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Synthesis of Hybrid Graphite-Mesoporous Silica Nanoplatelet Using 1-Hexadecylpyridinium Bromide Ionic Liquid as Novel Template

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ABSTRACT

We report the synthesis of hybrid graphite-mesoporous silica nanoplatelet (G-MSNp) prepared by separating graphite nanoplatelet (GNp) using mesoporous silica nanoparticles (MSNs). The resulting G-MSNp possesses high surface area, large aspect ratio and mesoporous structure. The use of ionic liquid is to replace cationic surfactants have effectively solves the incompatibility and aggregation problems between GNp and inorganic materials, at the same time serves as template for the formation of MSNs framework on the surface of GNp. In this work, 1-hexadecylpyridinium bromide ionic liquid was allowed to adsorb and self-assemble onto the surface of GNp in alkaline solution. As a result, the MSNs were formed around the surface of GNp. Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were used to investigate the morphology and microstructure of as-prepared G-MSNp. It was observed that the MSNs is homogenously coated on the surface of GNp and this was further confirmed by the element mapping images of carbon, silicon, and oxygen in the G-MSNp, in agreement with energy-dispersive X-ray (EDX) analysis. The analysis of nitrogen sorption analysis confirms the mesoporous nature of G-MSNp. The pore size distribution calculated by the Barrett–Joyner–Halenda (BJH) method is 8 nm, while the surface area is 128.41 m^2/g. This hybrid nanoplatelet may find promising application as adsorbents to sequester dyes and heavy metal ions from aqueous phase.

Keywords:
Graphite nanoplatelet, adsorbents, mesoporous silica, ionic liquid

1. Introduction

Graphene has emerged as a subject of enormous scientific interest because of its unique electronic, thermal, chemical, and mechanical properties for several promising applications. Graphene sheet (GS) is a single layer of carbon atoms packed in the graphite structure showing a 2-dimensional (2D) honeycomb lattice. This compound is the basic building unit for all graphitic materials, such as fullerenes, carbon nanotubes, and graphite [1].

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Graphite nanoplatelets (GNp), also called graphite nanosheet (GNs) or graphite nanoflake (GNf) is a type of 2D graphitic nanofiller consisting of stacked graphene layers. The stacked graphene layers are bonded to each other by weak Van der Waals forces with a typical d-spacing of 0.34 nm [2]. The thickness of GNp varies from several to dozens of nanometers, as compared to their diameter, usually in the microscale, which leads to the high specific surface area of GNp. However, due to the intrinsic Van der Waals interactions, graphene or graphene derivatives usually easily re-agglomerate, which limits their application. Agglomeration reduces the interface and thus limits the stress transfer across it strongly impacting the mechanical properties. Besides that it also decreases the aspect ratio of the nanomaterial and can even alter its shape reducing its reinforcing efficiency significantly. Thus it is necessary to overcome the extreme hydrophobicity of graphite which leads to aggregation in polar liquids [3].

Researches indicated that the modification of GNp is possibly the most versatile and easily scalable method [4]. The decoration of nanomaterials onto GNp helps to overcome the aggregation of individual graphene nanosheets and nanomaterials themselves [5]. Furthermore, decoration of the GNp with organic or inorganic materials about an important kind of graphene-based hybrid nanomaterials, thus enhances their application such as in catalysis, drug delivery, bio-imaging, tissue engineering, etc.

In this experiment, the GNp was modified with mesoporous silica nanoparticles (MSNs) to form graphene-based hybrid nanomaterials. Typical synthesis of MSNs was done by using organic surfactants such as centrimonium bromide (CTAB) and centrimonium chloride (CTAC) or block co-polymer (Pluronic P123) as structure directing agent (SDA) in acidic or basic condensation of alkoxysilanes. However for this particular experiment, ionic liquid (IL) was used as an alternative template because IL shows similar core structure as SDA used during MSNs synthesis. Ionic liquids are defined as salts with melting point below 100 ºC. Typical ionic liquid consists of two core components i.e. large organic cations and inorganic or organic anions. Therefore, IL is potentially used as the template for the synthesis of MSNs [6]. Significantly, hybrid materials based on GNp and mesoporous silica nanoparticles (MSN) have attracted significant scientific interest because of their remarkable properties that do not exist in the individual components [7,8]. Considering the outstanding properties of GNp and MSN, hybrid nanomaterials of graphite-mesoporous silica nanoplatelet (G-MSNp) would be one of the greatly popular and interest topics in the field of nanomaterial and nanotechnology [9].

2. Methodology

2.1 Chemicals and Reagents

Pyridine, 1-bromohexadecane, ethanol, diethyl ether, acetonitrile, trimethylamine (TEA), tetraethylorthosilicate (TEOS), hydrochloric acid (HCl) were purchased from Chemolab Sdn. Bhd. Graphene nanoplatelets (GNp) were purchased from XG Sciences, Inc. with approximately 2nm thick and average diameter is less than 2 μm average diameter with typical surface area of 750 m^2/g. All chemicals and materials are commercially available and of higher analytical grade unless otherwise specified. The chemicals were used without purification, unless otherwise stated.

2.2 Synthesis of 1-Hexadecylpyridinium Bromide Ionic Liquid ($C_{16}PyBr$)

Pyridinium ionic liquid with 16-carbon ($C_{16}PyBr$) chain length was prepared with modification from previously reported procedure [10]. Briefly, 40 mmol of 1-bromohexadecane and 33 mmol of pyridine were mixed and added into 10 mL of ethanol. The mixture was refluxed at 170°C for 24 hours. The resulting mixture was cooled below freezing point to allow precipitation. The precipitate was dissolved in a small amount of acetonitrile, before reforming as solid by adding diethyl ether. The final product of white powder was filtered and dried at room temperature.

2.3 Synthesis of Novel Hybrid Graphite-Mesoporous Silica Nanoplatelet (G-MSNp)

The MSNs synthesis procedure was adapted and further modified from previously reported method, where the silica precursor (TEOS) and base catalyst (TEA) undergo pre-treatment process [11,12]. 50 mg of GNp and 500 mg of $C_{16}PyBr$ ionic liquid was added into 20mL of deionized water. The mixture was sonicated for 90 minutes. Then, the mixture was stirred and heated at 90℃ for 1 hour. This mixture was denoted as solution A. Next, in a different vial, a mixture of tetraethylortosilicate (TEOS) and trimethylamine (TEA) was heated at 90℃ for 30 minutes. This mixture was referred as solution B. Later, solution B was added dropwise into solution A and the mixture was then further stirred an hour at 90^oC. The solid product was centrifuged, and washed several times with ethanol. The resulting material was refluxed overnight in an acidic ethanol solution in order to remove the ionic liquid template from the mesopores.

2.4 Characterization

The morphology of the particles was observed by using Field Emission Scanning Electron Microscopy (FESEM) with Electron Diffraction X-ray (EDX) Spectroscopy using NOVA NANO SEM 230 (FEI). The sample was placed on aluminium holder. Transmission Electron Micrographs (TEM) images were recorded on Tecnai G2 F20 operating at 200kV. Sample was dispersed in ethanol under ultrasonication for 20 minutes. One droplet of suspension was applied to a 400-mesh carbon-coated copper grid and dried in air. Brunauer-Emmett-Teller (BET) surface areas of the MSNs were measured by physisorption of N_2 at 77 K over a Micromeritics TriStar II 3020. Before measurement, the sample was degassed at 200°C for 6 hours to remove moisture and adsorbed gas. The crystallinity of G-MSNp hybrid nanomaterial was analysed using X-ray Diffraction (XRD) diffractometer (D8 DISCOVER, BRUKER) over 2θ range of $5\text{-}50^o$. To determine the presents of any functional groups and chemical bonds in the nanomaterial, the sample was characterized using Fourier transformed infrared (FT-IR) spectroscopy (Perkin-Elmer Spectrum 2000) in the range of 280 – 4000 cm^{-1}. The thermal stability of the material was examined using thermal gravimetric analysis (TA Instrument TGA Q500) with a heating rate of $10^oC/min$ under nitrogen flow.

3. Results

3.1 The Structural and Morphological Characterization of G-MSNp

Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were used to investigate the morphology and mesostructure of as-prepared G-MSNp. As shown by the FESEM images in Fig.1, it was observed that the MSNs were homogenously coated on the surface of GNp. The nanoparticles coated around the GNp exhibited spherical shape with particles dimension of hybrid MSNs-G is around 2.06 μm to3.48 μm. In addition to that, TEM images (Fig.2) also confirmed the coating of MSNs around the graphite nanoplatelets. It was observed that a dark layer which represents the graphite nanoplatelet was fully surrounded by the nanoparticles [13]. This was further confirmed by the element mapping images of carbon, silicon, and oxygen in the G-MSNp, in agreement with energy-dispersive X-ray (EDX) analysis in Fig.3 [14,15]. However, based on the TEM images, it can be seen that the nanoparticles that surround GNp are highly agglomerated with no visible pore structures.

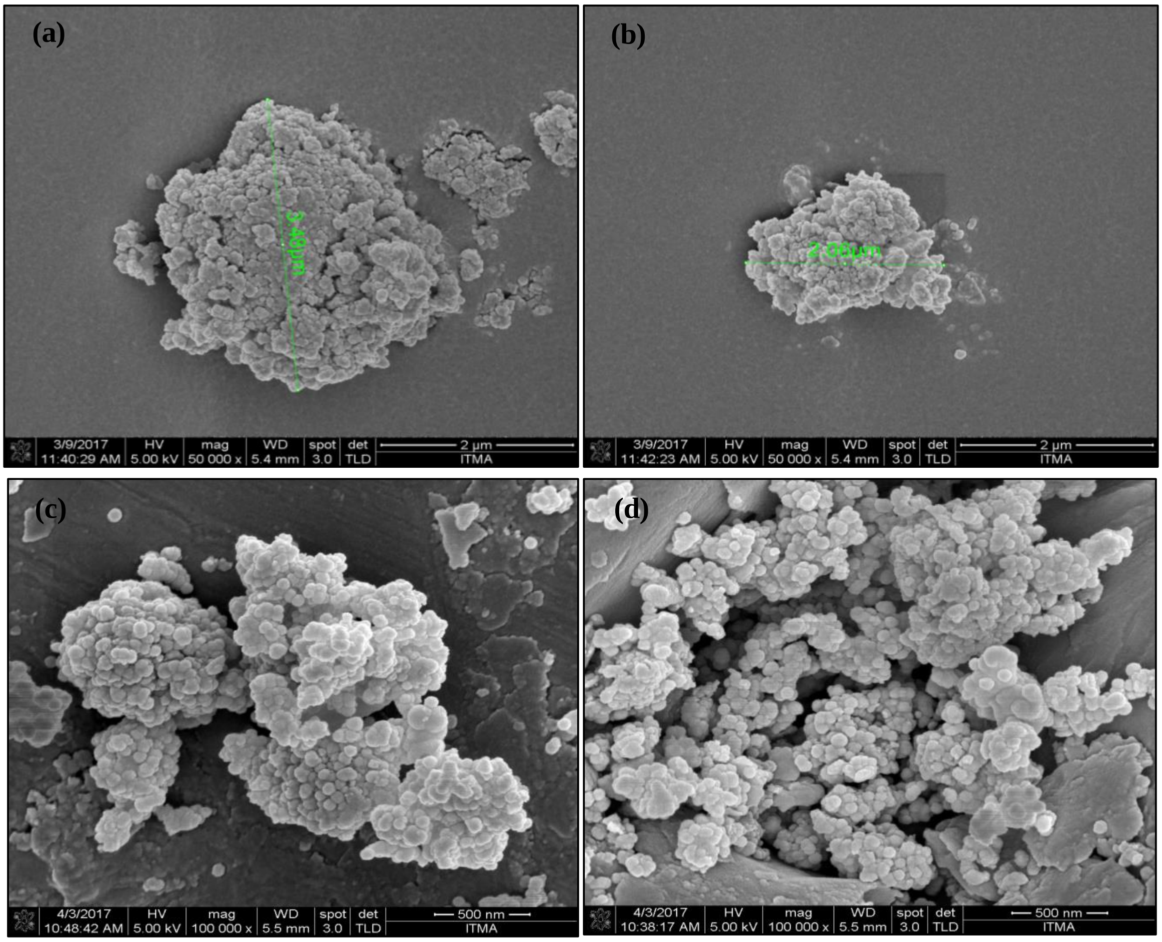

Fig. 1. FESEM images hybrid graphite-mesoporous silica nanoplatelets (G-MSNp)

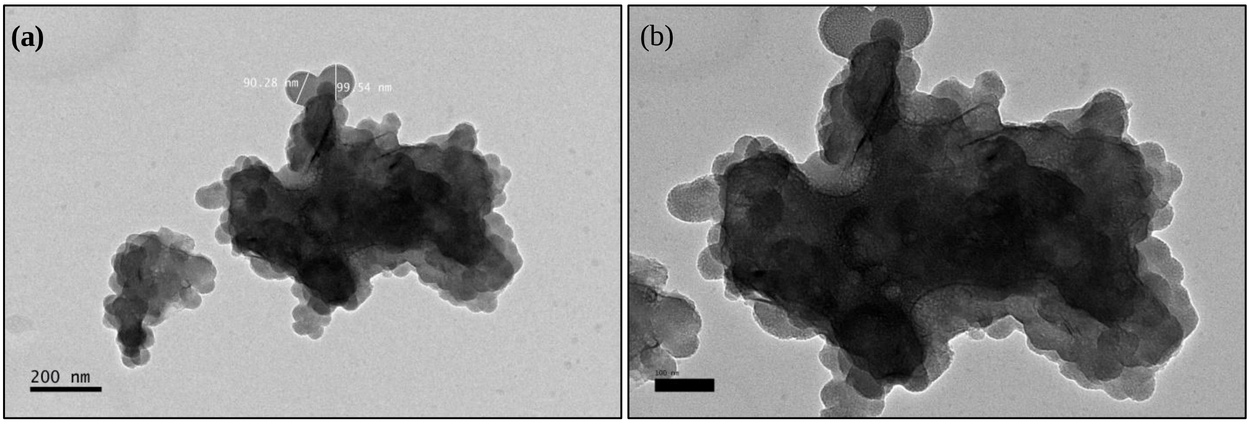

Fig. 2. TEM images hybrid graphite-mesoporous silica nanoplatelets (G-MSNp)

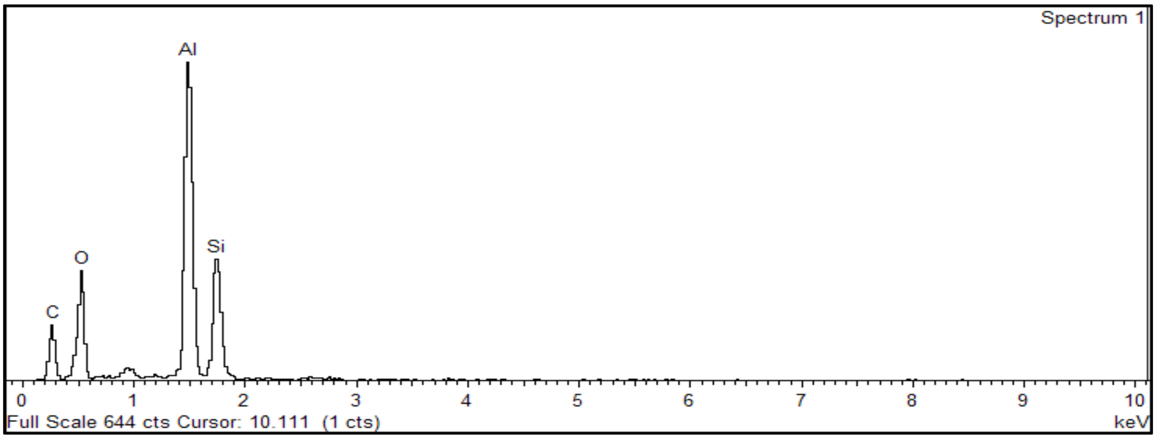

Fig. 3. EDX pattern of hybrid graphite-mesoporous silica nanoplatelets (G-MSNp)

3.2 Characterization of G-MSNp by XRD

The characterization using X-Ray diffraction spectroscopy was aiming to examine the nature of mesoporous structure of silica after combining with graphite. According to the XRD graph plotted (Fig.4), the hybrid GnP-MSN shows a broad peak at approximately 240˚ probably caused by the dominant effect of silica. Whereas, another peak that is seen to be sharper than the hybrid MSNs-G at 400˚ which originates from GNp. From the XRD plot also, it can be seen that the peak represent hybrid MSNs-G shifts more to the left side (lower 2ϴ) and otherwise, the pure GNp peak shift slightly more to the right side. This indicates that, the value d-spacing of hybrid MSNs-G has been increased from the original d-spacing of GNp. This may be due to the elongation in crystal structure of graphene which means the inter-graphene layer at GNp happen to be expended after the hybridization process with mesoporous silica particles. As it is known, the XRD pattern represents the exact unit cell dimensions and the unit cell volume. The shift pick point positions regard the expansion of the lattice. That means the analysed sample were in the nanoscale size which obtains an expansion in their lattice volume or lattice parameters due the crystal minimization to a nanoscale range size [16].

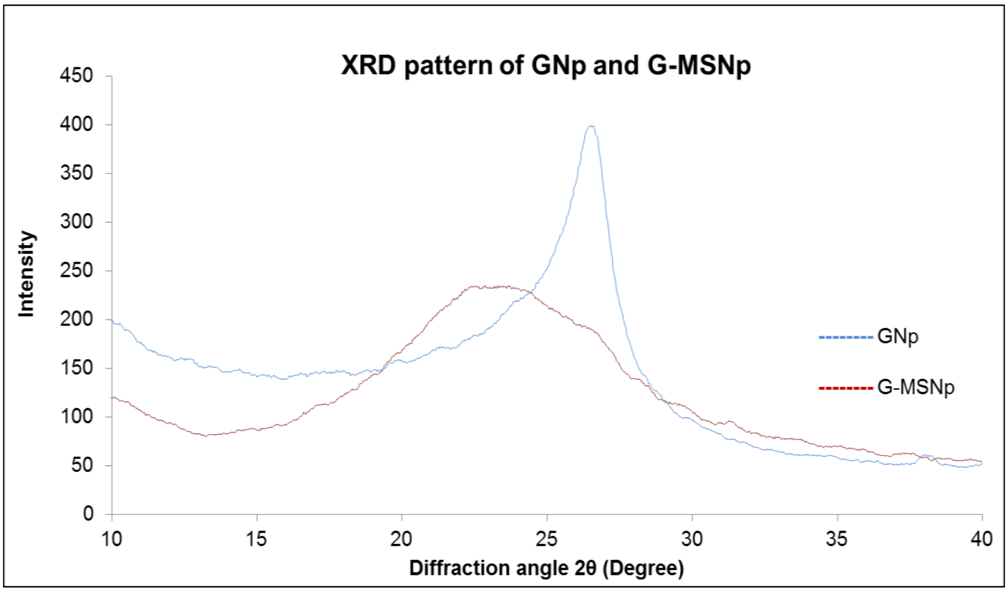

Fig. 4. XRD patterns of graphite nanoplatelet and hybrid G-MSNp

3.3 N_2 Adsorption – Desorption Analysis of G-MSNp

The porousity of G-MSNp sample was analysed using N_2 sorptions isotherm. Based on the result, the pore size distribution calculated by Barrett-Joyner-Halenda (BJH) method was 8 nm, while the BET surface area for MSNs-G and its pore volume was 128.41 m^2/g and 0.19 cm^2/g, respectively. The pores were actually come from the mesoporous particle, which are silica nanoparticles. This mesoporous material able to preserves its pores volume and structure due to the existence of C_{16}PyBr IL template. The template also helps it to produce a frame work with pristine graphite that will yield a very homogeneous particle. Fig. 5 represents the BET isotherm linear graph. According to the graph, at lower pressure region of graph is quite similar to Type II which only corresponds to a single monolayer adsorption. However, type IV adsorption shows the formation of monolayer followed by multilayer. Type IV isotherms confirmed that the silica nanoparticles are mesoporous [17]. The saturation level reaches at a pressure below the saturation vapour pressure. This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at pressure below the saturation pressure of the gas. From the graph we could determine the presence of pores from the hybrid MSNs-G nanocomposites by looking at the whole located between the lines of adsorption and desorption plotted. There is a small whole indicate the presence of pores comes from the mesoporous structure of silica nanomaterial [13].

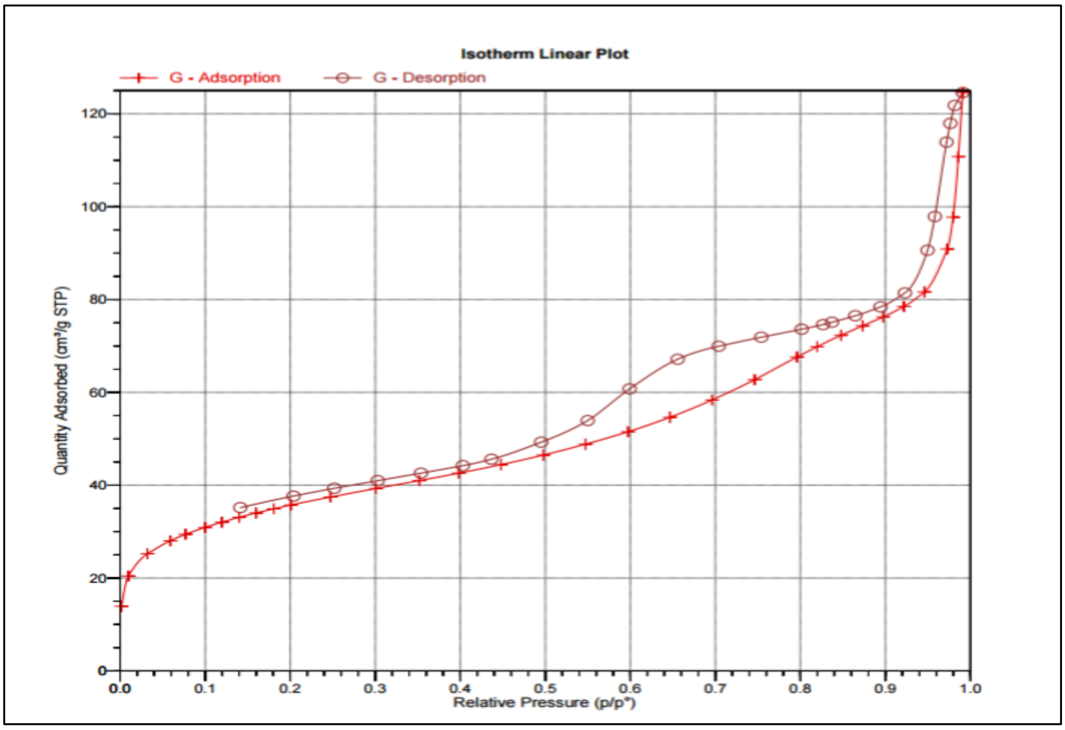

Fig. 5. The isotherm linear plot of MSNs-G 90 ^oC

Figure 6 shows all the functional groups and chemical bonding present in G-MSNp before and after annealing were identified using a Fourier-transform infrared spectrometry (FTIR). The possible functional group that may be obtained from this nanocomposite is C-H (aliphatic) at the range of 3300 cm^{-1} to 2700 cm^{-1}. This peak is considered to be a less intense as it shows only a small intensity in MSNs sample while in MSNs-G sample we could see that the peak almost disappear. This probably happen due to the dominant effect of silica. Besides that, peak observed at 1680 cm^{-1} until 1600 cm-

^{1} in MSNs-G was contributed by the C=C (aromatic) band where there is a broad peak with a small intensity. Next, the Si-O-Si band at 1080 cm^{-1} to 1090 cm^{-1} was detected in both MSN and MSNs-G samples. The peak presence was sharp with a slightly higher intensity due to the attribution of bending vibration with oxygen atom. Plus, in the range of 469 cm^{-1} to 800 cm^{-1}, a sharp peak with higher intensity presence in MSN graph while a broad peak with higher intensity observed at MSNs-G line graph. Both peaks indicate it as a Si-OH band where it is strongly absorb may be due to the higher electronegative different between these two atom [18]. Thus, it was strongly absorbed during both reactions. However, another desired peak that is Si – C in the range of 1350–1400 cm^{-1} was not form at the G-MSNp plotted graph [19]. This indicates that there is no covalent bonding or interaction form between the silica nanoparticles and graphite nanoplatelets. The silica only being "sandwiched" between the layers of graphite and only shows a physical interaction.

3.4 FT-IR Spectroscopy and TGA Analysis of G-MSNp

Based on Fig.7, it is observed that the thermal stability of single component of MSN has improves significantly when it hybridized with GNp. It is known that graphite is a material that possessed extreme thermal resistant. The hybrid of G-MSNp has successfully increases the properties of MSN in terms of thermal stability [20]. The GNp and MSN may not have any chemical interactions between them as there is no signal of Si – C bond observed on the FTIR spectrum. The strong attraction of highly dense packed graphite in a regular hexagonal pattern causes the graphene to nearly inert when in contact with almost any other material. When MSN was hybrid in the interlayer of graphite, the distance between the graphite layers increased. As MSN is tightly sandwiched between graphite layers, it improves the original properties of MSN without changing its nature.

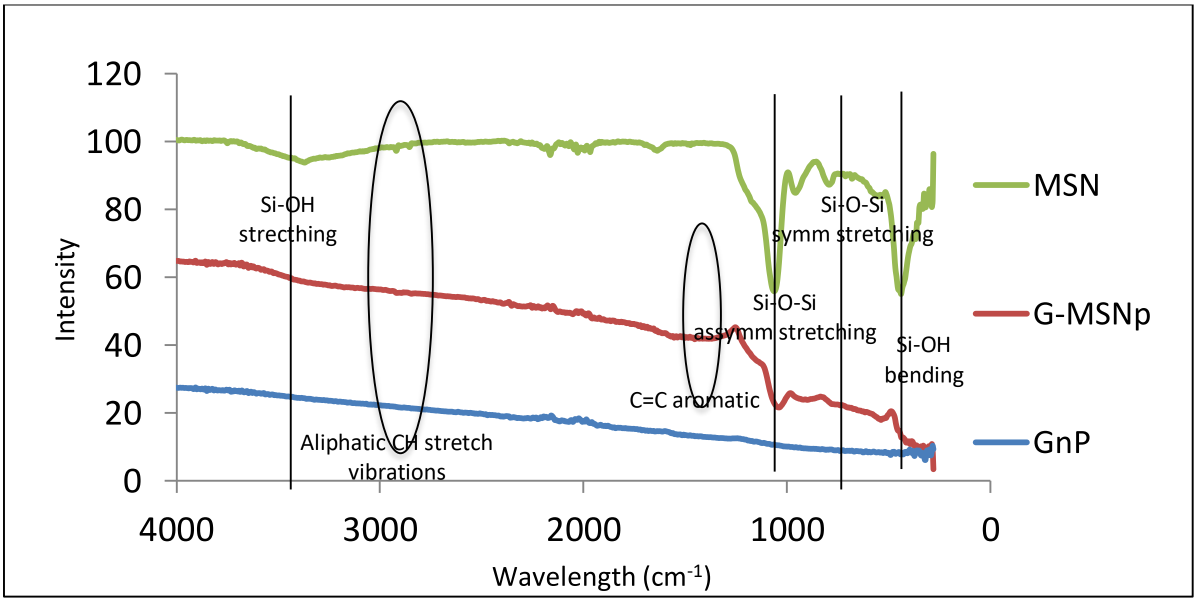

Fig. 6. FTIR spectra of MSN, graphite-nanoplatelet, and hybrid G-MSNp

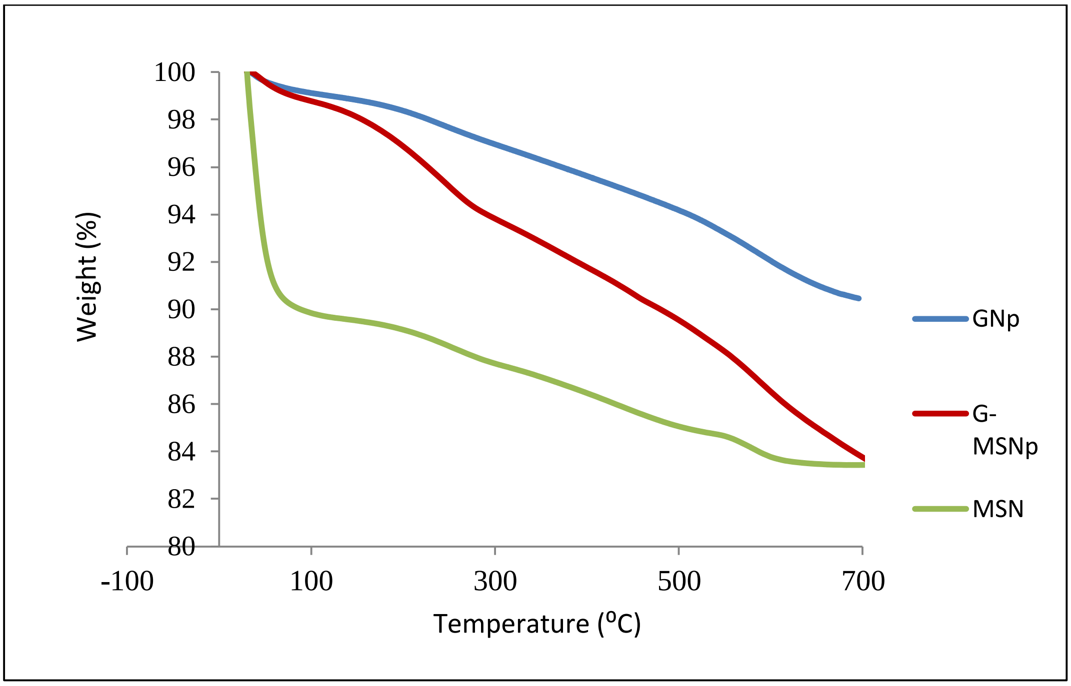

Fig. 7. TGA curves of GNp, MSN and G-MSNp

4. Conclusions

In conclusion, the target product which is graphite-mesoporous silica nanoplatelets (G-MSNp) were successfully synthesized by using 1-hexadecylpyridinium bromide ionic liquid as a surfactant. The particles synthesized exhibit spherical morphology and uniform particles size. Based on TEM and BET analysis, the G-MSNp proved to show relatively good porosity and thus have potential in drug delivery, VOC absorbent, tissue engineering, catalysis etc.

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