Palladium nanoparticles decorated graphite nanoplatelets for room temperature carbon dioxide adsorption

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ABSTRACT

In order to counteract the greater level of green house gases including CO_2, adsorption process has been found as one of the solution. Present work focuses on the high pressure CO_2 adsorption study of nanocomposite comprising of Pd nanoparticles decorated graphite nanoplatelets (GNP). Graphite nanoplatelets (GNP) were prepared by acid intercalation followed by thermal exfoliation. Functionalized graphite nanoplatelets (f-GNP) were prepared by further treatment of GNP in acidic medium. Palladium (Pd) nanoparticles were decorated over f-GNP surface by chemical method. Nanocomposite was characterized by electron microscopy, X-ray powder diffraction pattern, BET measurement, Raman spectroscopy and FTIR spectroscopy techniques. The CO_2 adsorption capacity was measured using high pressure Seiverts' apparatus by incorporating van der Waals corrections and adsorption of CO_2 was confirmed by FTIR spectroscopy. A remarkable enhancement of 15–20% is obtained in CO_2 adsorption by decorating Pd nanoparticles over functionalized graphite nanoplatelets. Dubinin–Radushkevitch (DR) equation is applied to the adsorption isotherm at room temperature and the results have been discussed.

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1. Introduction

The increasing demand of fossil fuel energy poses a great challenge in the control of CO_2 emissions in Earth's atmosphere. Among all the means to maintain optimum CO_2 level in the atmosphere, the geological sequestration and storage options of CO_2 are found environmentally and economically beneficial and thus have attracted worldwide attention among researchers [1,2]. As an alternative method for CO_2 capture, adsorption can be considered to be one of the more promising methods, offering potential energy savings compared to absorbent systems, especially with respect to compression costs. Pressure swing adsorption (PSA) using solid sorbents has gained interest due to its low energy and capital investment costs [3–6]. In terms of achieving high adsorption capacities, activated carbons (ACs), zeolite-based molecular sieves and chemically modified porous silica have shown much promise. ACs are often preferred over zeolites because of their relatively moderate strengths of adsorption for gases, which facilitates easier desorption [7–10]. CO_2 adsorption capacities of activated carbons depend not only on their pore structure but also on the surface chemistry properties [11,12]. Recently, enhanced CO_2 adsorption capacity is reported in nitrogen treated AC [13]. Along with ACs,

one dimensional carbon based nanostructures like single walled and multi walled carbon nanotubes also provide a good alternative for CO_2 adsorption due to their large surface area and high porosity [14]. Some metal based complexes such as metal organic frameworks, titanium covered graphene and palladium based complexes and metal oxides like Fe_2O_3, Al_2O_3 have been recently investigated for CO_2 adsorption [15–19].

Metal based complexes can be good adsorbent for CO_2 due to the affinity of metals towards polarized CO_2 molecules. But metal nanoparticles have greater tendency to agglomerate and thereby reducing their performance. Hence to avoid this problem, Pd nanoparticles were decorated over graphite nanoplatelets (GNP) in the present work. This Pd decorated GNP nanocomposite includes the adsorption property of GNP and Pd nanoparticles. Cost effective and easy preparation process of GNP, leads to the utilization of this Pd decorated GNP nanocomposite for industry. This low cost nanocomposite can be used as CO_2 adsorbent at high pressures, especially for the storage of CO_2 coming out from thermal power plants and cement industries by compressing the exhaust with some means. In addition, desorption of adsorbed CO_2 at high temperatures suggests the possible utilization of adsorbed CO_2 for food packaging. CO_2 adsorption capacity of Pd-GNP was studied using high pressure Seiverts' apparatus at three different temperatures (25, 50 and 100 °C). Adsorption capacity was calculated by incorporating van der Waals corrections in gas equation and room temperature isotherm was treated with Dubinin–Radushkevitch

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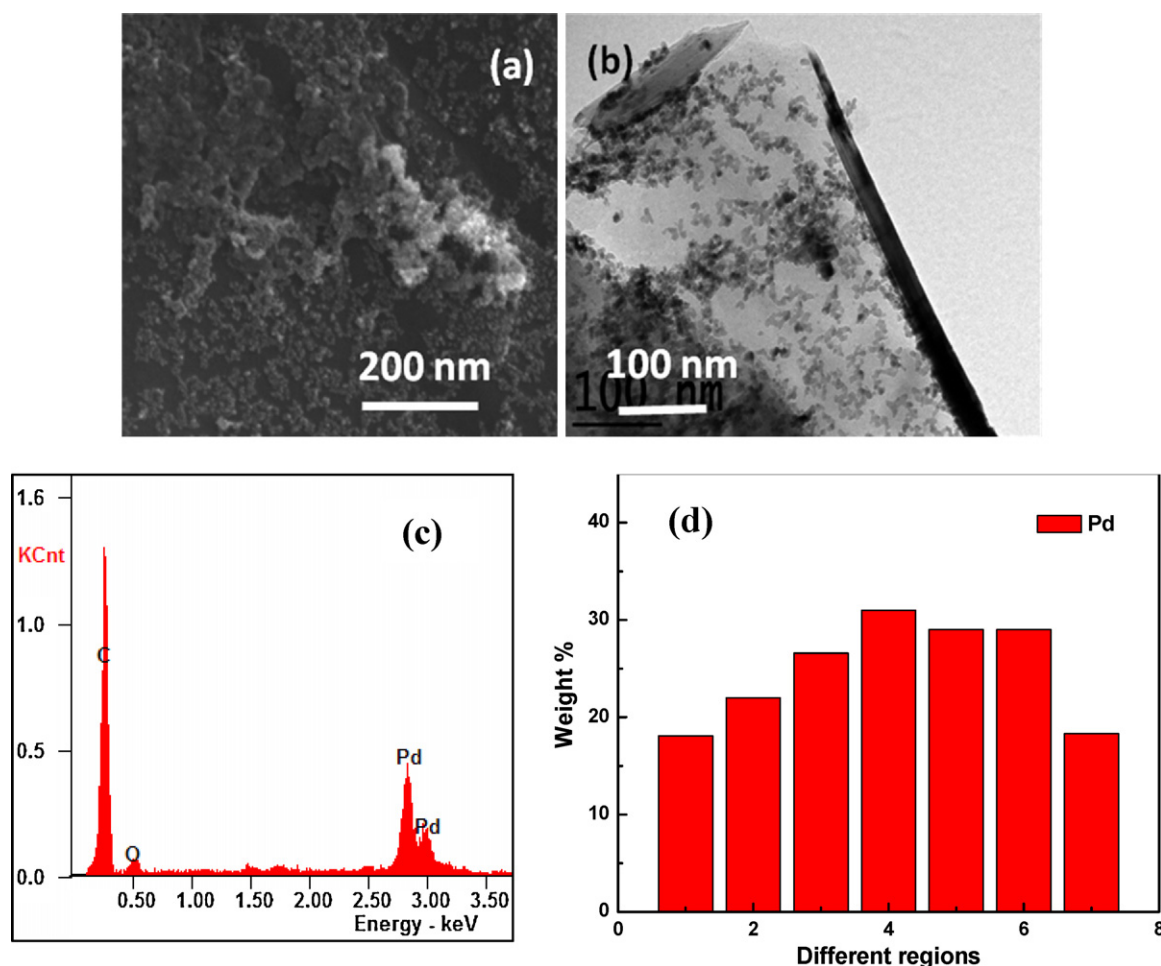**Fig. 1.** (a) SEM, (b) TEM images and (c and d) EDAX analysis of Pd-GNP nanocomposite.

equation. Desorption of CO_2 was performed at 150 °C under high vacuum ($\sim 10^{-9}$ bar).

2. Experimental

2.1. Preparation of Pd-GNP nanocomposite

Graphite was vigorously stirred with conc. HNO_3 and conc. H_2SO_4 in 1:3 ratios for 3 days. Vigorous stirring of graphite under strong acidic medium may cause the formation of acid intercalated graphite. This intercalated graphite was further thermally exfoliated at 1000 °C. This thermal shock may lead to the destacking of the graphite plates and hence formation of GNP [20,21]. This GNP was further treated with conc. HNO_3, which introduces hydrophilic functional groups (–COOH, –C=O, and –OH) at the surface of GNP. These functionalized graphite nanoplatelets (f-GNP) were further washed several times with water to achieve pH 7 followed by drying.

Decoration of Pd nanoparticles over the f-GNP surface was done by chemical technique. Functionalized GNP was suspended in de-ionised water by ultrasonication method. Functional groups at the surface of GNP provide the anchoring sites for metal nanoparticles and hence better decoration of nanoparticles at the f-GNP surface. Pd-GNP nanocomposite was prepared by reducing aqueous acidic solution of $PdCl_2$ and f-GNP with 0.1 M $NaBH_4$ and 1 M NaOH solutions followed by washing to neutralize with water [22].

2.2. Characterization techniques

Pd-GNP nanocomposite was characterized by FEI QUANTA 3D scanning electron microcope (SEM) and Philips JEOL CM12 transmission electron microscope (TEM). X-ray powder diffraction analysis was performed by X' Pert Pro PANalytical X-ray diffractometer. Raman analysis was performed by using HORIBA JOBIN YVON HR800UV Confocal Raman spectrometer, while FTIR study was performed by using PERKIN ELMER Spectrum One FT-IR spectrometer. Adsorption studies for CO_2 gas was performed using Seivert's apparatus. Surface texture study was performed by N_2 adsorption–desorption using Micromeritrix ASAP 2020 surface area analyzer. Surface acidity measurement was performed by NH_3 adsorption using Micromeritrix Autochem II 2920 analyzer.

2.3. Adsorption studies

Adsorption studies were carried out using high pressure Seivert's apparatus, which has been used well for high pressure hydrogen sorption studies [23]. The experimental setup consists of stainless tubes, tees, elbow joints and needle valves procured from NOVA, Switzerland. They can withstand up to 1000 bar pressure. The pressure transducers procured from Burster, Germany are used to monitor the gas pressure in the range 0–50 bar. Numbers of cycles were performed to recheck the adsorption capacity and the values were found to be consistent within the experimental error. Samples were degassed at 150 °C under high vacuum (10^{-9} bar) to