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# Versatile preparation of graphene-based nanocomposites and their hydrogen adsorption

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## ABSTRACT

We report the facile and versatile preparation of graphene-based nanocomposites of magnetite, silver, titania, nickel, and silicon by solid state mechanical mixing. The composites were directly employed for nitrogen and hydrogen gas adsorption studies at 77 K and equilibrium pressure of 1 atm. Under the experimental conditions the chemically synthesised graphene support had a solid state BET surface area of 499 m<sup>2</sup>/g and a total reversible hydrogen uptake of 0.5 wt.%. Among our prepared nanocomposite samples, the silver nanoparticles promoted the most significant increase in hydrogen uptake per metre squared of material by 30% when compared to the parent graphene sample. However, the total hydrogen uptake by weight percentage in the studied graphenic materials remains low. The hydrogen storage capacity observed for the graphene nanocomposites can be qualitatively accounted for by considering the contributions of the catalyst particles on the hydrogen storage, the contact between catalyst and graphene, and the structural nature of the graphene surface.

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## Introduction

Technologies utilising hydrogen as an energy carrier have the potential to curb greenhouse gas emissions [1]. Much attention has been directed towards hydrogen sorption materials capable of safe incorporation into portable cells. Increasing the surface area of a material or its affinity toward the adsorbent species can enhance the gas uptake capacity in the material [2]. Hence, an adsorbent with high surface area and pore volume has a large number of adsorption sites and is anticipated to be an excellent candidate as an adsorbent. This has made both carbon nanomaterials (*e.g.* graphite, activated

carbon, graphene, carbon nanotubes *etc.*) [3–8] and non-carbon nanomaterials (*e.g.* metal hydrides, metal-organic frameworks, polymers *etc.*) [1,9] potential candidates for solid-state hydrogen storage.

In the present nano-carbon based hydrogen storage methods, graphene materials are a popular choice due to their unique properties exhibiting the superior combination of lightweight, extremely large theoretical surface area, high thermal and electrical conductivity, mechanical strength, and relative chemical stabilities [10–12]. Synthesis of freely separated sheets of graphene in large quantities remains challenging as graphene sheets tend to aggregate in the solid state [13,14]. Often graphenic composite materials are prepared by

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high dispersion using chemical solvents, surfactants, or solutions prior to chemical modification [15]. Thus, recent reports of gas adsorption on graphene have indicated the use of graphene nanoplatelets or layered graphene sheets [16,17].

Ma et al. reported that a single layer of graphene could store 0.4 wt.% hydrogen near 1 atm. of pressure and cryogenic temperature [18]. At room temperature the adsorption capacity decreased to 0.2 wt.% close to 60 atm. pressure. Parambath et al. demonstrated hydrogen exfoliated graphene had a hydrogen uptake of 0.5 wt.% at room temperature and 20 atm. pressure [19]. In another study Choi et al. showed that potassium hydroxide activated carbon with a Brunner-Emmet-Teller (BET) surface area value (2965 m<sup>2</sup>/g) similar to the theoretical surface area of a double-sided separated graphene sheet (2630 m<sup>2</sup>/g) could store about 0.5 wt.% hydrogen at 60 atm. pressure and room temperature (0.2 wt.% at 20 atm. pressure, 298 K), with a clear correlation between adsorption capacity, BET surface area and micropore volume [20].

Such values lie within the typically agreed upon hydrogen uptake capacity of carbon materials [3,21]; generally less than 1 wt.% at room temperature and still well below values required for practical application targets [1]. At low and cryogenic temperatures, the reported hydrogen uptake capacity of carbon materials prepared by different methods remains higher than those at room temperature, although still below useful targets.

There are many reports that hydrogen storage at room temperature can be improved by a phenomenon known as 'spillover effect', initiated by nanoparticles, usually transition or noble metals, decorated over the carbon surface [9,22–26]. Metal atoms tend to aggregate easily because of the strong metal cohesion forces. Parambath et al. showed that the contact between the metal nanoparticles and supporting adsorbate material plays a major role in spillover mechanisms [19]. However, spillover does not occur in all circumstances, and may not be the sole explanation of the mechanisms taking place and the topic remains highly contentious [27].

Increases in hydrogen sorption have also been obtained by compositional doping and modification to the carbon morphology. For example, Jiang et al. demonstrated that nitrogen containing carbon spheres could store 2.21 wt.% hydrogen at room temperature and 80 atm. pressure [28]. It was further shown by Orimo et al. that mechanically-milled graphite can store about 7.4 wt.% hydrogen by chemisorption and interlayer diffusion [29]. In this article, we explore the possibility of combining the exceptional physical properties of graphene sheets with the versatility of metal, metal-oxide, and semi-metal particles for hydrogen sorption.

## Materials and methods

### Synthesis

To obtain the graphene material we employed a method based on solvothermal synthesis known to produce extended 3-dimensional networks of graphene [30]. The term 'solvothermal' denotes conditions involving reactions performed at a temperature above the boiling point of a solvent in a closed reaction vessel. In this case ethanol (5.00 mL,

85.8 mmol) was used as the alcohol feedstock for the solvothermal reaction with sodium metal (1.80 g, 78.3 mmol) at 493 K for 72 h in a 23 mL Teflon lined stainless steel Parr reaction vessel. The solvothermal reaction produced a solid product which was rapidly pyrolysed. The resulting carbon material was washed with water, then with acidified ethanol (2 M hydrochloric acid in ethanol, 1:4 vol./vol. ratio), and filtered under dynamic vacuum before drying in a vacuum oven at 473 K for 1 h.

The graphene supported composites were prepared by simple mixing of commercially available nanosize silicon (<150 nm, Nanostructured and Amorphous Materials Inc.), nickel (<100 nm, Sigma Aldrich), silver (<100 nm, Sigma Aldrich), magnetite (<150 nm, Sigma Aldrich), or titania (P25<sup>®</sup>, 25–30 nm, Sigma Aldrich) with the graphene material in a weight ratio of 1:1 by agate mortar (i.e. 50 wt.% nanoparticle). Negligible amounts of material was left in the mortar after mixing compared to the gram-scale quantities prepared.

### Characterization

The morphology and microstructure of the as-prepared graphene nanocomposites were characterized by a Hitachi S-900 'in-lens' field emission scanning electron microscope (SEM) capable of imaging at very high resolutions (~0.5 nm). The as-prepared materials were directly applied on to double sided carbon tape and analysed.

X-ray photoelectron spectroscopy (XPS) measurements were conducted to examine the elemental compositions at the surface of the graphene nanocomposites with an ESCALAB250Xi instrument manufactured by Thermo Scientific, UK. The background vacuum was better than  $2 \times 10^{-9}$  mbar. A monochromated Al K<sub>α</sub> (energy  $h\nu = 1486.68$  eV) was used as the source and a power of 164 W (10.8 mA and 15.2 kV) was used with a spot size of 500 μm. The photoelectron take-off angle was 90° and the pass energy was 100 eV for survey scans and 20 eV for high resolution surface region scans. Under the surface region scan conditions, a spectral resolution of 0.59 eV (full width at half maximum) can be achieved. The graphene nanocomposites were pressed directly onto indium foil for analysis.

Powder X-ray diffraction (PXRD) data was collected to assess particle size and distribution over the 10°–60° 2θ range with a 0.01° step size and 3°/min scan rate on a PANalytical X'Pert Pro diffractometer fitted with a solid state PIXcel detector (40 kV, 30 mA) using Cu-K<sub>α</sub> ( $\lambda = 1.5406$  Å) radiation and ½° divergence and 1° anti-scatter slits. No mathematical manipulation was performed on the presented data.

Adsorption isotherms were measured using a BELSORP-max instrument from BEL Japan Inc. Approximately 450 mg of sample was loaded into a glass analysis tube and outgassed for a minimum of 3 h under vacuum at 200 °C prior to measurement. N<sub>2</sub> adsorption and desorption isotherms were measured at 77 K and data was analysed using a BET model to determine the surface area [31]. H<sub>2</sub> measurements (up to 1 atm. pressure) were carried out on the BELSORP-max instrument as described above. The samples used to obtain the reported adsorption-desorption data were taken from a bulk gram scale sample batch which was tested for composition

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