

Manuscript

(This manuscript has been prepared based on the data in chapters 6 & 7 of my Ph.D. dissertation titled: 'Structuring and Modification of Open Surface Area Graphene Nanoplatelets to Enhance the Energy Density and Storage Capacity of Electrodes for Electrochemical Energy Storage Applications' (*ProQuest, 2014*), chapters 6 & 7 investigate the effect of few layer graphene nanoplatelet substrate and polymer surfactant on the crystal morphology/phase of manganese oxide deposits and the uniformity of deposition, a new method has been developed to synthesize Mn_3O_4 nanoparticles on few layer graphene nanoplatelets through a polyethyleneimine surfactant mediated method with the potential to find many different applications, this method is believed to have advantages over previously used methods, performance of the few layer graphene nanoplatelet/ Mn_3O_4 composite has been investigated as Lithium-ion battery anode)

Synthesis of Clustered Mn_3O_4 Nanoparticles through a Polymer Surfactant Mediated Route on Few-Layer Graphene Nanoplatelet Surface and Its Application for Electrochemical Energy Storage: Lithium-ion Battery Anode

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Abstract: clusters of Mn_3O_4 nanoparticles have been synthesized on few-layer graphene nanoplatelet (GnP) surface through a route involving Polyethyleneimine (PEI). Effect of PEI as a capping and as a reducing agent in transforming a network of ribbon-like Birnessite- MnO_2 to clustered Mn_3O_4 nanoparticles has been demonstrated. Composite of GnP-clustered Mn_3O_4 nanoparticles formed through this route has potential as Lithium-ion battery anode material.

1. Introduction

Composites synthesized through the deposition of Mn_3O_4 on graphene, carbon nanotube and other carbon based materials have attracted much attention recently as potential electrode materials for different electrochemical applications such as pseudocapacitor [1-5]; Lithium-ion battery [6-10]; and catalysis [11-15]. The primary reason Mn_3O_4 is grown on these substrates in spite of having high charge storage capacity as

pseudocapacitor or Lithium-ion battery electrodes on its own is to enhance its electrical conductivity and/or to impart flexibility to the electrode, which is difficult for a fully metallic electrode. Higher electrical conductivity prolongs the cycle life of an electrode. In addition, the substrate contributes capacity and thus, enhances the overall energy density of an electrode. Mn_3O_4 acts as a spacer and keeps graphene nanosheets separated when used as the substrate for capacitor electrode fabrication. This helps retain the high surface area of graphene nanosheets in the electrode which contributes additional capacitance. Mn_3O_4 supported on graphene and other carbon substrates have recently been investigated as catalyst for methanol electro-oxidation in alkaline media [11]; CO oxidation [12]; and Oxygen reduction reaction (ORR) [12-15]. High surface area substrate uniformly distributes metal particles and prevents their agglomeration and dissolution during catalytic process. In addition, high electrical conductivity of graphene and carbon substrates enhances the electronic conductivity of Mn_3O_4 which is of importance for superior catalytic activity. Composite of Mn_3O_4 combined with carbon based substrate has also found non-electrochemical application such as the removal of Pb and Cu ions from aqueous solution because of their adsorptive behaviour [16].

A myriad of procedures have been adopted for the synthesis of Mn_3O_4 on graphene or other carbonaceous substrates [1, 4, 5, 17, 18, 10, 19, 20, 21, 12, 14, 15, 22, 16, 23]. All of these methods involve one or more of the following factors that complicate the process, such as: long synthesis time; high synthesis temperature; use of hazardous/toxic chemicals; multistep process and the requirement for sophisticated device or highly controlled environment. In fact, the complications associated with the synthesis of Mn_3O_4 have already been acknowledged and investigations have been directed at finding relatively simpler route such as the use of microwave technique [2, 24, 9].

In this research, we report the synthesis of clusters of nearly octahedral shaped Mn_3O_4 nanoparticles on few-layer graphene nanoplatelet (GnP) surface through a simple, wet-chemical, polyethyleneimine (PEI) mediated route. Few-layer graphene nanoplatelets are ultrathin particles of graphite prepared through proprietary intercalation and exfoliation method (XG Sciences, Inc., Lansing, MI, USA). The components involved in this synthesis method are manganese salts (KMnO_4 and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$); water; PEI; and GnP as the substrate. The

synthesis is carried out at a temperature of 80°C only and in open air. Highly crystallized Mn₃O₄ particles, as observed by X-Ray Diffraction (XRD), can be synthesized on GnP surface. It has also been observed that PEI acts as a reducing agent and as a capping agent on a continuous network of ribbon-like Birnessite-MnO₂ (IV) to produce a nearly octahedral shaped nanoparticles of Mn₃O₄ (II, III). It has already been mentioned that composites of Mn₃O₄ on graphene or other carbonaceous substrates find a myriad of applications. Thus, our research findings to synthesize GnP-Mn₃O₄ composite through a simple method should be of interest to a broad group of researchers. In this research, we have investigated the performance of this composite system as a Lithium-ion battery anode only. Our preliminary investigations reveal that the Mn₃O₄ composite synthesized through this method has just as much potential as the ones prepared through other alternative methods.

2. Experimental Procedures

In order to illustrate the effect of PEI on manganese oxide structure, two types of composites were synthesized: GnP-manganese oxide composite in absence of PEI and GnP-manganese oxide composite in presence of PEI. A detailed description for the synthesis of composites; morphological, chemical, compositional characterization; and electrochemical performance evaluation can be found in section 1.1 of the supporting information.

3. Results and Discussion

Figure 1 (a) shows the SEM image [for additional images see figure S5 of the supporting information] of the manganese oxide synthesized in presence of GnP substrate without PEI surfactant (according to table S1 of the supporting information). A continuous network of ribbon-like structure is seen to have grown on the GnP surface. Figure 1 (b) shows the XRD pattern of the same structure seen in figure 1 (a). A comparison of diffraction peaks of the composite to previous literature [9, 25-30] on manganese oxide synthesis reveals that the network-like structure is Birnessite-MnO₂. The peaks in-between 2 θ 20°-30°, 50°-60°, and 70°-80° in figure 1 (b) arise from the GnP substrate [31]. Other diffraction peaks in figure 1 (b) at 2 θ 12°, 13°, and 66° can be indexed as the (001), (111), and (020) reflections of monoclinic Birnessite-MnO₂ [27]. Figure 1 (c) shows SEM

image [for additional images see figure S4 of the supporting information] of manganese oxide synthesized in presence of GnP substrate and PEI surfactant [according to table S2 of the supporting information]. It is clear that the structure of the deposit on GnP surface changes drastically in presence of PEI surfactant. Small and large islands of clustered nanoparticles are seen all over the GnP surface. The clusters are made up of almost octahedral shaped nanoparticles. Figure 1 (d) shows an XRD pattern of the same structure seen in figure 1 (c). The diffraction peaks in-between 2θ 20° - 30° , 50° - 60° , and 70° - 80° in figure 1 (d) arise from the GnP substrate [31]. Rest of the peaks in the diffraction pattern can be attributed to various planes of Mn_3O_4 (II, III) [6-10].

Figure 2 (a, b) show the galvanostatic discharge and charge profiles of the GnP- Mn_3O_4 composite electrode (at 40 mA/gm of composite electrode current rate). The slopes and plateaus in the profiles can be interpreted in terms of the mechanism of Lithium reactivity with Mn_3O_4 and the intercalation of Lithium ions in the interlayer spaces of graphene in GnP. The detailed mechanism of Lithium reactivity with Mn_3O_4 has been discussed in literature [6-10, 32]. In brief, the sloping parts from around 1.75V to 0.3V (point ‘a’ to ‘b’) in the galvanostatic discharge profile of first cycle correspond to two main processes: (i) formation of the solid electrolyte interface (SEI) on the GnP substrate and the Mn_3O_4 particles; and (ii) the initial reduction of Mn_3O_4 to MnO. These phenomena appear as peaks in the discharge part of the cyclic voltammetry (CV) profile of first cycle of the electrode at around 0.65V and 1.24V [see figure S2 of the supporting information]. The first galvanostatic discharge profile of first cycle from 0.3V to 0.01V (point ‘b’ to ‘d’) corresponds to the reactions related to Lithium reactivity with Mn_3O_4 [6-10] as well as the intercalation of Lithium ions [33, 34] in the interlayer spaces of graphene in GnP. The well-defined plateau at around 0.3V in the galvanostatic discharge profile of first cycle corresponds to the further reduction of MnO to Mn and the formation of amorphous Li_2O (point ‘b’ to ‘c’). The first galvanostatic discharge profile from 0.2V to 0.01V (point ‘c’ to ‘d’) corresponds to the intercalation of Lithium ions in the interlayer spaces of graphene in GnP [33, 34]. The peak in the CV profile at the end of the discharge part of the first cycle corresponds to both this transformation of MnO [6-10] as well as the intercalation of Lithium ions [33, 34] in the interlayer spaces of graphene in GnP. The plateau observed at 0.3V in the first galvanostatic discharge profile begins at 0.55V (point ‘a’ to ‘b’) in the discharge profile of the

second cycle which indicates the ease of Lithium reactivity beginning the second cycle [6-10]. This appears as a peak around 0.4V in the discharge part of the CV profile during the second cycle [6-10]. The intercalation of Lithium ion in GnP can be distinguished separately and appears at the end of the discharge part of the CV profile during the second cycle [33, 34]. The change in slope beginning at 1.2V and the following plateau (point 'e' to 'f') in the galvanostatic charge profile correspond to the oxidation of Mn to MnO [6-10]. Another relatively less distinguishable change in slope above 2V (point 'g' onwards) corresponds to the further oxidation of MnO to Mn₃O₄ [6-10]. These appear as a sharp peak at 1.25V and a depressed peak at 2.4V during the charging part of the CV profile [6-10]. The galvanostatic charge profile from 0.01V to 0.25V (point 'h' to 'i') corresponds to the de-intercalation of Lithium ions from the interlayer spaces of graphene in the GnP [33, 34]. The peaks at the beginning of the charging part of CV profile are representative of Lithium de-intercalation from the inter-layer spaces of graphene in GnP [33, 34]. These charging plateaus and peaks don't change from the first cycle to the second cycle.

Figure 2 (c) shows the galvanostatic discharge-charge cycle performance of the GnP-Mn₃O₄ composite electrode for 15 cycles (at 40 mA/gm of composite electrode current rate). The electrode delivers a discharge capacity of 704 mAh/gm during the 1st cycle with a coulombic efficiency of 68% only. In the 2nd cycle, the electrode delivers a discharge capacity of 491 mAh/gm with a coulombic efficiency of 96%. The discharge capacity and the coulombic efficiency are raised to 516 mAh/gm and 97% respectively at the end of the 15th cycle. High discharge capacity and low coulombic efficiency during the 1st cycle can be attributed to electrolyte decomposition and the formation of SEI layer. Pristine GnP delivers a discharge capacity of about 314 mAh/gm with a coulombic efficiency of 69% in the 1st cycle (at 40 mA/gm of pristine electrode current rate). It delivers a discharge capacity of 224 mAh/gm with a coulombic efficiency of 96% at 2nd cycle and a discharge capacity of 220 mAh/gm with a coulombic efficiency of 98% at 4th cycle [see figure S3 of the supporting information]. The charge capacity remains constant at 216 mAh/gm from 1st cycle to 4th cycle. According to Thermo- Gravimetric Analysis (TGA), the GnP-Mn₃O₄ composite has about 57.5wt% GnP content. This would yield a discharge capacity contribution from Mn₃O₄ itself of about 852 mAh/gm (at 40 mA/gm of composite electrode current

rate and if we assume that GnP delivers same discharge capacity in the composite electrode as that of the pristine GnP electrode) [see figure S6 of the supporting information].

Figure 2 (d) shows the galvanostatic discharge-charge cycle performance of the GnP-Mn₃O₄ composite electrode (at 100 mA/gm of composite electrode current rate) for 25 cycles. The electrode delivers a discharge capacity of 720 mAh/gm during the 1st cycle with a coulombic efficiency of 67%. In the 2nd cycle, the electrode delivers a discharge capacity 498 mAh/gm with a coulombic efficiency of 96%. A discharge capacity of 485 mAh/gm with a coulombic efficiency of 97.5% is obtained at 25th cycle. Please note that different two-electrode coin cells were assembled for the determination of discharge-charge performances at different current rates of the GnP-Mn₃O₄ composite electrode. The performances are reproducible.

Investigation of composites of Mn₃O₄ with graphene or other carbon substrates have been carried out under widely different conditions [6-10]. These conditions include different methods for Mn₃O₄ synthesis; Mn₃O₄ morphologies; substrates for Mn₃O₄ deposition; wt% of Mn₃O₄ in the composites; and experimental conditions such as different current rates and number of cycles etc. Wang et al. [7] have reported the performance of RGO (11.4 wt% in the composite) decorated with 10-20 nm diameter Mn₃O₄ particles. A capacity of 900 mAh/gm (normalized with respect to the weight of Mn₃O₄ in the composite) and 810 mAh/gm (normalized with respect to the total composite weight) at a current rate of 40 mA/gm of composite has been obtained at the end of 5th cycle. Free Mn₃O₄ delivers a capacity <300 mAh/gm in the first cycle and it falls to 115 mAh/gm at 10th cycle at a current rate of 40 mA/gm Li et al. [9] have reported the performance of 20 nm diameter Mn₃O₄ particles on graphene (18.8 wt% in the composite) substrate. This composite delivers a capacity of 900 mAh/gm at 50th cycle at 40 mA/gm current rate. A capacity >800 mAh/g is obtained even at 100 mA/g current rate. In this study, bare Mn₃O₄ shows a capacity nearly similar to that of the composite. However, the capacity falls continuously to 450 mAh/gm at the end of 50th cycle. Lavoie et al. [8] have reported that XGM-5 (34.3 wt% in the composite)/needle-like Mn₃O₄ composite delivers a capacity of 720 mAh/gm even at 100th cycle at a current rate of 75 mA/gm which is slightly better than the performance of RGO/Mn₃O₄ composite (675 mAh/gm). Free Mn₃O₄ particles initially deliver a high capacity; however, it falls rapidly below 300 mAh/gm under 20th cycle.

Li et al. [35] have reported the performance of 10-15 nm Mn_3O_4 particles on Ordered Mesoporous Carbon (OMC) substrate (79.7 wt% in the composite). A capacity of 795 mAh/gm has been obtained at 50th cycle at 100 mA/gm current rate. Free Mn_3O_4 particles deliver a capacity of around 400 mAh/g in the first cycle which falls to 148 mAh/gm at 50th cycle. Wang et al. [9] have reported the performance of nanorod-like Mn_3O_4 particles on carbon substrate (1.2 wt% in the composite). A capacity of 473 mAh/gm has been obtained at 50th cycle at a current rate of 40 mA/gm. Free Mn_3O_4 particles deliver a capacity of 155 mAh/gm at 50th cycles. Nam et al. [36] have reported the performance of Mn_3O_4 nanoparticles (72 wt% in the composite) on GNS substrate. The composite delivers a capacity of 500 mAh/gm with less significant capacity fade after 40th cycle at a current rate of 60 mA/gm. Free Mn_3O_4 particles deliver a high initial capacity which falls below 100 mAh/gm at 40th cycle.

The gravimetric capacity of our GnP- Mn_3O_4 composite anode exceeds by almost 270 mAh/gm compared to pristine GnP (491 mAh/gm for the composite anode compared to 224 mAh/gm for pristine GnP at 2nd cycle). This shows the effectiveness of this composite electrode. The fact that the electrode delivers nearly similar capacity even when the current rate is increased by a factor of 2.5 from 40 mA/gm to 100 mA/gm and the capacity performance remains nearly stable for 25 cycles shows the effectiveness of conductive GnP substrate on capacity and cycle performance. The capacity contribution from Mn_3O_4 itself in the composite is 852 mAh/gm (at 40 mA/gm of composite electrode current rate) as discussed already. This value is close to the theoretical capacity of Mn_3O_4 which is 937 mAh/gm [3]. This shows the effectiveness of our synthesis method.

4. Conclusion

PEI has been investigated for the synthesis of gold [37] and silver [38] nanoparticles. To our knowledge synthesis of transition metal oxide Mn_3O_4 through a PEI mediated route has not been reported yet. We are aware of some prior research works that have investigated the synthesis of transition metal oxide Mn_3O_4 through other surfactant mediated route without involving a substrate [39, 40-43]. However, we do believe that our method is the simplest method reported so far for Mn_3O_4 synthesis on a substrate considering the chemicals involved, synthesis temperature, and the synthesis environment as discussed already. It is also interesting to

point out that octahedron shaped Mn_3O_4 nanoparticles have attracted particular attention [39, 41, 43], of which we have proposed a simple synthesis method. In addition, our study demonstrates the effect of PEI on the oxidation state of Mn in its oxide structure as well as the morphology of the oxide. It should appeal to a broad group of researchers considering the versatility of application of manganese oxides and their composites. This research also demonstrates the applicability of this composite as a Lithium-ion battery anode which has the potential for further improvement through optimization. Since we have demonstrated that PEI affects both the oxidation state of manganese oxide as well as its morphology, it is not hard to imagine that other oxide structures of varying morphologies could be obtained by tuning the amount of PEI in the synthesis process.

Figures

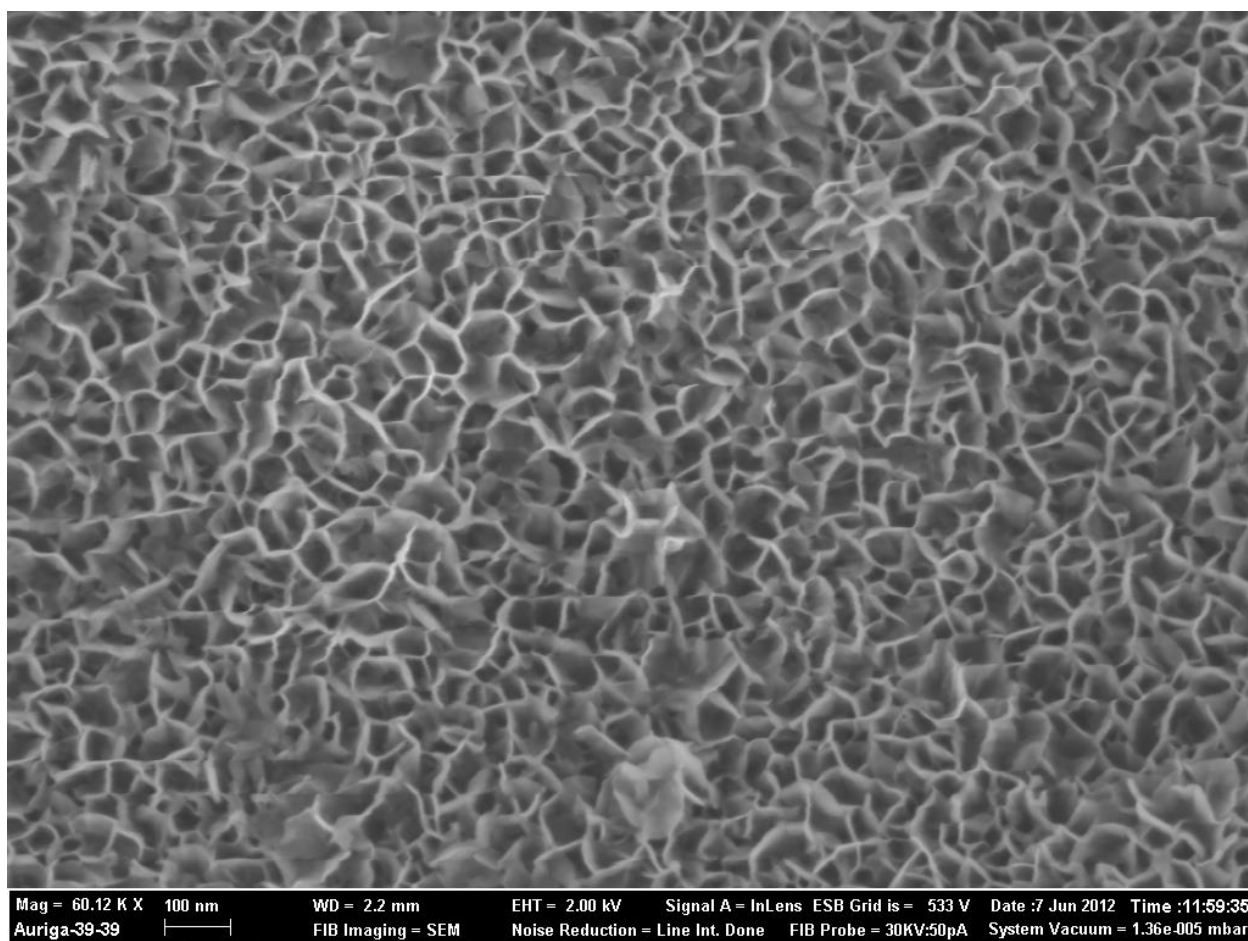


Figure 1 (a). network of ribbon-like structure on GnP surface (micron bar is 100 nm)

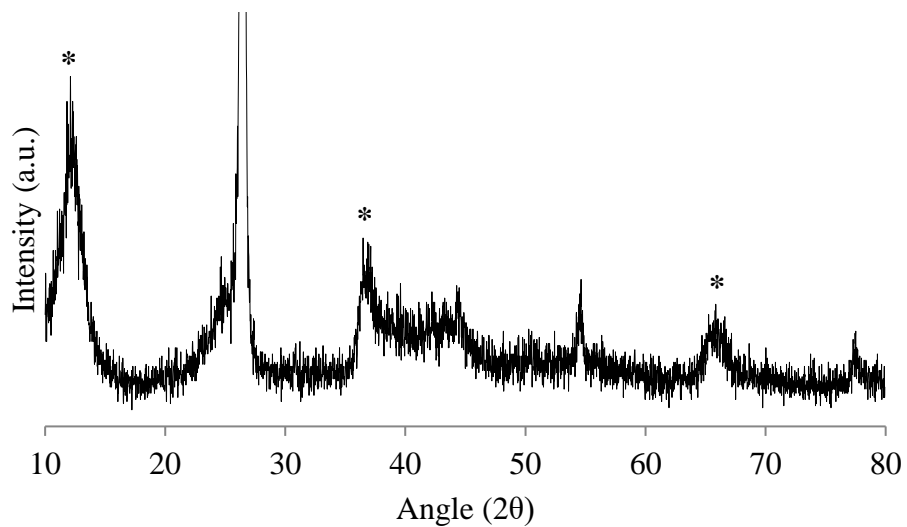


Figure 1 (b). XRD pattern of the composite of GnP and Birnessite-MnO₂ (* indicates metal oxide phases)

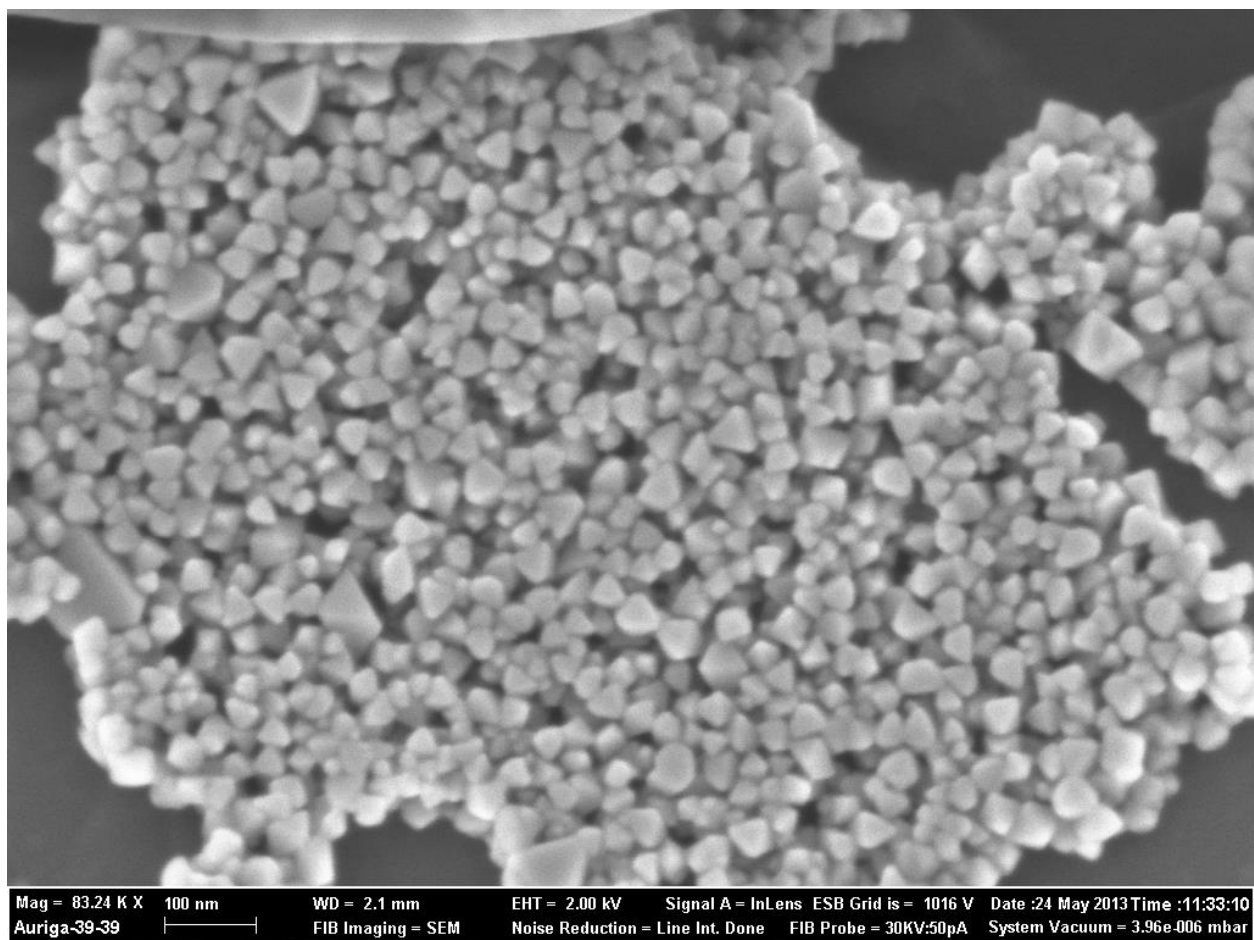


Figure 1 (c). cluster of nanoparticles on GnP surface (micron bar is 100 nm)

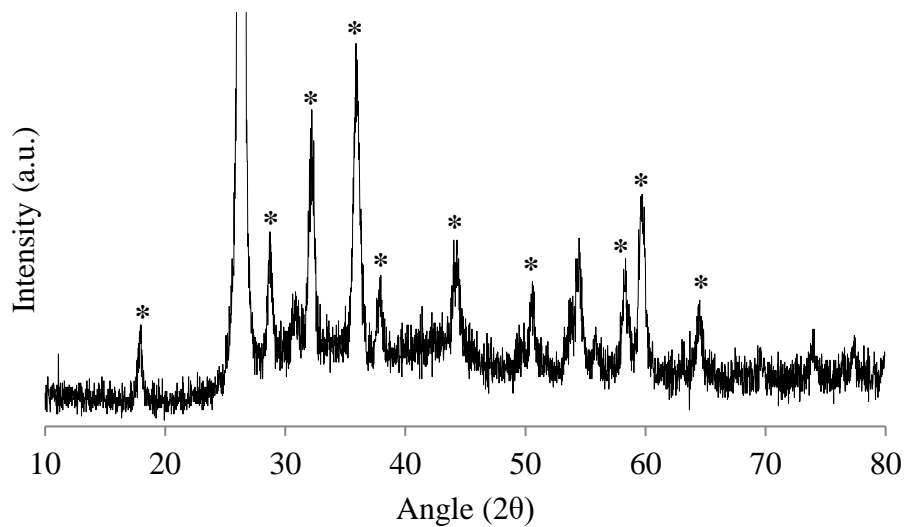


Figure 1 (d). XRD pattern of the composite of GnP and Mn_3O_4 (* indicates metal oxide phases)

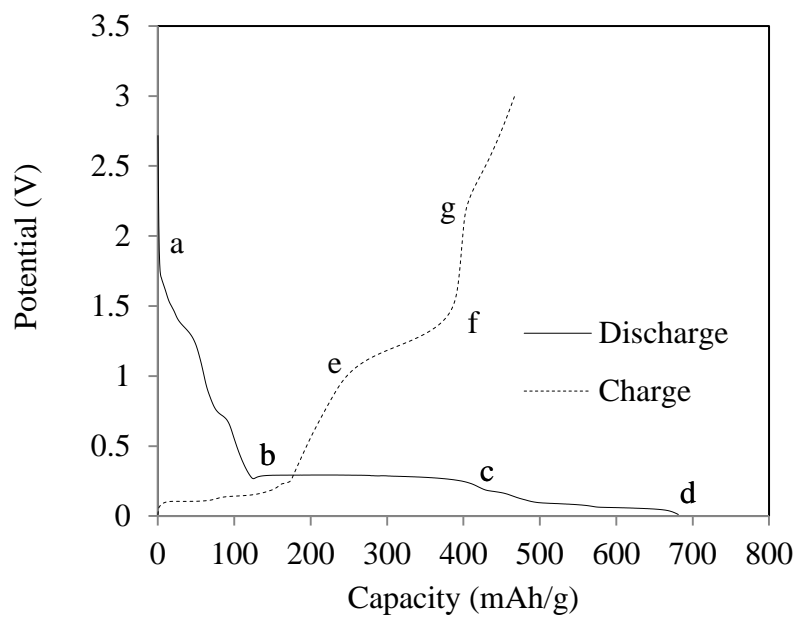


Figure 2 (a). galvanostatic discharge-charge profiles of first cycle

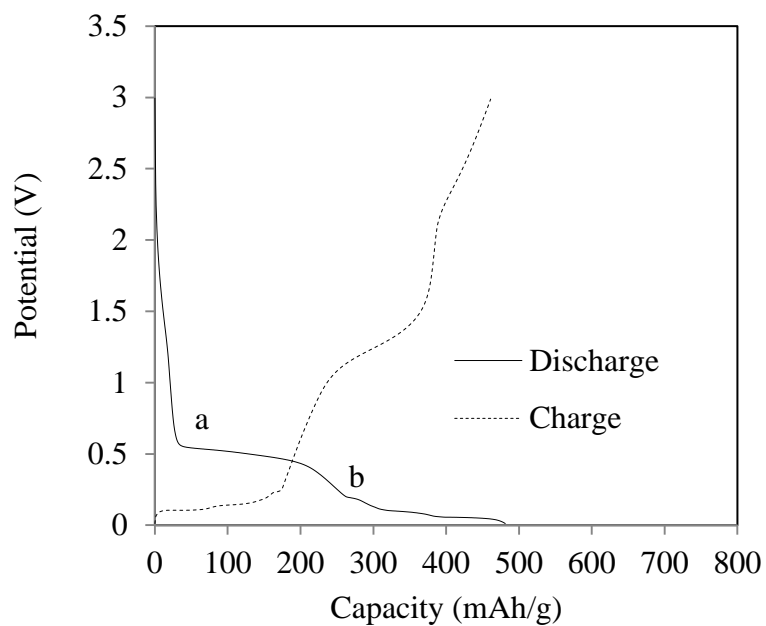


Figure 2 (b). galvanostatic discharge-charge profiles of second cycle

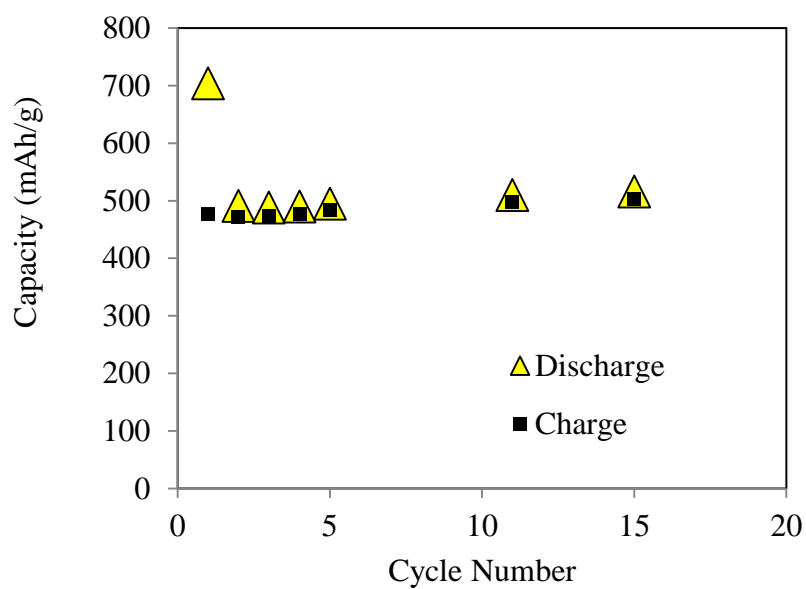


Figure 2 (c). galvanostatic discharge-charge cycle performance at 40 mA/gm current rate

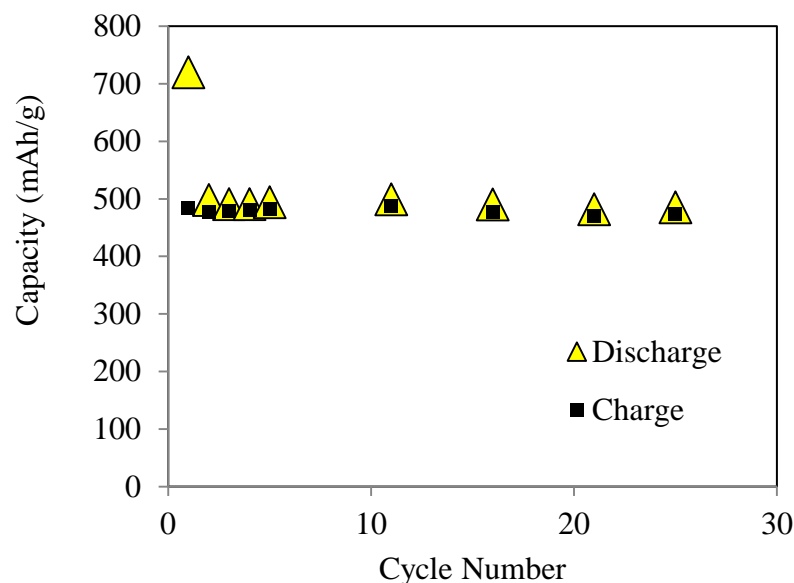


Figure 2 (d). galvanostatic discharge-charge cycle performance at 100 mA/gm current rate

Supporting Information

Experimental procedures; cyclic voltammetry profile of $\text{GnP-Mn}_3\text{O}_4$ composite electrode; discharge-charge performance of pristine GnP electrode; additional images of $\text{GnP-Mn}_3\text{O}_4$ composite synthesized in presence of PEI; TGA of $\text{GnP-Mn}_3\text{O}_4$ composite and related calculations-this material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Ribbon-like network of Birnessite-MnO₂ on few-layer graphene nanoplatform (left) changes to Mn₃O₄ on few-layer graphene nanoplatform (right) due to the presence of polyethyleneimine in the wet-chemical synthesis process

Supporting Information

Synthesis of Clustered Mn₃O₄ Nanoparticles through a Polymer Surfactant Mediated Route on Few-Layer Graphene Nanoplatelet Surface and Its Application for Electrochemical Energy Storage: Lithium-ion Battery Anode

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1.1 Experimental Procedures

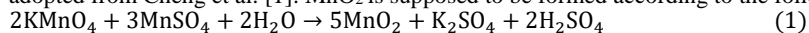
1.1.1 Synthesis of Clustered Mn₃O₄ Nanoparticles Decorated Few-Layer Graphene Nanoplatelet

Materials

Manganese sulfate monohydrate (MnSO₄.H₂O) (ReagentPlus>99%) and potassium permanganate (KMnO₄) (ACS reagent>99%) were purchased from Sigma-Aldrich. Branched polyethyleneimine (PEI) was also purchased from Sigma-Aldrich (average M_w 25,000 by LS, average M_n 10,000 by GPC). GnP-M-15 (120-150 m²/gm surface area, 15 µm average particle size) few-layer graphene nanoplatelet (GnP) (obtained from XG Sciences, Lansing, Michigan, USA) was used as the substrate for manganese oxides deposition. Few-layer graphene nanoplatelets (GnP) are ultrathin particles of graphite consisting of a few layers of graphene prepared through proprietary intercalation and exfoliation process.

Synthesis of clustered Mn₃O₄ nanoparticles decorated GnP in absence of PEI

First, 1.0 gm GnP is added to 150 ml reverse osmosis water and sonicated for 2 minutes. This is followed by heating to 80°C under constant stirring in the container attached to the recirculating heater as shown in figure S1. The container has a water jacket. The heater pumps heated water into the container jacket with an inlet pipe and reverses it back to the heater through an outlet pipe continuously. Heat is transferred from the water inside the jacket to the water stirring inside the container. The temperature of the heater is set slightly above 80°C to account for the heat loss in the process of heat transfer. Please note that a simple oil bath could be used if a container with water jacket and a recirculating heater as described here is not available. The water container is placed on a magnetic stirrer plate. The plate stirs a magnetic stirrer bar which is placed at the bottom of the water container and thus stirring the GnP-water solution at a uniform speed. MnSO₄.H₂O and KMnO₄ are dissolved separately in 25 ml. reverse osmosis water by stirring and heating to 80°C. The compositions along with the synthesis conditions are listed in table S1. The ratio of manganese salts is adopted from Cheng et al. [1]. MnO₂ is supposed to be formed according to the following equation.



First, MnSO₄.H₂O solution was added drop-wise with a glass pipet to the GnP-water solution. The significance of slow addition is that it prevents the solution temperature from deviating from 80°C. This is followed by a slow addition of KMnO₄ solution with a glass pipet. After addition of both salt solutions, the container is covered with a lid (not sealed) and the stirring continues for 1 hour. After 1 hour, the stirrer plate and the heater are turned off and the solution is allowed to cool for 2 hours. After cooling, the solution is filtered with a filter paper to collect the solid residue; a composite of GnP and Mn₃O₄. The composite is washed multiple times with reverse osmosis water. This is followed by a pre-drying step where the composite is dried in air under a hood. This is followed by a second drying step in a vacuum oven at 120°C for about 12 hours. The vacuum oven is allowed to cool naturally by turning off the heater before it is filled with air and the composite is taken out.

Synthesis of clustered Mn₃O₄ nanoparticles decorated GnP in presence of PEI

The synthesis process remains same except for the preparation of GnP/PEI/water dispersion. First, 1.0 gm GnP is sonicated for 2 minutes in 125 ml. reverse osmosis water. PEI is dissolved in 25 ml. reverse osmosis water; added to the GnP solution and stirred for 12 hours to prepare the dispersion. Please note that our GnP came in highly agglomerated form and a 12 hour time was allowed just to reduce the agglomeration to the best extent possible. For easily dispersible substrates a lesser time can be used. This dispersion is then heated to 80°C as described before and the rest of the steps for composite synthesis remain same. The compositions of the reagents along with the synthesis conditions are listed in table S2.

Water Volume (ml.)	KMnO ₄ (gm)	MnSO ₄ .H ₂ O (gm)	Molar ratio (KMnO ₄ :MnSO ₄ .H ₂ O)	GnP (gm)	Temperature (°C)
150	1.1	0.4	2.9:1	1	80

Table S1: Synthesis of GnP-Mn₃O₄ composite in absence of PEI

Water Volume (ml.)	KMnO ₄ (gm)	MnSO ₄ .H ₂ O (gm)	Molar ratio (KMnO ₄ :MnSO ₄ .H ₂ O)	GnP (gm)	PEI (gm)	Temperature (°C)
150	1.1	0.4	2.9:1	1	2	80

Table S2: Synthesis of GnP-Mn₃O₄ composite in presence of PEI



Figure S1: Setup for GnP-Mn₃O₄ composite synthesis

1.1.2 Scanning Electron Microscopy (SEM)

Morphology of the GnP-Mn₃O₄ composite was observed with a Carl Zeiss Auriga 39 scanning electron microscope

1.1.3 X-Ray Diffraction (XRD)

XRD patterns of the GnP-Mn₃O₄ composite was collected with a Bruker powder diffraction instrument in the range of 2θ 10°-80° at an incremental step of 0.02048° with a step time of 0.75 seconds

1.1.4 Thermo-Gravimetric Analysis (TGA)

TGA of the GnP-Mn₃O₄ composites was carried out in the temperature range of 25°C-800°C at a scan rate of 10°C/min in air

1.1.5 Preparation of Electrode

GnP-Mn₃O₄ composite electrode was prepared by coating a slurry of 1.3 g composite (95 wt %), 0.07 g Polyvinylidene Fluoride (PVDF) (5 wt %) and 15 ml. N-Methyl-Pyrrolidinone (NMP) on 15 µm thick copper foil. This coating was dried with a heater in open air at 120°C for 12 hours. This was followed by a second drying step in a vacuum oven at 120°C for another 12 hours to remove the residual NMP. 12.7 mm diameter discs were punched to be used as electrodes in coin cells. Each electrode had a material loading of about 1.2-1.3 mg.

Pristine GnP electrodes were prepared following the same method except that the content of the slurry was different. The slurry had following composition: 0.4759 g GnP (95 wt %), 0.025 g Polyvinylidene Fluoride (PVDF) (5 wt %) and 14 ml. N-Methyl-Pyrrolidinone (NMP)

1.1.6 Assembly of Two Electrode Coin Cells

CR-2032 coin cells were assembled in argon filled glove box (<1 ppm H₂O, <1 ppm O₂). Either pristine GnP electrode or GnP-Mn₃O₄ composite electrode was used as the anode; Lithium-foil (Alfa-Aesar, 0.75 mm thick, 99.9% metal basis) as the cathode; and glass microfiber (Whatman) soaked with 1(M) solution of LiPF₆ in 1:1 (V/V) (EC:DMC) as the electrolyte. EC (anhydrous, 99.7%) and DMC (99.7%) were purchased from Sigma-Aldrich.

1.1.7 Electrochemical Performance Evaluation

Discharge-charge performances of coin cells with GnP-Mn₃O₄ composite electrodes were measured at 40 mA/gm current rate for 15 cycles and at 100 mA/gm current rate for 25 cycles. Discharge-charge cycle performance of pristine GnP electrode was measured at 40 mA/gm current rate for 4

cycles. The cut-off potential limits for the discharge half cycle and the charge half cycle were 0.01V and 3V respectively. Cyclic Voltammetry (CV) profile of the $\text{GnP-Mn}_3\text{O}_4$ composite electrode was collected for the first and the second cycle in the potential window of 3V-0.01V at a scan rate of 0.1mV/sec.

1.2 Cyclic Voltammetry Profile of $\text{GnP-Mn}_3\text{O}_4$ Composite Electrode

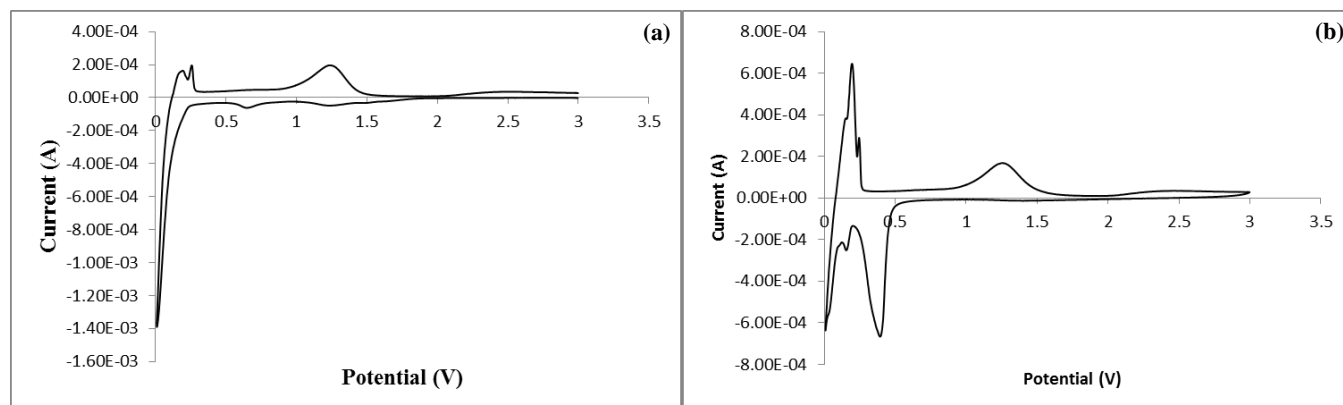


Figure S2: Cyclic Voltammetry profile of $\text{GnP-Mn}_3\text{O}_4$ composite electrode (a) first cycle; (b) second cycle at 0.1mV/sec scan rate

1.3 Discharge-Charge Performance of Pristine GnP Electrode

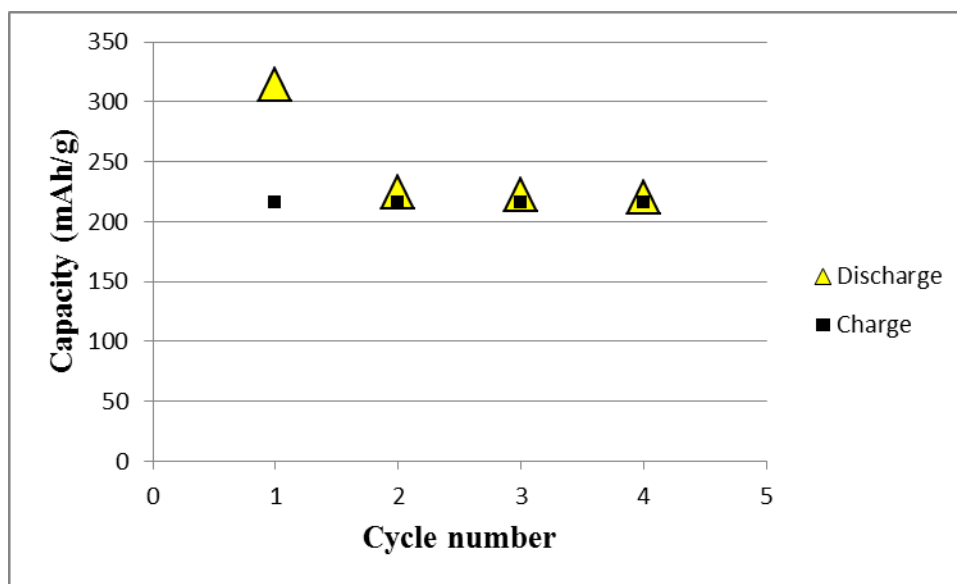


Figure S3: Discharge-charge cycle performance of pristine GnP electrode at 40 mA/gm of electrode current rate

1.4 Additional Images of GnP-Mn₃O₄ Composite Synthesized in Presence of PEI

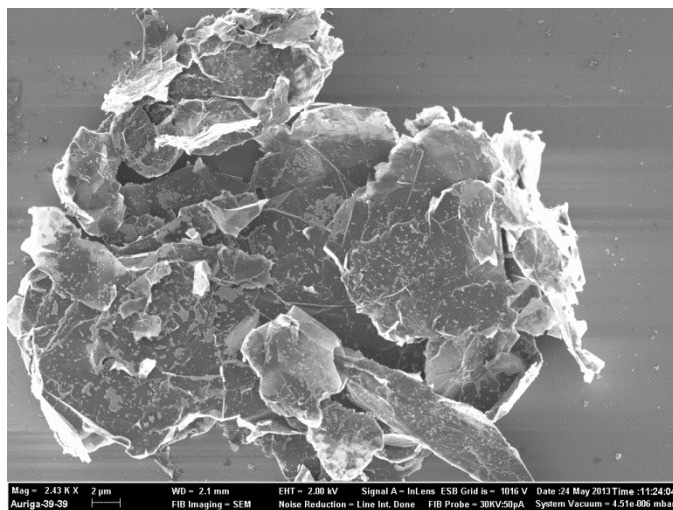
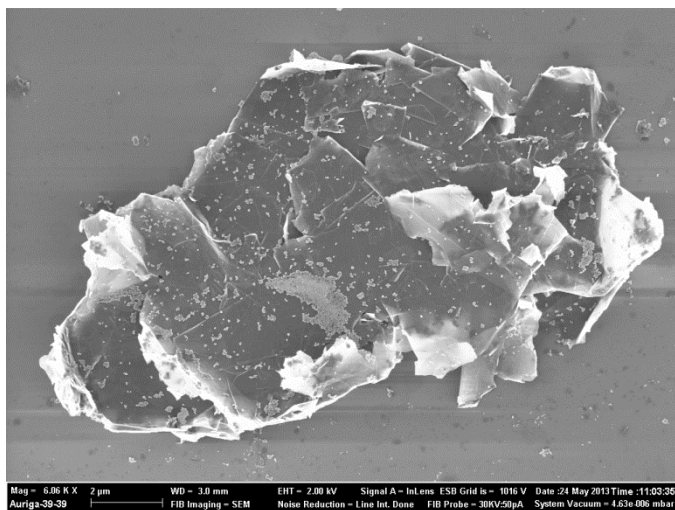
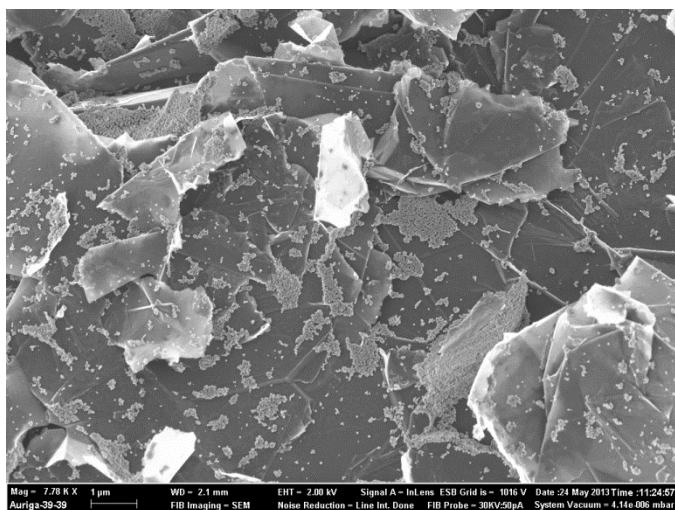


Figure S4: GnP-Mn₃O₄ composite synthesized in presence of PEI



1.5 Additional Images of GnP-Mn₃O₄ Composite Synthesized in Absence of PEI

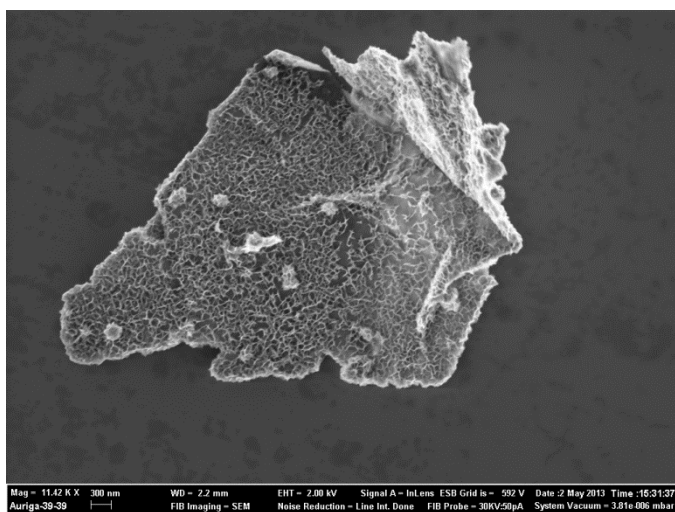


Figure S5: GnP-Birnessite MnO₂ composite synthesized in absence of PEI

1.6 TGA of GnP-Mn₃O₄ Composite and Related Calculations

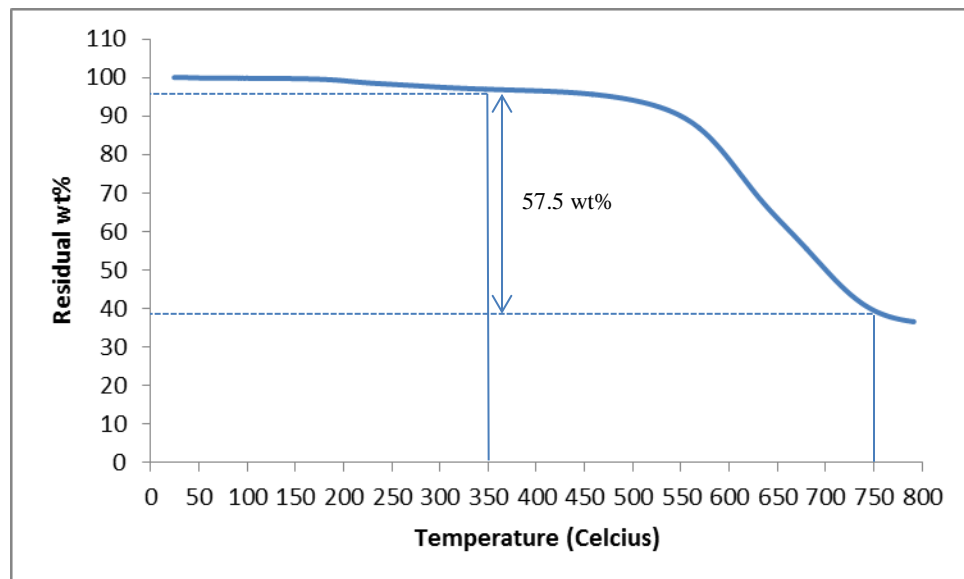


Figure S6: TGA of GnP-Mn₃O₄ composite

The weight loss beginning at 350°C and up to 750°C where the TGA profile begins to level-off is considered as the weight loss from the burning of GnP substrate. The weight loss below 350°C can be attributed to loss of water [2]. The amount of GnP in the composite is about 57.5 wt% and the amount of Mn₃O₄ is about 42.5 wt%.

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