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Hydrogen storage performance of palladium nanoparticles decorated graphitic carbon nitride

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ABSTRACT

Pd on nitrogen rich carbon material g-C$_3$N$_4$ has been synthesized by a simple cost-effective method. From the study of the hydrogen storage properties of host g-C$_3$N$_4$ matrix and Pd-g-C$_3$N$_4$ by pressure reduction method using Sievert's apparatus in the ranges $0.1 \leq P_{H_2}(MPa) \leq 4$ and $0 \leq T(°C) \leq 100$, it has been demonstrated that the hydrogen storage capacity of Pd-g-C$_3$N$_4$ reaches 2.6 wt% at 25 °C and 4 MPa. At room temperature, an increase of 66% in the hydrogen uptake capacity is accounted by Pd nanoparticles (Pd-NPs) decoration over host g-C$_3$N$_4$ matrix, clearly demonstrating the hydrogen spillover process. The good dispersion of Pd-NPs over host g-C$_3$N$_4$ matrix and strengthened interaction between the host g-C$_3$N$_4$ matrix and Pd-NPs catalyze the dissociation of hydrogen molecules and subsequent migration of hydrogen atoms to the host g-C$_3$N$_4$ matrix due to spill over mechanism. From the present study, it can be concluded that the nexus between the catalyst support and catalyst particles results in the high hydrogen uptake capacity.

Introduction

The long term reliance of humanity on the energy solely derived from fossil fuels, has led to a number of challenges, including global warming followed by climate changes due to the release of huge amounts of greenhouse gas CO$_2$. Most of the world's energy requirement for transportation and heating, which is the 2/3rd of the primary energy demand, is derived from petroleum or natural gas. Unfortunately, the combustion of hydrocarbon fuel contributes over half of all greenhouse gas emissions and a large fraction of air pollution. Thus the urgency of developing alternative fuels arises. Among various alternative energy vectors, hydrogen offers the highest potential benefits. For the past few decades, hydrogen has been promoted as a solution to the global warming and air pollution [1—10].

But different obstacles inhibit the popularization of a hydrogen economy. The most important one is the safe and efficient storage of hydrogen, particularly for mobile and automotive applications. Of all possible solutions the most reliable one is the storage in solid media as hydrides, which is free from the drawbacks experienced by compressed and liquid hydrogen. The released hydrogen from metal hydrides via safe endothermic process is of very high purity and hence can be directly used to run a Polymer Electrolyte Membrane fuel cell [1—10]. A wide literature support from various part of the world exists for the use of carbon nanomaterials as

effective hydrogen storage media. Hydrogen storage in high surface area carbon nanomaterials such as activated carbon, carbon nanotubes, Graphene has been well investigated [11].

It is already a proven fact that the presence of nitrogen or boron on carbon materials enhances the catalytic activity and hydrogen storage capacities pretty well. But the complexities involved in the procedure of nitrogen/boron doping will make the process cumbersome [12]. In this context, if a carbon material, which is already enriched with nitrogen, is used to store hydrogen will be interesting. In this point of view, graphitic carbon nitride (g-C_3N_4) is a promising candidate for hydrogen storage medium. The material itself is endowed with numerous meso/macro pores and is having a high amount of nitrogen content, but comparatively low surface area [12,13].

The first-principles study of Guangyong Koh et al., predicted the high storage capacity of g-C_3N_4 nanotubes due to its peculiar nitrogen structures. But in practice, for g-C_3N_4 nanopowders, the normal storage of hydrogen through physisorption cannot give the predicted efficiency [14] and one has to consider the occurrence of chemisorption also by use of transition metals, which can promote chemisorption [8]. From the first-principle theory, it is already predicting that the functionalization of metal atoms like Titanium (Ti) can improve the capacity of g-C_3N_4 nanotubes. However, it has been reported that for Ti functionalized g-C_3N_4 nanotubes, the calculated energy barrier for a hydrogen molecule penetrating into the tube interior is very high compared to that of pristine C_3N_4 nanotubes indicating that the hydrogen molecule faces difficulty to enter via pores [14]. In this regard, one can examine the mechanism of 'spill over' to improve the kinetics of hydrogen storage and hence the hydrogen storage capacity. It is reported from our group that the 'spill over mechanism' of Pd-NPs over graphene (G) and nitrogen-doped graphene (N-G) enhances the hydrogen storage capacity [15–17]. Here we report an efficient and simple method of Pd-NPs decoration over g-C_3N_4 and further the enhanced hydrogen storage capacity of Pd-g-C_3N_4 compared to pure g-C_3N_4. To the best of our knowledge, the hydrogen storage study on g-C_3N_4 and Pd-NPs decorated g-C_3N_4 have not been reported.

Experimental details

Material synthesis and characterization

Materials used
Analytical grade melamine powders, Palladium (II) chloride (99%), Ethylene glycol(99%) and Sodium Hydroxide pellets (all purchased from Sigma Aldrich), high purity Nitrogen gas(99.999%) were used. Deionized water is used through out the experiment.

Sample preparation
Graphitic carbon nitrate (g-C_3N_4). g-C_3N_4 Nano powder was synthesized by a simple method – low temperature thermal condensation of melamine [18]. Around 2 g of well ground melamine powder was taken in an alumina boat, which was placed in the central part of a quartz tube furnace. As the temperature reaches 600 °C, high purity nitrogen gas (99.999%)

was allowed into the furnace at a flow rate of 75–150 sccm for 4 h. The furnace was then allowed to cool to room temperature and the product was taken out and ground into fine powder [18]. This pale yellow powder is labeled as g-C_3N_4.

Palladium decorated graphitic carbon nitride (Pd-g-C_3N_4). Pd nanoparticles decoration on g-C_3N_4 is done by a modified ethylene glycol (EG) reduction method. In brief, around 250 mg of well ground g-C_3N_4 powder was dispersed in 200 ml of EG by 10 min by ultrasonification followed by 12 h mechanical stirring. The required amount of 1 wt % $PdCl_2$ solution was then added drop-by-drop to the stirring medium and allowed to stir for next 24 h. After that pH of the solution was adjusted to 11 by adding NaOH solution followed by 6 h refluxing at 125 °C. The final product was washed with DI water, filtered out and dried in vacuum oven 60 °C for 12 h. The dark-grey colored sample is collected and labeled as Pd-g-C_3N_4.

Material characterization
Powder X-ray diffraction (XRD) pattern was recorded using PANanalytical X-pert Pro X-ray Diffractometer with nickel filtered Cu-K$_\alpha$ radiation as X-ray source. The vibrational spectra of the samples were recorded via Raman instrument using 532 nm laser (Witec Alfa 300) with the excitation source in the range of 100–3000 cm^{-1}. The surface morphology of the samples was analyzed using Field Emission Scanning Electron Microscope [FESEM, FEI QUANTA 400F] and Transmission Electron Microscope (TEM, FEI Tecnai G^{2}20 S-TWIN, 200 keV). The Brunauer-Emmett-Teller (BET) surface area and porosity measurements were carried out using Micrometrics ASAP2020 analyzer. Thermo gravimetric analysis (TGA) was done using a NEZSCH analyzer from room temperature to 1000 °C in air atmosphere at a heating rate of 20 °C/min. Energy Dispersive X-ray (EDX) Analysis was done to confirm the elemental composition of the samples.

Hydrogen storage studies

The hydrogen adsorption/desorption studies and kinetic studies of pure g-C_3N_4 and Pd-g-C_3N_4 samples in the pressure range of 0.1–4 MPa and in the temperature range of ice temperature to 100 °C were carried out using high pressure Sievert's apparatus. Initially the unit was calibrated using high purity hydrogen (99.99%). The volumes of the gas in the empty sample cell were accurately measured by allowing various initial pressures at different temperatures. Degassing of the samples at 280 °C was done at high vacuum to remove the impurities like moisture and oxide layers. Again, two trial activation cycles were done to enable the gas adsorbing sites, followed by consecutive measurement cycles. In each activation process, the sample was first evacuated up to 10^{-6} Torr and then heated to 250 °C and kept at 250 °C for 2 h. Then the sample was cooled down to 100 °C at 10^{-6} Torr and pure hydrogen gas was allowed to the sample cell. Subsequently the temperature was reduced to 50 °C, room temperature and ice temperature and each time, the equilibrium pressure readings were noted down. The pressure-composition isotherms were obtained using the hydrogen storage weight percentage capacity calculated for different pressure drops. After each cycle, the sample was degassed for 2 h at 250 °C.