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# Lithium assisted enhanced hydrogenation of reduced graphene oxide-PANI nanocomposite at room temperature

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ABSTRACT

Present study, first time, reveals that lithium and ethylenediamine assisted Benkeser reaction enhanced the hydrogenation process where reduced graphene oxide-PANI (G-PANI) nanocomposites act as storage medium. Varying the weight ratio of graphene and PANI, several samples were synthesized and hydrogenated. The reduced graphene oxide-PANI (G-PANI) and hydrogenated reduced graphene oxide-PANI (HG-PANI) nanocomposites were characterized by high resolution transmission electron microscopy (HRTEM), field emission scanning electron microscopy (FESEM), Fourier transform infrared spectra (FTIR) analysis and thermo gravimetric analysis (TGA). The electrical conductivity with the variation of temperature for the nanocomposites has also been studied. The reduced values of electrical conductivity and percent weight loss in TGA suggested that the hydrogenation occurs. The degree of hydrogenation of reduced graphene oxide-PANI estimated by TGA, revealed 11% (30% reduced graphene oxide-PANI) and 16.04% (50% reduced graphene oxide-PANI), hydrogen storage, which is considerably higher than the reported values of hydrogen storage in individual storage materials like, PANI, graphene and carbon nano tube.

## 1. Introduction

Hydrogen has attracted a great deal of attention as a clean fuel for mobile and stationary purpose in the future. In the hydrogen life cycle, the production and storage using safe and efficient retrieval methods is given priority in research fields. Recently, Graphene has attracted strong interest for its exclusive and highly enviable electrochemical, electrical and mechanical properties [1–12]. Theoretical calculations predict that regular or irregular combinations of sp$^3$-bonded carbon atoms and graphene fragments are beneficial for molecular hydrogen storage [13]. It was also found by ab initio molecular orbital theory and DFT calculations that the physisorption energies are considerably increased on the curved and planar graphenes [14,15]. In this regard, it was reported that reported that 3.2 (weight%) wt% hydrogen were stored in multiwall carbon nanotubes (MWCNT) through Benkeser reaction [16]. As well as, graphene also stored 2.7 wt% hydrogen when particular experimental conditions were maintained (298 k and 25 bars), observed by Wenhui Yuan et al. [17]. In this study graphene nano-sheet were prepared using green approach (reduction through glucose). More recently, few layer of graphene has been hydrogenated through the arc discharge method and it has been exhibited that hydrogen plays a crucial role for conversion of sp$^2$ - to sp$^3$ - carbon configuration in graphene lattice under methane-mixed gas atmosphere [18].

In our previous report [19], we explored the hydrogenation of graphene using Benkeser's reaction. We showed, through this reaction, hydrogen can be incorporated into graphene matrix as high as 14.67% (weight %), which can be released upon heat treatment.

Regarding hydrogen storage research on Polyaniline (PANI), Cho et al. [20] reported 5.75 wt% hydrogen can storage on PANI. Inherently conductive polymer, for instance Polyaniline (PANI), has received significant interest due to its optical, electrical and electrochemical properties derived from conjugated π-electron system. More interestingly, it has been observed that more than 6–10 wt% hydrogen storage is possible in PANI structure due to the availability of many sites for physisorption as well as chemisorption [21]. In addition, Electrospun

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PANI fibers exhibits 3 to 10 wt% reversible hydrogen storage capacity at different temperatures varying from 25 °C to 125 °C [22].

Recently, graphene based composite materials like reduced graphene oxide-PANI (G-PANI) has attracted great attention due to it's enhance thermoelectric property [23] and electrochemical and physical storage ability of PANI. Demirocak et al. [24] illustrated that the Polyaniline nanocomposites and Cross-Linked Polyaniline stored hydrogen at room temperature, but the extent of storage did not fulfil the DOE targets.

However, the thermal stability of PANI may limit the hydrogen storage/release at higher temperature. In this context, the temperature dependence of the thermo physical and paramagnetic characteristics of polyaniline containing a variety of structured impurity centers has been reported in literature [25].

In the present study, reduced graphene oxide-PANI (G-PANI) nanocomposites with different weight percent of Polyaniline (PANI), were synthesized and hydrogenated at room temperature and atmospheric pressure. Benkeser's reaction was employed to introduce hydrogen in to the reduced graphene oxide-PANI unsaturated structure to a large extent, using tert-butanol and Lithium in ethylene diamine and to convert it to hydrogenated reduced graphene oxide-PANI; the incorporated hydrogen can be released upon heat treatment. Very specifically, to avoid the structure related problem of PANI, we introduced the reduced graphene oxide. On the other hand, PANI chains (containing double bonds) were introduced for enhancement of overall hydrogen storage/incorporation of the composite, especially at normal temperature.

## 2. Material and methods

Graphite, was obtained from Sigma Aldrich, while $N_2H_4$-$H_2O$ was obtained from RFCL Limited; $KMnO_4$, $H_2SO_4$, $H_3PO_4$, 5-Sulfosalicylic acid (SSA), Aniline ($C_6H_5NH_2$ purity 99.5%, density 1.02 kg/lit), Ammonium peroxsulfate or APS ($(NH_4)_2S_2O_8$). Ethylenediamine ($C_2H_8N_2$),Tert-butanol ($C_4H_{10}O$) and 30% $H_2O_2$ were all obtained from E MERCK.

### 2.1. Synthesis of graphene

Graphene was synthesized employing via simple chemical method. Here Graphite was oxidized and formed Graphite oxide (GO), as followed by our previous works [20,26–27]. Synthesized, dried brownish yellow colored GO was used for graphene preparation and hydrazine hydrate used as reducing agent.

### 2.2. Synthesis of reduced graphene oxide-PANI nanocomposites

The nano-composites of reduced graphene oxide-PANI (poly aniline) were prepared by the in situ chemical oxidative polymerization of aniline using 5-sulfosalicylic acid as a dopant and ammonium peroxydi-sulfate as an oxidizing agent, followed by the synthesis process reported by Mitra et al. [23].

### 2.3. Hydrogenation on reduced graphene oxide-PANI (G-PANI) nanocomposites

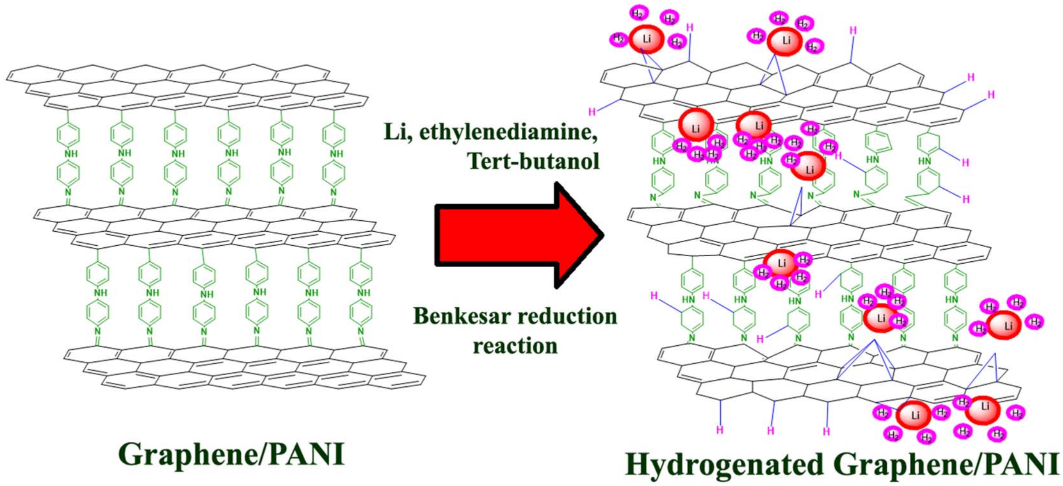
Synthesized G-PANI was hydrogenated through the Benkeser's reaction [16]. Basically, it is a modified form of Birch reaction. The entire hydrogenation process was performed under argon atmosphere. G-PANI (60 mg), ethylenediamine (80 ml), pieces of lithium (200 mg) and tert-butanol (5 ml) were used for this experiment. Step by step hydrogenation procedure is almost similar to our previous work [19].

### 2.4. Characterization of reduced graphene oxide-PANI and hydrogenated reduced graphene oxide-PANI

Fourier transformation infrared (FTIR) spectrum was recorded on FTIR Spectrometer (IR Prestige-21, Shimadzu, Tokyo, Japan) and an IR Affinity-1. The samples were compressed into a pellet with KBr. X-ray diffraction (XRD, BRUKER D8 Advance) spectra were obtained by using Cu-Ka radiation (l 1/4 1.5418 ˚A) in the range of 10–80° with a scanning speed of 5 $\text{min}^{-1}$. Transmission Electron microscopy (TEM) and high-resolution transmission electron microscope (HRTEM) images were obtained using A JEOL JEM 2100 (JEOL KOREA LTD., Seoul, Korea) at voltage of 200 kV. Field emission scanning electron microscopy. FESEM, Hitachi-4200 was utilized for surface morphology analysis of the nano-composites. Thermo-gravimetric analyses (TGA) were carried out by Pyris Diamond TG/DTA (Perkin Elmer, Singapore) with the operational temperature range of 32° to 1000 °C at15.00 °C $\text{min}^{-1}$ heating rate, under nitrogen atmosphere (circulation rate 150 ml $\text{min}^{-1}$).

## 3. Results and discussion

Different weight ratio of reduced graphene oxide-PANI (10%, 30%, 50%) composites were synthesized and hydrogenated by using lithium in ethylenediamine under Benkeser reduction reaction [16]. In this reaction, polycyclic aromatic hydrocarbons were catalytically hydrogenated using calcium or lithium metal and low molecular weight alkyl groups or primary amines ($-CH_3$, $-CH_2CH_2NH_2$, $-CH_2CH_3$, $-CH_2CH_2CH_3$) as reductants. The proposed scheme of Benkeser



**Scheme 1.** Proposed reaction scheme of Benkeser reduction reaction for hydrogen storage.

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