Enhanced hydrogen storage performance of reduced graphene oxide hybrids with nickel or its metallic mixtures based on spillover mechanism

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Abstract

In this work, as a fascinating 2-dimensional carbon material, reduced graphene oxide (rGO) has been decorated with Ni, Ni/Pd, and Ni/Ag/Pd nanoparticles on its surface to enhance its hydrogen storage performance based on the spillover mechanism. First, graphene oxide (GO) was fabricated from graphite by a modified Hummer method. Next the GO was dispersed in water and mixed with nickel chloride, palladium chloride, and/or silver nitrate to synthesize parental Ni(OH)₂/GO, Ni(OH)₂/Pd(OH)₂/GO, and Ni(OH)₂/Pd(OH)₂/AgOH/GO hybrids through hydrothermal treatment with HMTA as a capping and precipitation agent. After in situ reduction of these parental hybrids with hydrogen flow and heat treatment at 350°C, nanostructured Ni/rGO, Ni/Pd/rGO, and Ni/Ag/Pd/rGO hybrids were obtained. These Ni (Ni/Pd, or Ni/Ag/Pd)/rGO hybrids show great potential in hydrogen storage at ambient environment, as measured at room temperature (293.15K) and 800 mmHg, 0.007, 0.13, and 0.055 wt% hydrogen adsorption capacity was obtained from the Ni/rGO, Ni/Pd/rGO, and Ni/Ag/Pd/rGO hybrids, respectively.

Keywords: Graphene; Nickel; Metallic; Spillover; Hydrogen storage

Introduction

Hydrogen can be stored with different methods [1], including high-pressure tank, cryogenic-liquid storage, physisorption [2-5] and chemisorption [6,7]. However, conventional hydrogen storage methods have various problems such as high potential safety hazards, extreme storage conditions, low capacities, etc. Among various storage methods, adsorption in solid state materials is considered as a promising approach due to fast kinetics, excellent reversibility and high adsorption capacity possibly at low pressure and ambient temperature [8]. To store hydrogen efficiently, one of the most common ways is to enhance adsorption capacity of solid state materials via spillover mechanism [9,10]. Hydrogen spillover is a phenomenon describing the transport of dissociated hydrogen generated on the first surface (like Pd), then absorbed by second surface (like carbon) [11,12]. This mechanism enables us to use solid materials to store hydrogen at ambient environments.

Carbon materials such as graphene [13-15], carbon nanotubes [16,17] and activated carbon [18-20] are promising candidates as hydrogen absorbents because of their high surface areas and porous structures [13-20]. For example, M. C. Tellez-Juarez et al [21] prepared activated carbon with apparent surface areas higher than $3000 \text{ m}^2\cdot\text{g}^{-1}$ and obtained hydrogen adsorption as high as 6.8wt% at -193°C and 4 MPa. Guo et al [22] fabricated a hierarchical graphene material with a specific surface area up to $1305 \text{ m}^2\cdot\text{g}^{-1}$, which is composed of micropore ($\sim 0.8 \text{ nm}$), mesopore ($\sim 4 \text{ nm}$), and macropore ($>50 \text{ nm}$) and shows a capacity over 4.0% at atmospheric air pressure and 77K. To enhance the hydrogen adsorption capacity in ambient environment, especially at room temperature, noble metals like Pd [23] and Pt [24] have been utilized to dissociate hydrogen using spillover mechanism. As an example, Zhu et al [25] synthesized Pd/PC (porous carbon) composites exhibiting an ultrahigh surface area of $2734\text{-}3316 \text{ m}^2\cdot\text{g}^{-1}$ and large pore volumes of $1.789\text{-}1.991 \text{ cm}^3\cdot\text{g}^{-1}$. The excess hydrogen uptake of the Pd/PC-850 composite reached 4.6wt% at 77 K and 20 bar, but no measurements at room temperature were reported. Moreover, these noble metals are of great cost and limited supply. Therefore, common metals or their alloys/mixture with better performance are in demand to reduce the usage of noble metals. Alloying and core/shell mixing of metals have been

often used to ‘dilute’ expensive materials by cheaper ones in order to keep desired properties while lowering cost [26].

In this work, we synthesized nanoparticles of Ni and its derivative (i.e. Ni/Pd and Ni/Ag/Pd) hybridized with reduced graphene oxide (rGO) to store hydrogen at both ambient temperature and pressure. Compared to similar report on pure Pd doped carbon materials [27,28], our Ni/Pd/rGO hybrid shows better hydrogen adsorption capacity and excellent hydrogen reversibility. More specifically, with the use of hexamethylenetetramine (HMTA) as capping agent and in-situ reduction, we distributed Ni and its metallic mixture nanoparticles onto rGO flakes to obtain Ni (Ni/Pd, Ni/Ag/Pd)/rGO hybrid samples. More importantly, based on hydrogen adsorption performance measured at room temperature and atmospheric pressure, the 10 mmol Ni/5 mmol Pd/rGO hybrid demonstrates the best hydrogen adsorption capacity and the 5 mmol Ni/5 mmol Pd/5 mmol Ag/rGO possesses the best adsorption-desorption reversibility among the synthesized hybrid samples.

Experimental

2.1 Chemicals

Nickel(II) chloride hexahydrate ($\geq 98\%$), palladium(II) chloride ($\geq 99.9\%$), hexamethylenetetramine (HMTA, 99%), nitric acid (ACS reagent, 70%) and hydrogen peroxide (30-32%) were purchased from Sigma-Aldrich. Graphite powder (APS 7-11 micron, 99%) and potassium permanganate (98%) were obtained from Alfa Aesar, silver nitrate (ACS reagent) was from VWR scientific, sulfuric acid was from Acros, and hydrochloric acid was from Fisher scientific. All chemicals were used as received without further purification.

2.2 Synthesis of Ni/rGO, Ni/Pd/rGO and Ni/Pd/Ag/rGO hybrids

Graphene oxide (GO) was prepared from graphite flakes according to a modified Hummers’ method [29]. 1 g of GO was dispersed in 200 mL water by sonication for 30 min to form GO water dispersion, 15 mmol of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 30 mmol of HMTA were added into the dispersion, and then stirred for 20 min. The homogeneous mixture was separated and transferred to two 100 mL autoclave and hydrothermally reacted at 120°C for 1 hour to obtain parental $\text{Ni}(\text{OH})_2/\text{GO}$ hybrid. To make parental

Ni(OH)₂/Pd(OH)₂/GO hybrid, PdCl₂ and HMTA were added to the obtained parental Ni(OH)₂/GO hybrid followed with another hydrothermal reaction at 120 °C for 1 hours. To make parental Ni(OH)₂/AgOH/Pd(OH)₂/GO hybrid, AgNO₃ and HMTA were first added to the obtained parental Ni(OH)₂/GO hybrid followed with a hydrothermal reaction at 120 °C for another 1 hour. After that, PdCl₂ and HMTA were added to the Ni(OH)₂/AgOH/GO hybrid and followed with another hydrothermal reaction at 120 °C for 2 hours. Black solid products from the hydrothermal synthesis were separated by filtration, washed with DI water and dried at 70 °C under vacuum. After that, the black solids of these parental hybrids were reduced at 350 °C for 2 hours under continuous hydrogen flow to obtain Ni (Ni/Pd, Ni/Ag/Pd)/rGO hybrids. To be comparative, the total moles of metal salts initially introduced into 1 g of GO were kept at 15 mmol, i.e. 15 mmol of NiCl₂·6H₂O was used to generate the Ni/rGO hybrid, 10 mmol of NiCl₂·6H₂O and 5 mmol of PdCl₂ were used to generate the Ni/Pd/rGO hybrid, and 5 mmol of NiCl₂·6H₂O, 5 mmol of AgNO₃ and 5 mmol of PdCl₂ were used to produce the Ni/Ag/Pd/rGO hybrid. As a contrast, corresponding rGO sample without hybridizing with metallic nanoparticles was synthesized for comparison by processing the prepared GO through the whole synthesis procedure. The synthesis process for the Ni/rGO, Ni/Pd/rGO and Ni/Ag/Pd/rGO hybrids was schematically demonstrated as Figure 1 below.

Figure 1. Schematic diagram of the synthesis procedure of the Ni (Ni/Pd, Ni/Ag/Pd)/rGO hybrid samples.

2.3 Characterization

The morphology of the Ni (Ni/Pd, Ni/Ag/Pd) and rGO hybrid samples was investigated by a field-emission scanning electron microscopy (FESEM, Sigma VP Carl Zeiss, Germany). Energy-dispersive spectroscopy (EDS) was used to analysis element composite of these hybrids tested with EDAX detector equipped on the FESEM. The average diameter of the metallic nanoparticles was measured using the image analysis software Gatan Digital Micrograph (V2.3). Powder X-ray diffraction (XRD) was performed with a Rigaku Miniflex diffractometer. Raman spectra were taken by a SENTERRA Dispersive Raman Microscope which equipped with a 785 nm laser source. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K α spectrometer with monochromatic Al $_{K\alpha}$ radiation (1486.6 eV). The peak areas were quantified by its accompanying casaXPS (V2.3.16) software. Porosimetry analysis (BET surface area, BJH pore volume/pore area) and hydrogen sorption measurements were performed on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. A reference material (silica-alumina) provided by Micromeritics Company was tested to assure the accuracy of equipment. Nitrogen adsorption analyses were performed at 77 K after a preparatory degassing at 300 °C, 2 μ m Hg pressure for > 12 hours. Hydrogen adsorption analyses were performed at room temperature (295.15 K) after the same degassing procedure.

Results and discussion

3.1 SEM imaging

Figures 2a & 2b show the morphology of the GO and rGO samples, which were obtained with the modified Hummer method and with the same treatment at 350 °C under continuous hydrogen flow as the hybrid samples of rGO and Ni or its metallic mixtures, respectively. Figures 2c-h show the morphology and the EDS spectra of the corresponding Ni/rGO, Ni/Pd/rGO and Ni/Ag/Pd/rGO hybrid samples. The concentration of metal as per EDS spectra provided in supplemental inf.1. The SEM images illustrated that metallic Ni, Ni/Pd, Ni/Ag/Pd nanoparticles with diameter varying from 10 to 110 nm were well distributed on the rGO sheets. The diameters of the Ni, Ni/Pd, and Ni/Ag/Pd particles vary because of the difference of metal precursor introducing sequence and their

reduction activities. More specifically, Fig. 2c illustrated that the Ni nanoparticles were of ~13 nm. When the Ni precursor was firstly introduced, its low reduction activity resulted in the smallest particles in this series of samples. In Fig. 2e, it can be seen that the Ni/Pd nanoparticles grew to ~30 nm. The Pd precursor PdCl_2 was added into the $\text{Ni(OH)}_2/\text{GO}$ system and it is believed that metallic Pd layer was wrapped on the Ni NP surface as further confirmed by the EDS spectrum in Fig. 2f. Therefore the average diameter of the Ni/Pd nanoparticles increased. Fig. 2g clearly shows the diameter of the Ni/Ag/Pd particles varies from 40-110 nm. It is because the reduction activities of Pd and Ag precursors are much higher than that of the Ni precursor, thus some particles contain mainly Pd and/or Ag and have bigger size. The increasing trend of the diameter of these metallic nanoparticles following that of their reduction activity indirectly proved that they are composed of corresponding metal layers.

Figure 2. (a) SEM image of the GO; (b) SEM image of the rGO; SEM images and EDS spectra of the hybrids: (c & d) the Ni/rGO hybrid; (e & f) the Ni/Pd/rGO hybrid; and (g & h) the Ni/Ag/Pd/rGO hybrid.

Moreover, it can be clearly seen from these SEM images that the metal nanoparticles inserted into the rGO layers (Figures 2a&b vs 2c, 2e & 2g). It is believed that during the hydrothermal reaction, graphene oxide dispersed in water and reacted with the metal precursors. These metal precursors then hydrolyzed into metal hydroxide nanoparticles as assisted and controlled by the added HMTA, and these metal hydroxide nanoparticles decorated onto the GO surface. After the hydrothermal reaction, the GO sheets tended to stack back as shown in Fig. 2a but were prevented with the metal hydroxide nanoparticles decorated on their surface. Therefore, as observed here, the metallic Ni, Ni/Pd, Ni/Ag/Pd nanoparticles presented between the rGO layers after the hydrogen reduction process at 350 °C.

3.2 XRD patterns

Fig. 3A shows the X-ray diffraction patterns of the synthesized Ni (Ni/Pd, Ni/Ag/Pd)/rGO hybrids accompanied with that of the synthesized rGO. As seen, the rGO sample showed a very broad peak around $2\theta = 26^\circ$, all of the hybrid samples have this peak at the same position (shown in Fig. 3B), due to reduced graphene oxide is highly disorder, they can't show distinguish peaks, enlarged XRD peaks shows in Fig. 3B. And in Fig. 3C, there is a peak in 11° shows in GO sample, but no peaks at the same position for rGO or metal/rGO samples, which confirms the existence of rGO in these hybrid samples. XRD patterns of Ni/rGO demonstrated that there were two types of Ni crystal structures, i.e. cubic and hexagonal phases. By comparing the XRD patterns of the Ni/rGO, Ni/Pd/rGO and Ni/Ag/Pd/rGO hybrid samples, the intensity of corresponding Ni peaks decreased in this sequence, which confirms that the Ni percentage decreased in these samples as the initial amount (and so as the ratio) of the introduced Ni salt decreased in the sequence of Ni/rGO, Ni/Pd/rGO and Ni/Ag/Pd/rGO. This is also in agreement with the metal concentration change in EDS analysis (see Figure S1). Obvious intensity difference between the diffraction peaks from metallic Ni and Pd is consistent with the fact that the reduction activity of the used Ni precursor NiCl_2 was weaker than that of the Pd precursor PdCl_2 , which resulted in the observed phenomenon that the Ni nanoparticles is much smaller than its metallic mixture counterpart Ni/Pd and the relative percentage of Ni is low. In the XRD pattern of the Ni/Ag/Pd/rGO hybrid, the diffraction

peak intensities from Ag and Pd are at the same height due to the facts that these two metal precursors PdCl_2 and AgNO_3 have similar reduction activities and were added with the same molar amount. Blue shift of the Pd peak position was observed when comparing the XRD patterns from the Ni/Pd/rGO and Ni/Ag/Pd/rGO hybrids. The possible explanation for this phenomenon is because of slight substitution of Ag into Pd lattice due to their similar atom radii, which resulted in twists of the Pd crystal structure, as previously observed in Pd-Ag alloy sample [30].

Figure 3. (A) XRD patterns; (B) enlarged XRD patterns shown in (A) in the range of 20° – 30° ; (C) zoomed in XRD patterns shown in (A) in the range of 10° – 20° ; and (D) normalized Raman spectra of (a) GO, (b) rGO, (c) Ni/rGO, (d) Ni/Pd/rGO, and (e) Ni/Ag/Pd/rGO samples.

3.3 Raman analysis

Fig. 3D presents the Raman spectra of the GO, rGO, and Ni (Ni/Pd, Ni/Ag/Pd) and rGO hybrid samples with two distinct peaks of carbon at around 1355 cm^{-1} (D peak) and 1594 cm^{-1} (G peak). The intensity ratio of these two bands, $I(D)/I(G)$, can be used to characterize surface defect density of graphene sheets [31-33]. In high-defect-density regime, the intensity ratio $I(D)/I(G) = D(\lambda) \cdot L_D^2$, [34] where $D(\lambda)$ is the constant depend on laser excitation wavelength and L_D is distance between defects. According to the Raman spectra, the Ni/Ag/Pd/rGO hybrid had the highest $I(D)/I(G) \approx 1.64$, which revealed that its defect distance was the smallest, in other words, this Ni/Ag/Pd/rGO hybrid has more defects compared to the other samples. Compared to the Ni/rGO and Ni/Pd/rGO hybrids with $I(D)/I(G) \approx 1.37$ and 1.43 respectively, the Ni/Ag/Pd/rGO hybrid underwent the longest reaction time. Repeated heating-up and cooling-down during the synthesis made the Ni/Ag/Pd/rGO hybrid tended to generate the most atomic-scale defects while the Ni/rGO hybrid had the least defects on graphene layers.

Moreover, there were smooth board peak rises around 2700 cm^{-1} , where the 2D peak of graphene is located. It is reported that the Raman peaks of 2D graphene stacks would become boarder and shift to higher wavenumber because of increasing layers of graphene [33]. In Fig. 3B, the 2D graphene peak from the Ni, Ni/Pd, Ni/Ag/Pd/rGO hybrid samples shifted to higher wavenumber and became broader, which means graphene layers stacked back together and is in agreement with nitrogen adsorption isotherms shown in Fig. 5 below.

3.4 XPS analysis

Fig. 4 demonstrated the XPS C1s spectra of GO, rGO, Ni/rGO, Ni/Pd/rGO and Ni/Ag/Pd/rGO hybrid samples, which confirms the reduction of the parental metal hydroxide and GO hybrids into the corresponding Ni and its metallic mixture with rGO hybrids from these XPS measurements. As shown in Fig. 4a, the C1s spectra of GO can be convoluted into three peaks at 284.5 , 286.3 and 287.6 eV via gauss fitting, which corresponded to C-C/C=C, C-OH and C=O functional groups [35], respectively. It is also consistent with what have been reported in the literature that the major functional group of GO are hydroxyl, carboxyl and epoxy groups [36]. Comparing Fig. 4a to Fig. 4c-e, the

C-OH intensity in the metal/rGO hybrid samples decreased tremendously. Large quantity removal of C-OH and C=O groups and the increasing amount of C-C/C=C groups indicated the successful reduction of GO into rGO. This observation in agree with the previous study on similar Ni/rGO hybrids [37].

Figure 4. XPS C1s spectra of (a) GO; (b) rGO; (c) Ni/rGO; (d) Ni/Pd/rGO; and (e) Ni/Ag/Pd/rGO hybrids.

3.5 Porosimetry (BET surface area and BJH pore volume)

Fig. 5 shows the nitrogen adsorption isotherms taken at 77 K for GO, rGO, and Ni series rGO hybrids. The isotherms of Ni (Ni/Pd, Ni/Ag/Pd) with rGO hybrid samples exhibited

the typical type III adsorption, indicating the formation of adsorbate multilayers and the weak adsorbate-adsorbent interactions [38]. We found that Ni/rGO had a delay in N₂ desorption as the first N₂ adsorption-desorption hysteresis observed, however this hysteresis did not happen from other two hybrid samples. The Ni/rGO hybrid with the highest percentage of Ni is the only one who had delay in desorption. The difference of these hybrids was probably due to composition of metallic nanoparticles. It can be inferred that Pd and Ag may be helpful to reduce the hysteresis in gas adsorption and Ni alone might not be as good as these two metals. Thus it may be beneficial to control the Ni percentage in certain range for the reversible gas desorption of this type of hybrids while further study is necessary on this aspect.

Corresponding BET surface area and BJH pore volume values were calculated from the scale of relative pressure from 0.06 to 0.2 P/P₀ and shown in Table 1. After series of treatment, GO turns to curly rGO hence the surface area increase from ~33 to ~119 m²/g. And it can be observed that the Ni/rGO, Ni/Pd/rGO, Ni/Ag/Pd/rGO hybrids exhibited decreasing trend in BET surface area and pore volume as more types of metals were introduced into the hybrid system. This trend is because curly graphene surface were occupied by metal nanoparticles. As shown by the SEM images in Fig. 2, metal nanoparticles became bigger when more types of metals were added. Therefore the surface area and pore volume of the Ni (Ni/Pd, Ni/Ag/Pd)/rGO hybrid samples had reduced. According to Raman analysis in Fig. 3B, the graphene sheets in the hybrid samples stacked back, but they could not fully stack back to intense graphite structure due to the insertion of the metallic nanoparticles between the rGO layers. Hence Ni(Ni/Pd, Ni/Ag/Pd)/rGO hybrids have BET surface area of ~30 m²/g, which is similar to GO sample.

Figure 5. Nitrogen adsorption isotherms of the GO, rGO, Ni/rGO, Ni/Pd/rGO and Ni/Ag/Pd/rGO hybrid samples at 77 K.

Table 1 Porosity analysis of the GO, rGO, Ni/rGO, Ni/Pd/rGO and Ni/Ag/Pd/rGO hybrid samples from the nitrogen adsorption isotherm analysis at 77 K.

	GO	rGO	Ni/rGO	Ni/Pd/rGO	Ni/Ag/Pd/rGO
BET Surface Area (m²/g)	33.0275	119.7858	38.6597	25.4270	23.3813
BJH pore volume (cm³/g)	0.0743	0.0962	0.0734	0.0713	0.0645

3.6 Hydrogen storage application

Fig. 6 shows the hydrogen adsorption performance of the GO, rGO, and Ni/rGO, Ni/Pd/rGO, Ni/Ag/Pd/rGO hybrids at 295 K. At 295 K and 800 mmHg, the hydrogen uptake capacity of the Ni/rGO, Ni/Pd/rGO and Ni/Ag/Pd/rGO was measured to be 0.007%, 0.13% and 0.055%, respectively, while GO and rGO have negligible hydrogen uptake capacity as expected under the ambient conditions. In comparison with the GO and rGO contrast samples, the Ni/Pd/rGO and Ni/Ag/Pd/rGO hybrid sample demonstrated greatly enhanced hydrogen adsorption uptake capacity. Moreover, our

Ni/Pd/rGO and Ni/Ag/Pd/rGO hybrid samples possess higher hydrogen adsorption capacities than the Pd/carbon (activated carbon, graphene/activated carbon) hybrids at room temperature (298 K) and atmospheric pressure (0.1 MPa) reported on the literature with corresponding values of 0.08wt% [27] and 0.018% [28], respectively. Thus, the Ni mixtures of Ni/Pd and Ni/Ag/Pd are good candidates to replace bulk Pd as surface decoration catalysts on large surface carbon materials for hydrogen adsorption, especially based on the spillover mechanism at ambient conditions.

Hydrogen adsorption isotherms in Fig. 6 also reveal that the Ni/rGO hybrid does not have very active hydrogen adsorption performance due to the low spillover activity of Ni, and the high hydrogen storage performance of our Ni/Pd/rGO and Ni/Ag/Pd/rGO hybrid samples at ambient environment can be attributed to the excellent spillover activity of the Pd component [39]. The Ni/Pd nanoparticles on the rGO surface make Pd atoms from the Ni/Pd/rGO hybrid sample has high surface area to maintain good contact with H₂ molecules, even with low amount of Pd and eventually in the Ni/Pd/rGO hybrid. Therefore, it is believed that our Ni (Ni/Pd, Ni/Ag/Pd)/rGO hybrid approach and sample preparation procedure reported here are promising to enhance their adsorption capacity for hydrogen molecules by decorating high surface porous materials with metal nanoparticles. At the meantime, we also realized that not all the metallic particle mixtures are favorable for hydrogen storage based on the spillover mechanism. Particularly, the Ni/Ag/Pd/rGO hybrid did not show performance as good as the Ni/Pd/rGO sample. Therefore, the composition of metal particles [40] is also a very important factor affecting hydrogen spillover activities.

Moreover, the reversibility of adsorption and desorption performance of an adsorbent is another key factor for its commercial use as a hydrogen storage material [41]. For their full usage, hydrogen adsorbent materials need to be able to fully desorb hydrogen as well in ambient environment after adsorption. In our cases, the Ni (Ni/Pd, Ni/Ag/Pd)/rGO hybrid samples exhibited very good reversibility at room temperature and atmospheric pressure. Among these samples, the Ni/Ag/Pd/rGO hybrid had the best hydrogen adsorption-desorption reversibility performance even though its hydrogen uptake capability is only half of the Ni/Pd/rGO hybrid. This is because the size of the Ni/Ag/Pd metallic nanoparticles in the Ni/Ag/Pd/rGO hybrid sample is the biggest compared to

those in the other two hybrids. The contact and space between rGO surface and the Ni/Ag/Pd metallic nanoparticles provide a ‘highway’ for H₂ gas molecules to quickly adsorb and desorb, therefore the Ni/Ag/Pd/rGO hybrid sample shows the best reversibility.

Figure 6. Hydrogen adsorption performance of the GO, rGO, Ni/rGO, Ni/Pd/rGO and Ni/Ag/Pd/rGO hybrid samples measured at 295 K.

Conclusions

In this study, Ni (Ni/Pd, Ni/Ag/Pd) and rGO hybrid samples have been successfully prepared by a hydrothermal reaction using HMTA as capping agent and hydroxide source followed with in-situ reduction by heat treatment with H₂ flow. Metallic Ni and its Ni/Pd and Ni/Ag/Pd nanoparticles with diameter varying from ~10-110 nm were well dispersed on reduced graphene oxide sheets. The Ni/Pd/rGO sample showed the best hydrogen uptake capacity of 0.13wt% at room temperature (295.15 K) and atmospheric pressure (800 mmHg) while the Ni/Ag/Pd/rGO had the best hydrogen adsorption-desorption reversibility. The promising results encourage further studies with the replacement of Pd by Ni mixtures/alloys for hydrogen storage through spillover in ambient environment.

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