Performance of palladium nanoparticle–graphene composite as an efficient electrode material for electrochemical double layer capacitors

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ABSTRACT

Palladium nanoparticle–graphene nanosheet composite (PdNP–GN) is demonstrated as an efficient electrode material in energy storage applications in supercapacitors. Palladium nanoparticle (PdNP) decorated graphene nanosheet (GN) composite was synthesized via a chemical approach in a single step by the simultaneous reduction of graphene oxide (GO) and palladium chloride from the aqueous phase using ascorbic acid as reducing agent. The materials were characterized by scanning and high resolution transmission electron microscopy, Raman, X-ray diffraction and energy dispersive X-ray spectroscopy which demonstrate that the metal nanoparticles have been uniformly deposited on the surface of graphene nanosheets. The synthesized material has been analyzed by cyclic voltammetry, electrochemical impedance spectrometry and chronopotentiometry using 1M KCl as the supporting electrolyte for its application in electrochemical double layer supercapacitors. PdNPs-GN composite showed improved electron transfer kinetics and superior capacitive performance with large specific capacitance of 637 F g⁻¹, excellent cyclic performance and maximum energy and power densities of 56 Wh kg⁻¹ and 1166 W kg⁻¹, respectively at a current density of 1.25 A g⁻¹. This highlights the importance of the synergetic effects of electrochemically efficient Pd nanoparticles and graphene for energy storage applications in supercapacitors.

Key words: Graphene, Palladium nanoparticles, Supercapacitors, Energy density.

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1. Introduction

There is currently a growing interest in the development of high-performance, low-cost and environmental-friendly electrode materials for energy storage devices. Among all energy storage devices, supercapacitors (SCs), also called electrochemical supercapacitors (ESCs) have attracted major attention due to their long cycle life, high power performance and low maintenance cost [1, 2] and potential applications in diverse technologies, such as hybrid electric vehicles, portable electronic devices and for power backup purposes [1-3]. Compared with secondary batteries, supercapacitors can provide high power in short-term pulses, and can be used as peak-power sources in hybrid electric vehicles, memory backup devices, or back-up supplies to protect against power disruption [4]. Supercapacitors can be categorized into two main types depending upon the specific charge-storage mechanism: (i) electrical double-layer capacitors (EDLCs), where the electrical charge is stored at the interface between the electrode and the electrolyte; (ii) redox electrochemical capacitors, where capacitance arises from reversible Faradaic reactions at the electrode/electrolyte interface [1].

Among the materials investigated recently, carbonaceous materials [5], transition metal oxides [6–11] and conducting polymers [12–15] have emerged as promising candidates for electrodes in SCs. However, each material has its unique advantage and disadvantage for SC application. For example, carbon based SCs have high power density and long life cycle, but the small double layer capacitance limits its application. SCs based on transition metal oxides, hydroxides and conducting polymers show fast redox kinetics with relatively higher capacitance while their relative low mechanical stability and cycle life are major limitations for the SCs [16-20]. However, the composite electrodes based on active carbon materials and metal oxide nanoparticles which combine the advantages of EDLCs and pseudocapacitors can overcome

these limitations [17, 21]. Furthermore, the composites based on carbon-based materials and active metal nanoparticles, such as palladium and platinum which do not show pseudocapacitive behavior but are expected to enhance the electrical double layer capacitance by providing larger electrochemically active surface areas for the adsorption of ions, offer additional advantages.

Graphene nanosheets (GN) with a hexagonal atomic layer structure and unique properties, such as its high electron mobility, large surface area, thermal, chemical and mechanical stability and ease in surface modification have attracted a great deal of interest in recent years for the development of new composite materials for a wide range of applications including sensors and supercapacitors [22-27]. Large scale synthesis of graphene can be carried out in different ways like mechanical exfoliation [28], thermal decomposition of SiC [29], oxidation of graphite [30] and liquid-phase exfoliation of graphite [31]. One of the most promising and scalable approaches to obtain graphene is to convert graphene oxide generated by the oxidization and subsequent exfoliation to graphene via chemical reduction or thermal treatment [32, 33]. However, monolayer graphene sheets undergo restacking due to the van der Waals interactions during the reduction process, which leads to a dramatic decrease of specific surface area of graphene, adversely affecting potential applications of GN. One way to overcome this problem is to decorate graphene layers with functional nanomaterials, which not only prevent the restacking of graphene layers but also provide larger electrochemically active surface area for the adsorption of ions and effectively accelerates the electron transfer rate [26, 27].

Various approaches have been recently used [34-36] to decorate GN with functional materials. In our earlier work, porous CuO was used to decorate graphene for use as electrode in SC. The resulting graphene-CuO composite showed superior cycling performance as well as specific capacitance [37]. Palladium nanoparticle decorated graphene hybrid materials have

been used for catalysis [38-40] and electrochemical sensing applications [26, 41]. However, research on the palladium metal nanoparticle decorated graphene composite as material for supercapacitor applications remains a challenge. Further, the use of common reducing agents such as NaBH_4 , ethylene glycol and hydrazine for graphene synthesis are toxic to the environment.

Here we present the use of Pd-NP decorated graphene as an efficient electrode material in ECDL supercapacitor. The PdNP-graphene composite is prepared in a simple, top-down (chemical reduction) approach, wherein graphene oxide and Pd-ions are simultaneously reduced together by friendly ascorbic acid. In this approach, ascorbic acid, an environmentally friendly reducing agent is also believed to be act as a capping agent for PdNPs. The PdNP-graphene composite demonstrates excellent electrochemical and environmental properties as ECDL supercapacitor electrode.

2. Experimental

2.1. Chemicals and materials

Natural graphite (99.5% pure, particle size $<50\mu\text{m}$) was obtained from s. d fine chem ltd. Sulphuric acid (AR grade, 98%), potassium permanganate (AR grade, 99%) were obtained from s. d. fine chem. ltd. Ascorbic acid and palladium (II) chloride (99%) were procured from Sigma Aldrich. All the chemicals were used without any further purification. Double distilled water was used throughout analysis.

2.2. Synthesis of PdNPs-GN composite

Graphite oxide was prepared by the Hummers method as previously described [42]. 500 mg of graphite oxide was exfoliated into graphene oxide (GO) by sonication in 100 ml of water for 2 h. Palladium nanoparticle-graphene composite was prepared in a simple way by dispersing

GO in water using ultrasonication. Acidified PdCl_2 solution was added in the GO dispersion and the reduction was initiated using ascorbic acid. With a given concentration of GO (50 mg) dispersed in 50 ml water by sonication, various amounts of PdCl_2 (11.0, 22.0, 44.0 and 88.0 mg) were added to the GO dispersion to load on graphene during reduction for the best electrochemical performance. Simultaneous reduction of graphene oxide (GO) and palladium chloride from the aqueous phase was achieved using ascorbic acid as reducing agent, avoiding the use of highly toxic NaBH_4 and hydrazine as reducing agents. An additional advantage of using ascorbic acid as reducing agent the possibility of its oxidized product acting as capping agent in stabilizing Pd NPs. The slurry obtained after adding ascorbic acid and sonicated for 60 min was stirred magnetically for 7 hours at room temperature. The mixture was allowed to stand for 10 h. The resulting black precipitate was separated from the aqueous supernatant by filtration using Millipore filter membrane and washed with water and methanol three times (20 ml each) and dried at 100°C overnight in a vacuum oven. 44 mg of PdCl_2 in 50 ml of distilled water acidified with conc. HCl added to the GO dispersion showed the best electrochemical performance when 362.2 mg of freshly prepared ascorbic acid was used. Pristine GN were synthesized independently using the same procedure but in absence of PdCl_2 .

2.3. Characterization methods

The crystallographic structures of the materials were characterized by powder X-ray diffraction (XRD) using Maxima 7000S XRD (Shimadzu, Japan) equipped with CuK_α radiation ($\lambda=0.154$ nm). Data was collected for 2-theta values from 2° to 80° for GO and GN and 2° to 120° for GN-PdNPs composite at a scan speed of $3.0^\circ/\text{min}$ and preset time of 1.0 s. Raman spectra were recorded using Renishaw micro-Raman spectrometer (RE-04) equipped with solid state laser with the diode pumped at 514 nm. The microstructure of the samples was investigated

by scanning electron microscopy (SEM) obtained from S-4800 field emission SEM system (FEI Quanta 200) operating at 20.0 kV equipped to perform elemental chemical analysis by energy dispersive X-ray spectroscopy (EDX). Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) were observed on a JEOL JEM 2100F microscope at 200 kV using an Orius SC1000 camera to further characterize the microstructure of the samples. For this, all the samples were dispersed in DMF and then the suspensions were bath sonicated at room temperature for 30 minutes. The solutions containing the sample were then drop casted on a holey carbon grid and let dry. Once the solvent was evaporated, the sample would be held on the grid.

2.4. Electrode preparation and electrochemical measurements

GCE was mechanically polished with a 0.05 mm alumina slurry and then sequentially sonicated in dilute nitric acid, anhydrous ethanol and redistilled water for 15 min. Next, the cleaned GCE was dried under nitrogen stream. 10 mg of each of GN and PdNPs-GN composite were dispersed in 5 mL dimethylformamide by sonicating in an ultrasound bath for 30 min to form a stable suspension. The suspension of 10.0 μ L was cast onto the GCE surface by a micropipette, and then thoroughly dried under an infrared lamp. Subsequently, the electrode was rinsed several times by distilled water and dried in air before use; the final obtained electrode was denoted as PdNPs-GN//GCE. For comparison, the GN/GCE was prepared using the GN dispersion alone by following the same procedure.

All voltammetric measurements were performed with a CHI electrochemical workstation (CH Instruments Model CHI1100B series). The conventional three-electrode geometry was adopted. The working electrode was a PdNP-GN composite modified glassy carbon electrode and the auxiliary and reference electrodes were platinum wire and Ag/AgCl/3M KCl,

respectively. The capacitive behavior of PdNP-GN/GCE was studied by cyclic voltammetry (CV) in 1 M KCl electrolyte at room temperature. Chronopotentiometry was used to study the galvanostatic charging-discharging characteristics of the material at different current densities. Electrochemical impedance measurements were performed using Eco Chemie, Electrochemical Work Station, model Autolab PGSTAT 30 using GPES software, version 4.9.005 and Frequency Response Analyser, software version 2.0 and measured in the frequency range from 10^6 Hz to 0.1 Hz. An Ag/AgCl/3M KCl and a platinum electrode were used as reference and counter electrodes, respectively.

Measurement of capacitance in the development of electrochemical supercapacitors is necessary to evaluate performance, application, and trouble-shooting when designing and re-designing active electrode materials. Determining the capacitance (C) or specific gravimetric capacitance (C_p) from CV experimental results often requires the integration of the current response in a cyclic voltammogram and can be calculated by using the equation [2, 37, 42].

$$C = \frac{\int I dv}{\Delta V \cdot v} \quad (1)$$

where, C is capacitance (F), I is the average current in the complete CV loop response (A), $\Delta V = V_f - V_i$ (where, V_f and V_i are the integration potential limits of the voltammetric curve. v is the potential scan rate ($V s^{-1}$). The specific capacitance of the material has been calculated from the CV curves according to the following equation:

$$C_{sp} = \frac{\int I dv}{\Delta V \cdot v \cdot m} \quad (2)$$

where C_{sp} ($F g^{-1}$) is the specific capacitance, m (g) is the mass of the electroactive materials in the electrode.

The discharge capacitance (C) of the electrodes at the constant current density was calculated using chronopotentiometry from the slope of the discharge curve obtained at different current densities using the equation [2, 27, 43].

$$C_{sp} = \frac{I}{m} \times \frac{dt}{dv}, \quad (3)$$

where C_{sp} is the specific capacitance in ($F\ g^{-1}$), I the discharge current in ampere (A) and $\frac{dt}{dv}$ is the inverse of the slope of the discharge curve in volts per second ($V\ s^{-1}$) and m is the mass of the electroactive material (g). The mass of as-synthesized electrode material used was 20 μg . The maximum energy density values were calculated using the equation:

$$E = \frac{1}{2} C_{sp} V_i^2 \quad (4)$$

where C_{sp} is the specific capacitance and V_i is the initial potential of the discharge curve [43].

3. Results and discussion

3.1. Structural and microstructural characterizations of GN and PdNP-GN composite

Scheme 1 shows the schematic representation of synthesis of PdNP-GN composite. The presence of epoxy and hydroxyl groups on basal planes and carbonyl and carboxyl groups on edges of GO act as anchoring sites for PdNP attachment [36, 44]. It is important to note that while defect-free GN have excellent electrical and electronic properties, the same is not true for GO. The presence of oxygenated species on the surface and edges of GO severely impair their electrical properties. Thus, simultaneous reduction of GO to GN and deposition of nanoparticles is expected to form an electrochemically active and electrically enhanced conductive composite material. Ascorbic acid, used as reducing agent removes most of the oxygen-containing groups whereby the conductivity of GN is recovered. When Pd (II) chloride is added in the GO suspension, the Pd^{+2} ions are adsorbed on the GO nanosheets by coordination with the surface

functionalities of GO. Ascorbic acid simultaneously reduces the metal ions, which get deposited on the surfaces of nanosheets as nanocrystals and GO into graphene. This results in the formation of a graphene-metal nanocrystals hybrid.

Scheme 1

Fig. 1A shows the XRD pattern of as synthesized graphene oxide with two characteristic peaks at 10.13° and 42.12° and Fig. 1B shows the XRD pattern of graphene with its characteristic peak at 24.3° indexed to the (002) crystal face of graphene [44]. Figure 1C shows the XRD pattern of palladium nanoparticle-graphene composite (PdNPs-GN). The successful reduction of GO to GN is indicated by the absence of characteristic diffraction peak of GO and appearance of peak at $2\theta \approx 24.3^\circ$ for graphene in the XRD pattern of PdNPs-GN composite. As shown in figure, prominent peaks at 2θ values of 40.0° , 46.5° , 67.9° , 81.5° and 86.0° due to the Bragg reflections with d-spacings of 2.25, 1.95, 1.37, 1.18 and 1.12 Å correspond to the characteristic of face centered cubic crystalline Pd nanoparticles. These d-spacing values correspond to (111), (200), (220), (311) and (222) planes with lattice constant, $a = 3.871$ Å, matching with that of JCPDS file (#05-0681). XRD line corresponding to most intense peak and from the half-width of (111) was used to calculate the average crystalline size of the Pd nanoparticles using Debye-Scherrer formula [45]. The average size of the Pd nanoparticles estimated from the Debye-Scherrer formula is 7 nm.

Raman spectroscopy is widely used to characterize the structural changes of graphitic materials and to determine ordered and disordered crystal structures of graphene [46]. Fig.1D shows the Raman spectra of (a) GN and (b) PdNPs-GN composite. GN is characterized by two main peaks namely the D-band and a more intense G-band at 1351 cm^{-1} and 1502 cm^{-1} corresponding to the disorder induced band and in-phase lattice vibration, respectively [39, 47,

48]. As the degree of disorder in graphene increases, the intensity for D-band of the Raman spectra increases [48]. Also, a second-order overtone of a different in-plane vibration with a strong frequency dependence on the excitation laser is obtained at 2690 cm^{-1} . However, its behavior is more intricate in comparison to the frequency shift seen for the G band [48]. It is also observed from the Fig. 1D (b) that the I_D/I_G intensity ratio for the PdNPs-GN composite is higher than the I_D/I_G intensity ratio for GN (Fig. 1D (a)). The I_D/I_G ratio increases from 0.23 in GN to 1.23 in PdNP-GN composite. This indicates that the graphene sheets decorated with Pd nanoparticles have become smaller in size and also a probable chemical interaction between palladium nanoparticles and GN [49]. It is proposed that due to the presence of some carbon vacancies and defects in graphene during the reduction of graphene oxide to graphene may enhance the interaction between Pd nanoparticles and graphene [50, 51]. Similar behavior has also been observed previously with GN, GO and carbon nanotubes decorated with other metal nanoparticles [38, 52, 53]. Moreover, all the D, G and 2D bands of graphene are shifted to lower frequency in PdNP-GN composite (1295 , 1555 , and 2675 cm^{-1} , respectively) which further supports the PdNP- graphene interaction during the reduction process [38, 54].

Fig.1A, B, C, D

The SEM image of as-synthesized GO [Fig. 2A] shows the typical crumpled and wrinkled flakes of graphene oxide stacked together forming a typical multi-layer structure. Fig. 2B shows the SEM image of graphene in the dry state, in which most of the graphene nanosheets are curled and entangled together with a layered structure. Fig. 2C shows the SEM image of PdNP-GN composite in which the Pd nanoparticles appear as discrete bright spots and homogeneously distributed on the surfaces of graphene sheets. However, there is a broad distribution in the size of PdNPs (7-70 nm) decorated on graphene. It is also observed from the

figure that PdNPs deposited onto the edges and planes of GN, enter between graphene sheets as spacers to prevent the restacking of graphene sheets, and thus avoid the loss of their high active surface area. Graphene layers interacting via van der Waals forces form an open pore system, through which electrolyte ions easily access the surfaces of graphene, which facilitate the formation of electric double layers and improve the electrochemical utilization of Pd nanoparticles. The PdNP-GN composite was further characterized by EDAX. The EDAX spectrum of PdNP-GN (Fig. 2D) shows the peaks corresponding to C, O and Pd elements. The wt. % of C, O and Pd calculated from EDAX are 55.3, 10.43 and 33.27 respectively, revealing a good loading of Pd nanoparticles on GN sheets, which is consistent with the SEM observations.

The microstructure of synthesized GN and PdNP-GN composite was further characterized by transmission electron microscopy (TEM) and high resolution TEM (HRTEM). The TEM image [Fig. 3A] of synthesized graphene and the inset show its corresponding FFT pattern. The hexagonal FFT pattern confirms that the synthesized graphene is highly crystalline and free of defects. Fig. 3B and 3C shows the HRTEM images taken from the graphene and PdNPs respectively. The fringes from the multilayer graphene are clearly visible in the Fig. 3B. The lattice spacings, calculated from Fig. 3C is equal to 2.25 Å which confirms the 111 plane of the fcc phase crystalline Pd. Fig. 3D shows the TEM image of PdNP-GN composite where well dispersed PdNPs are immobilized on the surface of the graphene nanosheets which are clearly distinguishable. The particle size of PdNPs lies in the range of 10-80 nm. The selected area electron diffraction (SAED) pattern is shown in Fig. 3E. The lattice spacings calculated from the SAED pattern and the standard values (Table 1) from the JCPDS card # 5-0681 were also compared by rotational average method [55]. The excellent agreement between the standard

values and the calculated d-spacings proves that the PdNps are highly crystalline and free of impurities. All these studies confirm a good dispersion of Pd nanoparticles with graphene.

Fig. 2(A, B, C, D)

Fig. 3(A, B, C, D)

3.2. Electrochemical characterizations of PdNPs-GN composite

Electrochemical behavior and electron transfer characteristics of PdNP-GN modified GCE were investigated with the help of cyclic voltammetry using $[\text{Fe}(\text{CN})_6]^{4-}$ as a standard electrochemical probe in 1M KCl as supporting electrolyte. Fig. 4A shows the CVs of (a) GO, (b) GN and (c) PdNP-GN modified GCE at a scan rate of 100 mV s^{-1} . It is evident from the figure that a large peak current is obtained at PdNP-GN modified GCE in comparison to those obtained with GO and GN modified GCE. This indicates that PdNP-GN composite offers a fast electron transfer rate due to its reduced charge transfer resistance and larger effective surface area as a result of Pd nanoparticles loading. A well-defined redox couple of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{2-}$ system is obtained at PdNP-GN/GCE which shows a direct electron transfer reaction between PdNP-GN composite and electroactive species [56, 57]. Also, as the scan rate increases, the anodic as well as the cathodic peak currents increase with simultaneous shift in anodic and cathodic peak potentials towards the more positive and more negative, respectively (Fig. 4B). Therefore, the apparent electron transfer rate as indicated by redox peak separation is found to correlate to both the exposed area of the graphene nanosheets and the Pd nanoparticles density on the surface.

The plot of anodic and cathodic peak currents vs. square root of scan rates shows a linear dependence from 0.01 to 0.50 V s^{-1} ($R = 0.998$ and 0.994 and linear Randles' slope of 3.04×10^{-2} and -2.62×10^{-2} for anodic and cathodic peaks, respectively) which corresponds to a diffusion

controlled non-surface process (Fig. 4C). The effective surface area of the electrode was calculated using Randles' -Sevcik equation; $I_p = (2.65 \times 10^5) n^{3/2} A D^{1/2} C v^{1/2}$ where, D is diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), C is concentration of probe (5.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$) and n is the number of electrons ($=1$) [57, 58]. The effective surface area (A) of PdNP-GN composite modified GCE was calculated to be $0.112 \pm 0.01 \text{ cm}^2$, which is larger than the geometric area of the electrode (0.071 cm^2). Peak separation (ΔE_p) is a function of a dimensionless kinetic parameter (Ψ) and is related as through the equation [56, 57] with the square root of scan rate ($v^{1/2}$)

$$\Psi = k^0 (D_o/D_r)^{\alpha/2} \sqrt{RT/(\pi n F D)} / v \quad (5)$$

where, k^0 is the heterogeneous charge transfer rate constant, D_o is the diffusion coefficient of $\text{K}_3[\text{Fe}(\text{CN})_6]$ ($0.76 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$), D_r is the diffusion coefficient of $\text{K}_4[\text{Fe}(\text{CN})_6]$, α is the electron transfer coefficient (assumed as 0.5), and R , T (298 K), π and F have their usual meanings. The plot of peak potential separation (Ψ) at different scan rates vs. the inverse of square root of scan rate is shown in Fig. 4D. From the slope of the curve, the value of k^0 was estimated as 0.92 cm s^{-1} . This shows that the value of heterogeneous rate constant of ferricyanide for PdNP-GN is higher than that of ferricyanide for grapheme [59].

Electrochemical impedance spectroscopy (EIS) was used to study the electron transfer characteristics and to compare faradaic resistance and capacitive traits of the electrode material using 0.1 M $[\text{Fe}(\text{CN})_6]^{3-/4-}$. The Nyquist plot has two parts; the semicircular part and the linear part. The semicircular part in the high frequency region represents electron-transfer-limiting process with its effective diameter equal to the faradic charge transfer resistance (R_{ct}), which contributes to the electron transfer kinetics of redox reactions at the interface between electrode and electrolyte solution [60]. Fig. 5 shows the Nyquist plots for (a) GN/GCE and (b) PdNP/GN/GCE. It is seen from the plot that the R_{ct} values for GN/GCE and PdNP/GN/GCE as

measured from the diameter of semicircle are 31.5 and 19.5 ohm, respectively. Thus the PdNP/GN composite displays a significantly reduced R_{ct} value and thus enhanced electronic properties as a result of loading of highly conducting Pd nanoparticles. The Nyquist plot in the low frequency region is a vertical line corresponding to a diffusion-limiting process for an ideal electrode material. The more vertical, the better is the capacitive behavior [15, 37, 61] of the system. It is evident from the Figures, compared with GN/GCE, PdNP/GN/GCE show more vertical line (less inclined), suggesting ideal capacitive behavior of the composite electrode possibly by forming more uniform diffusion paths for ions within PdNPs-GN composite [5, 38].

Fig. 4 (A, B, C, D)

Fig. 5

3.3. Electrochemical double layer behavior of PdNP-GN composite modified GCE

Fig. 6A shows the CV profile of (a) GN/GCE and PdNP-GN modified GCE at different concentrations of PdCl_2 loading viz; (b) 7.3 %, (c) 14.6 %, (d) 29.3 % and (e) 58.6 % at a scan rate of 100 mVs^{-1} in 1 M KCl. It is observed that the shape of CV loop for GN/GCE is quasi-rectangular. However, compared with the pure GN/GCE and at the same scan rate of 100 mVs^{-1} , PdNP-GN/GCE shows a typical rectangular behavior along the current–potential axis without obvious redox peaks with enhanced charge propagation following the electric double layer formation. This indicates an excellent capacitive behavior of PdNP-GN composite. Further, the current under the CV loop increases with increase in Pd (II) ion loading from 7.3 % to 58.6 %. However, an ideal rectangular CV loop is observed for 29.3 % of Pd (II) loading which was taken for subsequent studies. This higher capacitive behavior and increased current can be attributed to the large specific surface area of Pd nanoparticles and suitable porosity of GN layers

for easy insertion/de-insertion of ions. CVs of PdNP-GN modified GCE under the different sweep rates are shown in Fig. 6B. No obvious distortion is seen in the CV curves as the potential scan rates are increased. The observed rectangular type plots are indicative of good capacitive behavior. Further, the obvious increase of current with scan rates means a desirable rate capability for PdNP-GN composite electrode. Also, the specific capacitance decreases as potential scan increases because at low scan rate electrolytes ions are completely diffused into inner active sites of material which take part in electrical double layer formation. However, at higher scan rate electrolyte ions cannot diffuse completely into inner active sites of material. As a result it cannot make full use of the inner surface. Hence, decrease in specific capacitance is observed at higher potential scan rate. The specific capacitances of GN/GCE and PdNP-GN/GCE obtained from CV loops are 138 and 634 F g⁻¹, respectively at a scan rate of 100 mV s⁻¹.

Fig. 6(A, B)

Figure 7A demonstrates the galvanostatic charge/discharge curves of pure GN and PdNP-GN modified GCE tested from 0.35 to 0.8 V at a constant current density of 1.75 A g⁻¹. Both curves exhibit a triangular-shape, implying good supercapacitive performance. However, despite having a similar shape, the curve for the PdNP-GN modified GCE, show significantly higher charge and discharge time as compared to GN/GCE. This is due to the modification of electrode by PdNP-GN to accommodate more number of ions for the stronger electrical double layer formation which is responsible for the higher specific capacitance for PdNP-GN based electrode [62]. Fig. 7B shows the charging and discharging characteristics of PdNP-GN/GCE as a function of different current densities at (a) 1.25 A g⁻¹, (b) 1.75 A g⁻¹, (c) 2.5 A g⁻¹, (d) 3.75 A g⁻¹ and (e) 5.0 A g⁻¹ in 1M KCl. The specific capacitances decrease with increasing the current densities,

because of the presence of fewer electrolyte ions in the inner space of electrodes at high current densities. On increasing the current density from 1.25 A g^{-1} to 5 A g^{-1} , 81.57% of the specific capacitance was retained for PdNP-GN/GCE (Fig.7C) whereas only 30.56% specific capacitance was retained for GN/GCE at 5 A g^{-1} . This shows much enhanced performance, with excellent discharge efficiency and electrochemically dynamic properties, for PdNP-GN/GCE [5]. The maximum specific capacitances at 1.25 A g^{-1} for GN/GCE and PdNPs\GN/GCE are estimated to be 129 F g^{-1} , and 637 F g^{-1} respectively, which are consistent with the CV results. The maximum energy and power densities for PdNP-GN/GCE were calculated to be 56 Wh kg^{-1} and 1166 W kg^{-1} much higher than the corresponding value of 17.51 Wh kg^{-1} and 616 W kg^{-1} for pristine GN/GCE, respectively.

Fig. 7A, B, C, D)

3.4. Cyclic stability test

The long-term cyclic durability of a supercapacitor is important for its practical applications. The cyclic stability testing was evaluated in this study by repeating the cyclic charging-discharging test between 0 V and 0.9 V (vs. Ag/AgCl) for 10000 cycles at a current density of 1.25 A g^{-1} . Fig. 7D shows the variation of specific capacitance with cycle number for the GN/GCE and PdNP-GN/GCE at a constant current density of 1.25 A g^{-1} . The charging/discharging profile of initial ten cycles for PdNP-GN/GCE is shown in Fig. 8. All curves are linear and symmetrical with no obvious “IR drop” suggesting that the low internal resistance of the electrode is due to the well- formed electrode/electrolyte interface. From the cyclic stability testing, it is observed that the PdNP-GN based supercapacitor is found to exhibit excellent stability over the entire cycle, its specific capacitance still remains at 580.0 F g^{-1}

(91.4%) after 10000 cycles of testing (Fig. 7D). However, in GN/GCE, the specific capacitance drops to 72.5%, due to restacking of graphene sheets.

The Coulombic efficiency (η), calculated as the ratio of charging (T_c) and discharging (T_d) times, for the PdNP-GN/GCE super capacitor composite was found to decrease from an initial value of 96 % to 91 % after 10000 cycles, also showing a good cycle stability. This shows that the PdNP/GN based supercapacitor has a longer life cycle, compared to graphene. The excellent stability of PdNP-GN/GCE can be attributed to the Pd nanoparticles stabilizing GN sheets against restacking.

Fig.8

4. Conclusion

Supercapacitor applications of Pd nanoparticle–graphene composite (PdNP–GN) is first t demonstrated for the first time. The PdNP-GN composite was prepared using green synthetic approach by reducing GO and Pd (II) ions simultaneously together in a single step using ascorbic acid as reducing agent. Reduction of the GO recovered the conjugated structure in graphene and removed the electrochemically unstable oxygen groups, greatly improving the electron transfer kinetics and capacitive properties of PdNP-GN composite. The PdNP-GN composite and GN materials were characterized using different surface analytical techniques which demonstrated that the Pd nanoparticles are uniformly deposited on the surfaces of graphene nanosheets. The capacitive behaviors of pure GN and PdNP-GN composite-based supercapacitors were investigated using cyclic voltammetry and galvanostatic charging/discharging in 1M KCl as the supporting electrolyte. The PdNP-GN composite-based supercapacitor showed remarkable properties with a maximum specific capacitance of 637 F g^{-1} , energy density of 56 Wh kg^{-1} and power density of 1166 W kg^{-1} at a current density of 1.25 A g^{-1} . The fabricated supercapacitor

device also exhibits excellent cycle life with 91.4 % of the initial specific capacitance retained after 10000 cycles.

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Figure captions

Scheme 1. Schematic representation for the synthesis of Palladium nanoparticles-graphene composite by simultaneous reduction of Pd^{2+} and GO

Fig.1 PXRD pattern of (A) GO, (B) GN, (C) PdNPs-GN hybrid and (D) Raman spectra of (a) GN and (b) PdNPs-GN composite

Fig. 2(A) SEM images of exfoliated graphene oxide (B) GN and (C) PdNPs-GN composite (D) EDAX of PdNPs-GN composite

Fig.3. TEM images of (A) GN, (B)) PdNPs-GN composite,(C) selected area electron diffraction (SAED) pattern of PdNPs-GN composite and (D) Corresponding rotational average profile of PdNPs-GN composite.

Fig. 4 (A) Cyclic voltammograms of (a) GO/GCE (b) GN/GCE and (c) PdNPs-GN /GCE in 5.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ containing 1.0 M KCl at a scan rate of 100 mV s^{-1} . (B) CVs at PdNPs-GN/GCE at different scan rates of 10, 20, 30, 40, 50, 80, 100, 150, 200, 300, 400, 500 mVs^{-1} with the arrow indicating increasing scan rates. (C) Plot of anodic and cathodic peak current vs. square root of scan rate. (D) Plot of peak potential separation vs. inverse of square root of scan rate.

Fig. 5 Nyquist plots of (a) GN/GCE and (b) PdNPs-GN/GCE in 1.0 M KCl containing 0.1 M $\text{K}_4[\text{Fe}(\text{CN})_6]/\text{K}_3[\text{Fe}(\text{CN})_6]$ at an amplitude of 5 mV vs. Ag/AgCl over the frequency range of 0.1 Hz and 10^6 Hz. Z' : real impedance. Z'' : imaginary impedance. **Insert is the equivalent-circuit model used for fitting the Nyquist plots**

Fig.6(A) Cyclic voltammograms at (a) GN/GCE, (b) PdNPs-GN/GCE (7.3 % PdCl_2), (c) (14.6 % PdCl_2), (d) (29.3 % PdCl_2) and (e)(58.6 % PdCl_2)) in 1 M KCl at a scan rate of 100 mVs^{-1} . (B)

Cyclic voltammograms of PdNPs-GN/GCE at different scan rates of 10, 25, 50, 75, 100, 150 and 200 mV s^{-1} (arrow indicates increasing scan rate).

Fig. 7A Galvanostatic charge–discharge curves of (a) GN/GCE, (b) PdNPs-GN/GCE at current density of 1.75 A g^{-1} . (B) Galvanostatic charge–discharge curves for PdNPs-GN/GCE at different current densities of (a) 1.25 A g^{-1} , (b) 1.75 A g^{-1} , (c) 2.5 A g^{-1} , (d) 3.75 A g^{-1} and (e) 5.0 A g^{-1} in 1M KCl. (C) Specific capacitance of GN/GCE and PdNPs-GN/GCE as a function of the current density. (D) The cycling stability tests of GN/GCE and PdNPs-GN/GCE at a current density of 1.25 A g^{-1} .

Fig.8 Initial ten charging/discharging cycles for the PdNPs-GN/GCE at 1.25 A g^{-1} .

Scheme

Scheme 1

Figures

Fig.1 (A,B,C,D)

Fig. 2(A,B,C,D)

Fig. 3A,B,C,D

Fig. 4(A,B,C,D)

Fig. 5

Fig. 6(A, B)

Fig.7 (A,B,C,D)

Fig.8

Table

Table1. The values of lattice spacings calculated from the SAED pattern and the standard values from the JCPDS card # 5-0681 for palladium nanoparticles.

h	k	l	d(Å)	d(Å)
			JCPDS 5-0681	This work
1	1	1	2.2460	2.2405
2	0	0	1.9450	1.9313
2	2	0	1.3760	1.3743
3	1	1	1.1730	1.1683
2	2	2	1.1232	1.1330
4	0	0	0.9723	0.9670
3	3	1	0.8924	0.8994
4	2	0	0.8697	0.8616

Graphical abstract