



Research paper

Binder free platinum nanoparticles decorated graphene-polyaniline composite film for high performance supercapacitor application



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ABSTRACT

Conventional supercapacitors use insulating binders with active materials for fabricating working electrodes. Use of such binder reduces electrical conductivity of the electrode, thus causing energy wastage of supercapacitor. To overcome this, herein, we report binder free Platinum (Pt) nanoparticles (NPs) decorated Graphene–Polyaniline (Gr-PANI) composite modified electrode for supercapacitor application. Pt decorated Gr-PANI composite was prepared by template-free electrochemical polymerization method followed by electro-deposition of Pt NPs. Detailed structural and chemical characterization of the composite were done by SEM, EDX spectroscopy and Raman scattering. FESEM image of Pt decorated Gr-PANI composite revealed nano-fibrous structure of PANi (average diameter of 50–100 nm) with Pt NPs uniformly deposited on its surface. Interconnected network of PANi nanofibers made matrix highly porous, thereby, providing an improved electrode/electrolyte interface area and shorter diffusion lengths for electrolytic ions. The electrochemical behavior of Pt NPs decorated Gr-PANI composite film was studied by cyclic voltammetry while galvanostatic charge–discharge measurements were carried out to investigate its capacitive performances. Pt decorated Gr-PANI composite based supercapacitor exhibited higher specific capacitance of 922.5 F/g which was ~ 1.75 folds greater than that of only Gr-PANI based electrode at same current density (1 A/g) and much higher than previously reported Gr-PANI composite based supercapacitors. The developed Pt decorated Gr-PANI composite modified electrode exhibited charge capacity of 0.57 mAh/cm² and discharge capacity of 0.29 mAh/cm² which were 2.4 folds and 1.81 folds higher than only Gr-PANI electrode respectively. The significant improvement in specific capacitance with excellent sustainability to higher current, superior rate capability, charge storage capacity and cycling stability can be attributed to the synergistic effect of electrical double-layer capacitance and pseudocapacitance resulting from Gr and PANi respectively and excellent catalytic ability of Pt NPs. The as-synthesized Pt decorated Gr-PANI composite offers simple, promising and binder free electrode material for energy storage devices.

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1. Introduction

Recently, electrochemical supercapacitors that bridge the gap between batteries and conventional capacitors have attracted wide attention as next-generation energy storage devices due to their high power density, wide thermal operating range, low maintenance cost, longer cyclic life and environment friendliness [1–3]. On the basis of charge storage mechanisms, supercapacitors can be classified into two categories: electrical double layers (EDL) capacitor and pseudo-capacitor [4]. For EDL capacitors, carbon based materials such as activated carbon [5], mesoporous carbon

[6] etc. are usually used as electrode materials wherein the capacitance arises from the charge separation at the electrode–electrolyte interface without faradaic reactions. For pseudo-capacitors, transitional metal oxides or conductive polymers are widely used as electrode materials where electrostatic energy is stored by faster surface redox reactions [4,7]. EDL capacitors possess high power densities and longer cycle life but relatively lower specific capacitances whilst pseudo-capacitors exhibit high energy densities and higher specific capacitances but poor cycling stability resulting from the accumulation of irreversible components at the surface of the electrode during charging/discharging process. Therefore, to overcome the shortcomings of a single phase material and enhance overall performance, development of hybrid supercapacitors combining the advantages of both the EDL capacitors and pseudo-capacitors has gained much attention.

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Gr, a single-atom thick sheet of sp^2 bonded carbon atoms arranged in a perfect honeycomb lattice is considered as one of the best electroactive carbon materials due to its higher surface-to-volume ratio, excellent electrical and thermal conductivity [8]. Xia et al. synthesized 2D porous Gr which showed specific capacitance of 261 F/g and capacitance retention of 98.5% at 5 A/g after 1000 cycles [9]. Although Gr offers longer cycle life during the charging/discharging process, it exhibits lower specific capacitance (generally, in the range of 100–300 F/g) because of unavoidable aggregation of Gr nanosheets [9,10]. Similarly, PANi is a well-known and widely used conducting polymer in the field of pseudocapacitors due to its attractive properties like higher specific pseudocapacitance, low cost, high chemical durability, environmental stability and ease of synthesis [11]. Guan et al. demonstrated PANi nanofibers based supercapacitor with specific capacitance value of 548 F/g at current density of 0.18 A/g [12]. Nevertheless, its poor stability during the charging/discharging process limits its practical application in supercapacitors [10]. Therefore, Gr-PANi composites which combine the synergistic properties of both constituents have been widely explored. Wu et al. reported Gr-PANi flexible supercapacitors with specific capacitance value of 210 F/g at 0.3 A/g [13] while Kumari et al. synthesized Gr-PANi nanohybrid based supercapacitor with specific capacitance value of 630 F/g at 0.5 A/g [14]. On the other hand, noble metals like Pt have been investigated extensively in the field of electrode materials of supercapacitors owing to their excellent conductivity wherein nanostructured metals facilitate faster transport of ions and thereby offering higher reversible capacitance [15]. However, integration of Pt NPs with other sustainable and low-cost electrode materials due to its insufficiency and high cost is now-a-days being considered as one of the most attractive pathways to utilize their properties optimally and minimize their cost and consumption.

Most composite materials reported for supercapacitor applications are in powder form and need to be processed into an electrode by the physical mixing of composite with an insulator binder (e.g. nafion or poly-tetra fluoro ethylene (PTFE)) in a solvent and casting with resultant mixture [16,17]. Use of such binders not only makes the fabrication procedure complicated but also reduces the electrical conductivity of the electrode and hinders the diffusion of ions, thus causing energy wastage of supercapacitor [18,19]. Hence, it is essential to develop a simple method to fabricate binder-free Gr-PANi composite based electrode. Tang et al. reported binder free 3D reduced graphene oxide (rGO)-PANi composite electrode for supercapacitor with specific capacitance of 243 F/g at current density of 1 A/g [20] and Meng et al. developed porous Gr-PANi composite film based flexible supercapacitors with specific capacitance of 385 F/g at current density of 0.5 A/g [21]. Their methods either involve sophisticated and complex synthesis techniques such as $CaCO_3$ as a template or exhibit lower specific capacitance value owing to the lack of synergistic effect of Gr and PANi.

Herein, we report a simple and efficient electrochemical approach to fabricate binder free Pt NPs decorated Gr-PANi based electrode for high performance supercapacitor application. First, Gr-PANi composite was synthesized by electro-deposition of PANi on the surface of Gr modified Glassy Carbon Electrode (GCE) using cyclic voltammetry technique and Pt NPs decorated Gr-PANi composite was prepared by electro-deposition of Pt nanoparticles (NPs) at an applied potential of -0.2 V vs. Ag|AgCl for 900 sec on the surface of Gr-PANi/GCE. This method has been chosen mainly because it offers a simple and controlled approach of synthesizing nano-composite film with unique morphology and distribution by tuning the deposition parameters using the versatility of electro-deposition technique. Moreover, it eliminates the complexities associated with other techniques such as high precursor loading, high temperature synthesis, template removal etc. The Pt NPs

decorated Gr-PANi composite based electrode exhibited enhanced specific capacitance of 922.5 F/g at same current density of 1 A/g than that of only Gr-PANi composite based electrode (525.6 F/g) which can be ascribed to the synergistic effect of both Gr and PANi and excellent catalytic ability of Pt NPs. The as-fabricated supercapacitor electrode also exhibited good rate capability, charge storage capacity and cycling stability compared to other reported literature. To the best of our knowledge, this is the first study to be reported on Pt NPs decorated Gr-PANi composite based electrode for high performance supercapacitor.

2. Experimental

2.1. Materials

Gr flakes (average flake thickness: 12 nm (30–50 monolayers)) were procured commercially from Graphene supermarket, US. Aniline, chloroplatinic acid hexa-hydrate ($H_2PtCl_6 \cdot 6H_2O$), sulfuric acid (H_2SO_4), N, N-dimethyl formamide (DMF) [$(CH_3)_2NC(O)H$], hydrochloric acid (HCl) were procured from Sigma Aldrich and used in the experiments as received. DI water from a Millipore system (~ 18.2 M Ω cm) was used throughout the experiments.

2.2. Apparatus

Electrochemical measurements were performed on CHI 660E electrochemical workstation at room temperature. A three electrode cell configuration in which Pt NPs decorated Gr-PANi composite modified GCE (3 mm in diameter) as the working electrode, Ag|AgCl electrode (SHE) as the reference electrode and Pt wire as the counter electrode was employed. Cyclic voltammetry (CV) curves and galvanostatic charge–discharge measurements were performed in 1 M H_2SO_4 electrolytic solution.

2.3. Electrochemical supercapacitor design and fabrication

Prior to the electrode modification, GCE was polished with alumina powders (0.3 and 0.05 μ m), and ultra-sonicated in DI water for 3 min. To obtain Gr stock solution, 0.5 wt.% Gr was dissolved in DMF and continuously stirred at 750 rpm for 2 h. A 15 μ L of this stock solution was drop-casted onto the cleaned GCE surface and dried at 70 °C in an oven for 10 min. The modified GCE was then subjected to electro-polymerization using CV in the potential range of -0.4 V to $+1.1$ V vs. Ag|AgCl in 0.5 M H_2SO_4 electrolytic solution containing 0.1 M aniline at the scan rate of 50 mV/sec. After electro-deposition, the Gr-PANi composite modified electrode was washed with DI water and then dried. The growth of Pt NPs on the surface of as-prepared Gr-PANi composite modified GCE was accomplished by potentiostatic electro-deposition in 0.1 M HCl electrolytic solution containing 10 mM H_2PtCl_6 at an applied potential of -0.2 V vs. Ag|AgCl for 900 sec and the obtained Pt NPs decorated Gr-PANi/GCE was washed carefully with DI water and then dried at room temperature for further use. To compare the electrochemical capacitive performances, GCE was also modified with only Gr-PANi composite film.

2.4. Characterization of materials

Morphology of the as-synthesized materials were characterized by field emission scanning electron microscope (FE-SEM) operated at an accelerating voltage of 5 kV. The composition of as-prepared materials was determined by energy dispersive X-ray spectroscopy (EDX) attached on FE-SEM instrument while the phase information was studied by Raman spectroscopy. Raman spectra were collected

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