispersed in deionized water to form GO dispersion. The colloidal dispersion of GO using the sonication technique was shown as the simplest method to produce the exfoliated GO with thinner layer. TEM images revealed the GO sheets are multilayered, wrinkled and overlapped in deionized water. The presence of oxygenated group in GO and -SO_3H in SGO were confirmed by FTIR analysis. The addition of –SO_3H group into GO is expected to enhance the proton conductivity especially when incorporated into polymer-based membrane.

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