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Supercapacitive behaviour of a novel nanocomposite of 3,4,9,10-perylenetetracarboxylic acid incorporated Captopril-Ag Nanocluster decorated on graphene nanosheets

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Abstract

A nanocomposite of PTCA incorporated silver nanocluster and graphene nanosheets was synthesized by a single step facile methodology. The G/PTCA/Capt-AgNC nanocomposites were characterized by UV-Vis, photoluminescence (PL), FTIR, Raman, X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy (HRTEM), Scanning electron microscopy (SEM) and X-ray diffraction. Electron microscope revealed a sheet-like nanomaterial decorated with ultra-small (~ 2-4 nm) silver nanoclusters. It was found that the synthesized nanocomposite forms a remarkably stable suspension in solvents and exhibit exceptional fluorescence quantum yield (QY ~ 0.32) in comparison to the previously reported metal nanoclusters. To test the potential utility of the nanocomposite as charge storage material, electrochemical capacitance measurements were carried out. A drastic increase in the specific capacitance (C\textsubscript{m}) of G/PTCA/Capt-AgNC was observed in comparison to PTCA/Capt-AgNC. The as-prepared nanocomposite shows significant charge-discharge reversibility even at a high current density of 137 A g\textsuperscript{-1}. The method for the synthesis of the nanocomposite reported here provides a facile and straightforward approach to decorate graphene sheets with metal.
nanoparticles and it may be readily expanded to other classes of hybrid graphene for flexible
electronic, sensor and charge storage applications.

1. Introduction

Materials that have drawn substantial attention in recent years possess characteristics such as
flexibility, deformability, lightweight, bendability, transparency, and inexpensive due to their
versatile applications. These are found to be enormously useful for the modern-day consumer
electronics like digital displays, integrated sensors, thin-film transistors, solar cells, touch panels,
and transparent electrodes for optoelectronic and energy storage systems including batteries and
supercapacitors \(^1\)\(^-\)\(^8\). Currently, supercapacitors have drawn much attention as it has desirable
characteristics of high power density, fast charge-discharge, and long cycle life \(^9\),\(^10\). Nanocomposites with organic materials meet several advantages as active electrode material in
supercapacitors such as structural versatility, optical tunability, and higher theoretical
capacitance. However, the major drawbacks with recently explored organic materials like
conducting polymers\(^11\), organosulphur compounds\(^12\), organic radical compounds\(^13\), and
carbonyl compounds\(^5\),\(^14\) mainly suffer from poor electrical conductivity and dissolution in low
molecular weight organic electrolyte\(^5\).

Therefore, designing and modifications of suitable organic active materials with
significantly enhanced charge transport property are required. Recently carbonaceous materials
such as carbon nanotubes (CNT), carbon nanofibers, graphitic carbon nitride, onion-like
carbon\(^15\)\(^-\)\(^17\), multi-walled CNTs, carbon nanoparticles consisting of multiple concentric graphitic
shells, carbide-derived carbon, graphene and reduced graphene oxide (rGO) have been
investigated for the fabrication of micro-supercapacitors (MSCs)\(^10\) and other flexible electronic
devices\(^7\). However, despite having good energy density and power output, their specific
capacitance is generally found to be low\(^17\). Various highly conducting polymers such as
Polypyrrole\(^18\), polyaniline\(^19\) etc. are used to make nanocomposite with graphene or reduced
graphene oxide (rGO) to increase the specific capacitance of the material, but they have to suffer
with poor cycling stability because of the faradaic reaction mechanism involved. Inorganic
materials, indium-tin-oxide (ITO) is optically transparent and electrically conductive material
that is used for making transparent conductive thin films\(^2\) and current collector in
supercapacitors. Metal oxides such as RuO\(_2\)\(^20\), MnO\(_3\), mesoporous Co\(_3\)O\(_4\) nanoparticles (NPs),
NiO nano/microspheres, Ni/NiO core/shell NPs\textsuperscript{21}, α and β-Ni(OH)\textsubscript{2} NPs on Ni foams, hollow Co\textsubscript{3}O\textsubscript{4} nanowires on nickel foam, Ni(OH)\textsubscript{2} nanotubes with porous walls have been tested for showing excellent performance in electrochemical supercapacitor application\textsuperscript{1}. Though they are found to have many advantages, some metal oxides such as RuO\textsubscript{2} are expensive and not environmentally benign. Metal oxides and conductive polymers have high specific capacitance but they lack in stability cycling.

A combination of both inorganic and carbonaceous materials could potentially result in more efficient electrochemical supercapacitor and other electronic devices\textsuperscript{7}. For example, metallic nanoparticles ligated to graphene nanosheets results an efficient material can be useful in the transparent conductive film (TCFs) applications\textsuperscript{1}. Although, transition metal oxide (such as MnO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{3}O\textsubscript{4}, and V\textsubscript{2}O\textsubscript{5}) NPs mixed, embedded, or deposited onto carbonaceous materials are found to have considerable specific capacitance, but they generally found to be less conductive than its carbonaceous backbone and have low rate capability\textsuperscript{7}. An important class of hybrid graphene-organic composite materials in electronics has drawn a lot of attention in recent days. It has been found that the organic semiconductors can be used for better processing of graphene-like materials and to modulate its properties for various applications. The organic semiconductors have been constantly drawing increasing demand in the development of organic electronics, because of its key features like low cost, biocompatibility, low-temperature solution-based processibility. One such chemically stable organic semiconductor (OSC) is 3,4,9,10-perylenetetracarboxylic acid (PTCA), which contains a perylene ring and conjugated carboxylic groups. OSC molecules bound to carbon matrices with excellent conductivity such as reduced graphene oxide (rGO) have been explored\textsuperscript{6}. Furthermore, it has been found that graphene-like nanosheets could restack and precipitate from the dispersion medium. It limits its use as a transparent thin film with agglomerated rGO nanosheet. In order to prepare a stable dispersion and reduce the stacking of graphene-like nanosheets, various strategies have been followed such as grafting of polymers, incorporating organic semiconductors such as PTCA, decorating metal nanoparticle onto the surface, and use of phenyl groups to attract graphene nanosheets (GNS). PTCA also protects the electronic structure of the carbon materials in harsh conditions. Another promising strategy, which has been explored in recent days is the fabrication of transparent conducting thin film by decorating metal nanoparticles (Pt, Au, Pd, and Ag)\textsuperscript{2,22–25} on graphene-like nanosheet. It has also been reported that metal nanoparticles act as a nanoscaler and its
binding with GNS inhibits the agglomeration and improve the dispersibility. The stability of the metal nanoparticle is highly essential to be used as a nan spacer. Furthermore, ligands play an important role in the stability of the metal nanocluster. Captopril is one such suitable biocompatible ligand for the facile synthesis of metal (Ag) nanocluster which has been explored by our group \(^{26,27}\). The metal nanoclusters owing to its ultrasmall size when incorporated onto GNS along with OSC molecule can not only act as a nanospacer, but it can also display several simultaneous coexisting properties e.g. optical sensing, electrochemical sensing, catalysis, electrical conductivity, and specific capacitance. One of the unique properties of noble metal nanocluster which could be cleverly utilized is its tunable emission properties with suitable modification of its ligand shell \(^{28}\).

Herein, for the first time, we have prepared a novel nanocomposite of PTCA, silver nanocluster, and graphene by a solution based facile synthetic methodology. In this study, the \textit{in situ} loading of PTCA/capt-AgNC onto the surface of graphene nanosheet is adopted as a new strategy to synthesize the nanocomposite to be used as electrode material for supercapacitor. The as-synthesized material was then used as active electrode to test the electrochemical performance. There is huge increase in the capacitance of the nanocomposite material (PTCA/Capt-AgNC) after incorporation with GNS. The fluorescence intensity and dispersibility of the nanocomposite (G/PTCA/Capt-AgNC) were observed to be significantly high. We believe that the present strategy paves the way to fabricate multifunctional materials having high potential in the development of flexible electronic devices, energy storage systems, and full-color organic light-emitting diodes (OLED).

2. Experimental Methods

2.1 Instrumentation Details

X-ray diffraction (XRD) technique was used to determine the structural information of as-prepared nanocomposites using a Bruker X-ray diffractometer with Cu- \(\text{K}\alpha\) (\(\lambda = 1.5406 \ \text{Å}\)) radiation. Raman and Photoluminescence spectra were collected using a WITec, Germany, and Parkin Elmer spectrophotometer, respectively. Scanning electron microscopy (SEM) images were obtained using SEM Jeol JSMIT300 instrument. High-resolution transmission electron microscopy (HRTEM) studies were carried out on a JEOL 2100 TEM microscope with 0.2 nm point resolution and using 200 kV acceleration voltages. Elemental compositions of
G/PTCA/Capt-AgNC were measured using energy dispersive X-ray (EDAX) spectrometry associated with HRTEM. Nitrogen adsorption-desorption analysis was done at 77 K on an Autosorb iQ2 instrumental setup to examine the surface area by Brunauer Emmett Teller (BET) method. The pore size distribution was computed by the nonlocal density functional theory (NLDFT) technique. The samples were degassed at 120°C for more than 12 h under vacuum conditions. X-ray Photoelectron Spectroscopy was performed on PHI 5000 VersaProbe III system equipped with a monochromatic Al Kα945 X-ray radiation source. Fourier transform infrared (FTIR) spectroscopy was carried out on Perkin Elmer FTIR spectrometer at room temperature. A Regulated DC power supply (Sigma, 30 V/10 A) was used for the exfoliation of graphite electrode. Electrochemical measurements like cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) were performed on a CHI 760E electrochemical workstation. For the electrochemical characterizations, glassy carbon (GC) was used as a working electrode, Ag/AgCl (3M KCl) as a reference electrode and platinum wire as a counter electrode.

2.2 Synthesis of graphene via electrophoretic exfoliation method:

The synthesis of graphene was carried out via electrophoretic exfoliation method as explored in our previous reports\textsuperscript{29,30} with a few modifications. In a typical method, graphite plates of area (1×2) cm\textsuperscript{2} and thickness of 0.5 mm were used as both working and counter electrodes, which were immersed in a dilute orthophosphoric acid (1M H\textsubscript{3}PO\textsubscript{4}) solution and placed parallel to each other. A distance of 2 cm was maintained throughout the experiment between the electrodes. When a positive voltage of 8 V was applied from a direct current (DC) power source for 30 minutes to a graphite electrode, the graphite flake at +ve terminal began to expand, quickly dissociated and dispersed into the solution. The resulting exfoliated material was subjected to ultrasonication for one hour to form a homogenous dispersed solution and to break the large graphene sheets. The exfoliated material was then collected by centrifugation at 7000 rpm and washed with mili-Q water and ethanol repeatedly to remove the residuals. The washing was continued until the pH reached neutral. The sample was then, dried at 70 °C in hot air oven for 12 hours and named as exfoliated graphene (G). The obtained sample was further directly used for the characterization and thereby, nanocomposite formation.
2.3 Synthesis of G/PTCA/Capt-AgNC nanocomposite:

In a typical synthesis method (as demonstrated in Scheme 1), 70 mg (~ 0.4 mM) AgNO₃ was dispersed into a 20 mL methanol poured into 100 mL round bottom flask followed by addition of 125 mg (~ 0.23 mM) tetraoctylammonium bromide (TOABr) into the flask. The suspension was stirred and after 20 minutes, 130 mg (~ 1 mM) of captopril was added. It was kept under continuous stirring at 1000 rpm for another 40 minutes. Then, 20 mg of PTCDA/PVP microstructure (synthesized by following the reported method[31]) was poured into the mixture and stir the mixture sustainably. After 20 minutes, as prepared exfoliated graphene (100 mg) was added under continuous stirring. Finally, 10 mL ice cold aqueous solution of 2M NaBH₄ (500 mg) was slowly added with vigorous stirring. After the complete addition of sodium borohydride, the mixture was kept at 80°C under constant stirring for 6 h. The color of the suspension gradually changed to bottle blackish green. The temperature of the suspension was allowed to cool to room temperature (RT) and then acetone (20 mL) was added to precipitate the product. The product was harvested by centrifugation at 14500 rpm for 10 min, the supernatant was discarded and the solid product was collected. The product was then, vacuum dried and stored in a desiccator.

Scheme 1. Schematic illustration of the synthesis procedure of G/PTCA/Capt-AgNCs.
The electrochemical behavior of the as-prepared nanocomposite (G/PTCA/Capt-AgNC) was compared with the nanocomposite in absence of GNS (i.e. PTCA/Capt-AgNC). PTCA/capt-Ag nanocomposite was prepared by following the same procedure as described elsewhere. In order to compare the electrochemical capacitance behavior of organic semiconductor-based nanocomposite with other inorganic semiconductor-based materials (PTCDA/Nb$_2$O$_5$ and TiO$_2$/Nb$_2$O$_5$/Capt-AgNCs were prepared. The nanocomposite TiO$_2$/Nb$_2$O$_5$/Capt-AgNCs used here was synthesized by following the method reported elsewhere. The detailed synthetic methodologies of these materials are described in the supporting information. The as prepared Nb$_2$O$_5$ nanostructures and PTCDA/Nb$_2$O$_5$ nanocomposites were characterized using SEM (Fig. S1), XRD (Fig. S2) and FTIR spectroscopy (Fig. S3). Fig. S4 represents the HRTEM micrograph of TiO$_2$/Nb$_2$O$_5$/Capt-AgNCs nanocomposite.

2.4 Formulas to calculate the specific capacitance of the electrode materials:

The specific capacitance can be calculated from cyclic voltammetry via following equation (1)

\[ C_{sp} = \frac{I_{avg}}{m \Delta v} \quad \text{(1)} \]

Where \( I_{avg} \) is the average current obtained from cathodic and anodic sweeps, \( \nu \) is the scan rate, and \( m \) is the active mass of the G/PTCA/Capt-AgNC material.

The specific capacitance \( C_{sp} \) was also calculated from galvanostatic charge-discharge curves by equation (2) as follows:

\[ C_{sp} = \frac{I \Delta t}{\Delta V \cdot m} \quad \text{(2)} \]

Where, \( I \) (in A) is the discharge current, \( \Delta t \) (in sec) is the discharge time, \( m \) (in g) is the active mass of the material and \( \Delta V \) (in V) is the working voltage.

2.5 Supercapacitor Electrode Fabrication:

A three electrode system was designed (as described earlier) for the measurements of the electrochemical performance of as-fabricated materials in which a cleaned glassy carbon (GC) electrode was used as a conductive current collector, Ag/AgCl (3M KCl) as reference electrode and platinum wire as a counter electrode. Before use, the GC electrode was polished with fine
alumina powder and repeatedly washed with DI water followed by sonication in water. A homogeneously dispersed solution was prepared by mixing the active materials (PTCA/Capt-AgNC and G/PTCA/Capt-AgNC) in 1:1 isopropanol-water mixture followed by sonication for 15 minutes. The solution was then drop casted on the pre-cleaned GC electrode and dried overnight at room temperature in vacuum. The loading of all the active materials on GC electrode was 0.5 mg cm\(^{-2}\). Then, the electrode was subjected to all electrochemical measurements performed in a three-electrode system. All the electrochemical measurements were performed between a potential window of 1 V in 1 M H\(_2\)SO\(_4\) aqueous electrolyte.

3. Results and Discussion

The choice of the material G/PTCA/Capt-AgNC reported here is to offer a solution to some of the major limitations of any graphene-like materials in practical applicability as a supercapacitor. The major disadvantages of GNS are the loss of electronic conductivity due to structural damages in harsh acidic conditions and difficulty in making of a thin film because of its poor colloidal dispersibility\(^3\). These drawbacks could be countered by the binding of GNS with PTCA/Capt-AgNC. PTCA is a bifunctional molecule, which contains aromatic perylene rings and four carboxyl groups. The aromatic perylene group could strongly interact with the GNS. This allows the nanocluster to be anchored with GNS and reduce the aggregation of the nanosheets. Moreover, the presence of –COOH group makes the nanocomposite superiorly dispersible in solvents. Thus, the resulting material prepared here has a potential application in transparent thin-film sensor and supercapacitor applications. The as-prepared nanocomposite is characterized by various spectroscopic and electron microscopic techniques to confirm the nanocomposite formation.
In order to have deeper insight into the internal structures and nanocomposites formation, X-Ray diffraction analysis was carried out. The diffractogram for the red-pigmented pristine PTCA and the prepared nanocomposites are shown in Fig. 1a and 1b. The high intensity peaks of PTCA and PTCA/Capt-AgNC shows that the both the materials are highly crystalline in nature. Figure 1b shows the magnified XRD pattern of G/PTCA/Capt-AgNC nanocomposite which includes the sharp peaks corresponding to graphene and PTCA, and broad reflection peaks corresponds to Ag-NC. The peaks at 2θ values of 38.1°, 44.3°, 64.4°, and 77.4° corresponds to the lattice planes (111), (200), (220) and (311) of cubic structured silver (JCPDS No. 65-2871). The peaks observed at 2θ values of 31.4°, 32.1° corresponds to PTCA which indicates the

**Figure 1.** (a) X-Ray Diffraction pattern of PTCA, PTCA/Capt-AgNC and G/PTCA/Capt-AgNC, (b) shows the magnified XRD pattern of G/PTCA/Capt-AgNC. (c) Raman spectrum of G/PTCA/Capt-AgNC
incorporation of PTCA. A sharp peak at 25.9° and a broad peak at 43.6° could be assigned to the C (002) and C (100) of GNS which is exactly matched with XRD pattern of exfoliated graphene only (see in the supporting Fig. S5). The presence of various lattice planes of all the components as observed in the diffractogram verifies the successful preparation of nanocomposite.

In the Raman spectrum (Fig. 1c), two typical characteristics peaks are observed at 1580 and 1350 cm$^{-1}$. The peak around 1580 cm$^{-1}$ (G band) is assigned to the E$_{2g}$ phonon of sp$^2$ carbons. The D band (1350 cm$^{-1}$) determines the extent of defects and disorder and is generally assigned to the breathing mode of k-point phonons of A$_{1g}$ symmetry. The intensity ratio of D and G band was calculated ($I_D/I_G$) and found to be 0.95, which indicates lower defects in the as-prepared GNS. This could be attributed to the functionalization of PTCA with GNS. The other Raman modes observed here are 2D (second-order D band) and S3 band. A prominent 2D band can be seen at ~ 2690 cm$^{-1}$. It is well known that the decoration of silver nanoparticles on GNS enhances the Raman signal via surface-enhanced Raman spectroscopy (SERS) effect.

The formation of the nanocomposite was further confirmed by UV-Vis and PL spectroscopic measurements. The absorption and emission spectra are shown in Fig. 2a. In general, the peak positioned at 249 nm attributed to the $\pi-\pi^*$ transition of aromatic C=C of graphene which is shifted from its position (265 nm). This hyposochromic shift is due to the formation of nanocomposite of graphene with PTCA/Capt-AgNC. However, the bathochromic

![Figure 2](https://example.com/figure2.png)

**Figure 2.** (a) UV-Visible and Photoluminescence spectrum of G/PTCA/Capt-AgNC, (b) FT-IR spectra of G/PTCA/Capt-AgNC.
shift observed in comparison to the graphene oxide which in general appears at ~225 nm confirms the removal of oxygen containing surface functional groups and restoration of electron conjugation within graphene nano-sheet \(^{39,40}\). One of the other starting materials used in the synthesis of the nanocomposite, PTCDA (3, 4, 9, 10-perylenete-tracarboxylic dianhydride) shows the maximum absorption peaks at around 570 nm and the observed electronic transition is called the Q-band\(^{41}\). Here there is an in-situ conversion of PTCDA to PTCA, which is then incorporated into the nanocomposite. This is evidenced by the appearance of a new peak with absorption maximum around 415 nm. It could be attributed to the \(\pi-\pi^*\) electronic transition of perylene moiety and absorption peak of captopril protected silver nanocluster \(^{26}\). This suggests the formation of PTCA functionalized silver nanocluster/GNS nanocomposites. Strong greenish fluorescence was observed upon excitation at 350 nm for a neutral aqueous dispersion of the nanocomposite as shown in Fig. 2a. The fluorescence spectra exhibited two peaks one at 480 nm and another at 520 nm correspond to the \(0\rightarrow0\) and \(0\rightarrow1\) electronic transitions of PTCA, respectively\(^{42}\). The PL quantum yield was calculated using rhodamine 6G (Rh6G) as standard by following eq-3.

\[
\phi_x = \phi_{\text{std}} \frac{D_x A_{\text{std}} n_x^2}{D_{\text{std}} A_x n_{\text{std}}^2} \tag{3}
\]

Where \(\phi_x\) and \(\phi_{\text{std}}\) are the quantum yield of unknown and standard (Rh6G) solutions. \(D\), \(A\), and \(n\) are the integrated fluorescence, absorbance, and refractive index of the solvent respectively. The calculated quantum yield of fluorescence was found to be ~ 0.32 in reference to the standard aqueous solution of Rh6G (0.92). The quantum yield of fluorescence is several orders of magnitude higher in comparison to the previously reported metal nanocluster (usually <0.01). The possible mechanism for the high quantum yield of fluorescence could be due to the synergistic interaction between graphene and PTCA/Capt-AgNC. The high PL intensity of the composite is also due to the adsorption of graphene onto PTCA/Capt-AgNC via electrostatic interactions and van der Waal forces \(^{43}\). The constituents of the composite can interact with C=C groups of graphene, PTCA and captopril. Additionally, there are \(\pi-\pi^*\) interactions between the aromatic unit of graphene and perylene. The high intensity of PL is also because of coupling of silver nanocluster with GNS which improve radiative recombination rate. The similar
mechanism of high intensity of PL has been reported. It has been reported earlier that the high PL intensity could be achieved due to synergistic effect of the constituents of a ternary composite. Rigidity of the surface ligands of noble metal nanocluster restricts the rotation of the surface functional groups and found to play a pivotal role in reducing the non-radiative pathways of relaxation. The nanosheet of graphene provides the rigidity of the ligand shell of the nanocluster and prevents the non-radiative pathways. Thus, the reduction of nonradiative relaxation pathways enhances the fluorescence intensity.

The FTIR spectra of graphene and corresponding nanocomposite are presented in Fig. 2b. The peaks at 1579 cm\(^{-1}\) and 1595 cm\(^{-1}\) are due to C=C stretching of PTCA, and the peak at \(~1660\) cm\(^{-1}\) is due to C=O stretching vibration of carboxylic group of PTCA. The broad peak at \(~3411\) cm\(^{-1}\) is assigned for the adsorbed water or other functional groups on the surface of graphene during exfoliation process. The peaks observed at 1178 and 1073 cm\(^{-1}\) corresponds to the stretching frequency of C-O epoxide group. The characteristic peaks of graphene can be found at 1620 cm\(^{-1}\), which corresponds to the skeletal stretching of C=C alkene group with low intensity. This confirms that GNS is decorated with PTCA/Capt-AgNC.

Surface morphology, elemental composition and topographical details of as-prepared nanocomposites were analyzed by SEM, EDAX and HRTEM micrographs as shown in Fig. 3a-h. The inspection of surface morphology of PTCA/Capt-AgNC in Fig. 3a shows an aggregated and poor \(\pi\)-stacked structural morphology with an irregular shape. Moreover, TEM image of PTCA/Capt-AgNC shown in Fig. 3b reveals the formation of tiny nanoparticles of PTCA/Capt-AgNCs having a size of \(~2-4\) nm (red circles include the nanoparticles). Incorporating GNS with PTCA/Capt-AgNCs, a corrugated surface was observed in the SEM images Fig. 3c and 3d. It indicates that graphene nanosheets were effectively wrapped around PTCA/Capt-AgNCs. The EDAX analysis (Fig. 3e) shows that the composite mainly consists of elements i.e. C, N, O and Ag, inset table shows the atomic weight percentage of C, N, O and Ag (49.6\%, 44.8\%, 5.1\%, and 0.5\%), respectively. The wrapping structure was further confirmed by TEM, as shown in Fig. 3f and 3g. The transparent and corrugated GNS were homogenously distributed and PTCA/Capt-Ag nanoclusters with ultra-small size of \(~2-4\) nm (marked with red circles) are decorated all over the surface of GNS. The high magnification TEM micrograph (Fig. 3g), indicates that the
interlayer spacing of the graphene sheets was found to be \(~0.34\) nm, which corresponds to (002) plane of few layered graphene-like nanosheets \(^{6,46}\). The lattice plane of silver with a spacing of \(0.24\) nm could be seen in inset of Fig. 3g, which corresponds to (111) fcc plane of silver nanocluster. The selected area electron diffraction (SAED, Fig. 3h) pattern of G/PTCA/Capt-AgNC shows two diffraction ring with six diffraction spot in each ring clearly indicating crystalline structure of PTCA/Capt-AgNC with the presence of Ag (111) facet and hexagonal graphene-like lattice.

![Figure 3](image)

**Figure 3.** (a) SEM and (b) TEM images of PTCA/Capt-AgNC; (c,d) SEM images of G/PTCA/Capt-AgNC at 10 \(\mu m\) and 5 \(\mu m\) scale respectively (Inset shows the SEM image of G/PTCA/Capt-AgNC at 2 \(\mu m\) magnification); (e) EDAX spectrum of G/PTCA/Capt-AgNC; (f, g) TEM and HRTEM images of G/PTCA/Capt-AgNC; (h) SAED micrograph of G/PTCA/Capt-AgNC.
BET surface analysis is a very useful measurement technique for the determination of surface area and porosity of the as-prepared materials. The surface area to volume ratio of nanomaterial plays very significant role in determining the material’s properties like porosity. When the particle size decreases, there is gain in the surface area to volume ratio. The reactive surface area and pore size distribution of G/PTCA/Capt-AgNC was analyzed by adsorption/desorption under liquid nitrogen in 120°C temperature by BET measurements. The calculated effective surface area values of the PTCA/Capt-AgNC and G/PTCA/Capt-AgNC nanocomposites are 3.07 m² g⁻¹ and 74.7 m² g⁻¹, respectively (Fig. 4a) and active material pore size distribution was calculated from nitrogen desorption curve to be 1.89 nm (Fig. 4b).

The surface composition and the chemical state of the nanocomposites were investigated by measuring the XPS spectra. The survey XPS spectra of the nanocomposites are shown in Fig. 5 and Fig. S6. The characteristic peaks of C (1s), Ag (3d), N (1s), O (1s) and S (2p) as showed in survey XPS spectra (Fig. 5a) reveals the presence of all the elements in the nanocomposite. Surface elemental composition of the nanocomposites were also measured from survey XPS spectra and summarized in Table-1. Deconvolution of C1s and Ag 3d XPS spectra of G/PTCA/Capt-AgNC are demonstrated Fig. 5b and 5c respectively. As can be seen in Fig. 5b, the deconvoluted C1s XPS band contains four major contributing components with most intense...
peak centered at the binding energy of 284.6 eV (sp$^2$ C=C, C-C and C-H bonds). The other deconvoluted peaks with decreasing intensities centered at binding energies 285.5 eV (aliphatic C-C, C-O, C-N), 286.5 eV (C-O-C) and 289.1 eV (O=C-O) are primarily attributed to oxygenated carbons. The intense peak of sp$^2$ C=C and lower intensities of peaks of oxygen containing carbon bonds indicate the graphitic carbon and oxygenated carbon during exfoliation process in the as prepared nanocomposite, respectively. Figure S6b shows the deconvolution of C1s peak of PTCA/Cap-AgNC and reveals signature of aliphatic, aromatic C-C and oxygen containing carbons. The high resolution Ag 3d XPS spectrum of the nanocomposite (G/PTCA/Capt-AgNC) shows the presence of doublet with binding energies of 368.58 eV (3d$_{5/2}$) and 374.58 eV (3d$_{3/2}$). The observed characteristics bands of Ag (3d) core level confirm the incorporation of AgNC in the nanocomposite.

![Figure 5](image)

**Figure 5.** (a) Survey XPS spectra and deconvolution of XPS peak of (b) C 1s and (c) Ag 3d of G/PTCA/Capt-AgNC.
bands of Ag (3d) of PTCA/Capt-AgNC were found to appear at lower binding energies at 367.96 eV and 373.96 eV as compared to G/PTCA/Capt-AgNC. These positive shifts in binding energies of spin orbit doublet peaks of G/PTCA/Capt-AgNC could be due to the electron transfer from AgNC to GNS \(^{49,50}\). The similar shifts in binding energies of doublet of Ag (3d) have also been observed previously and our results agree with the earlier reported results. Moreover, the splitting due to spin orbit coupling of Ag (3d) is found to be 6 eV and it also strongly supports the presence of Ag\(^0\) in the composite \(^{51}\).

**Table.1** Surface elemental composition of PTCA/Capt-AgNC and G/PTCA/Capt-AgNC

| Sample             | Element Content (at. %) |
|--------------------|-------------------------|
|                    | C  | N  | O  | Ag  |
| PTCA/capt-AgNC     | 47.97 | 1.34 | 46.84 | 1.5 |
| G/PTCA/capt-AgNC   | 50.95 | 0.01 | 46.01 | 1.9 |

**Electrochemical Analysis:**

Electrochemical performances were measured to evaluate the potential applications of the PTCA/Capt-AgNC and G/PTCA/Capt-AgNC as active electrode materials in both acidic and basic electrolyte medium using three-electrode setup. Cyclic voltammetry (CV) response for PTCA/Capt-AgNC shows higher capacitance in acidic medium (1 M H\(_2\)SO\(_4\)) at a scan rate of 0.1 Vs\(^{-1}\) acquiring a voltage window of 1V as compared to the capacitance value in basic medium exhibited in Fig. 6a. The CV and Galvanostatic charge-discharge (GCD) response for PTCA/Capt-AgNC gives higher specific capacitance as compared to the as-prepared inorganic semiconductor based nanocomposites such as Nb\(_2\)O\(_5\)/PTCDA and TiO\(_2\)/Nb\(_2\)O\(_5\)/Capt-AgNCs in 1M H\(_2\)SO\(_4\) electrolyte (Fig. 6b and c). The calculated specific capacitance values for composite materials PTCA/Nb\(_2\)O\(_5\), PTCA/Capt-AgNC, and TiO\(_2\)/Nb\(_2\)O\(_5\)/Capt-AgNC are 0.795 F g\(^{-1}\), 1.622 F g\(^{-1}\) and 0.550 F g\(^{-1}\), respectively (Fig. 6b and 6c). The increase in the specific capacitance value of PTCA/Capt-AgNC in comparison to other nanocomposites could be attributed to the presence of higher \(\pi\)-conjugated perylene moieties surrounding Ag nanoclusters \(^{52}\). A high electron density per unit mass can be attained through effective \(\pi\)-conjugation of condensed aromatic perylene cores which in turn provides the higher capacitance. Furthermore, the capacitive current
enhances when PTCA/Capt-AgNC incorporated with GNS maintaining the rectangular shaped CV (Fig. 6d). This is mainly due to effectively wrapped GNS around PTCA/Capt-AgNC forming a laminating structure (clearly visible in SEM image Fig. 3d and TEM images Fig. 3f and g). The highly conductive GNS were distributed all over on the outer surface as well as between the adjacent PTCA/Capt-AgNC blocks to form a three-dimensional conductive network which is more favorable for electron transport than pristine PTCA/Capt-AgNC. The specific capacitance ($C_m$) value of graphene electrode is 8.71 F g$^{-1}$ and for G/PTCA/Capt-AgNC with respect to PTCA/Capt-AgNC, the gravimetric capacitance increases from 0.822 F g$^{-1}$ to 14.11 F.

Figure 6. Cyclic Voltammetry curve (a) for PTCA/Capt-AgNC in acidic (1M H$_2$SO$_4$) and basic medium (1M KOH). A comparison CV (b) and GCD (c) curves for PTCDA/Nb$_2$O$_5$, PTCA/Capt-AgNC and TiO$_2$/Nb$_2$O$_5$/AgNC, respectively at a scan rate of 0.1 V s$^{-1}$ in acidic medium. (d) A comparative CV curve for PTCA/Capt-AgNC exfoliated graphene electrode and G/PTCA/Capt-AgNC at a scan rate of 0.2 V s$^{-1}$ in 1M H$_2$SO$_4$. 
g⁻¹ at a scan rate of 0.2 Vs⁻¹ in aqueous electrolyte. This is due to the increased active surface area via incorporating exfoliated graphene sheets to the nanostructure of PTCA/Capt-AgNC, which favours the fast charge storage capacity of the electrode.

Furthermore, the potential window of G/PTCA/Capt-AgNC electrode was optimized in aqueous electrolyte to avoid the interference of oxygen-evolution reaction as depicted in Fig. 7a. A

![Graphs](image)

**Figure 7.** Galvanostatic charge-discharge (GCD) curves (a) for G/PTCA/Capt-AgNC electrode to optimize the working voltage of the electrode. Cyclic Voltammetry curves (b, c) for G/PTCA/Capt-AgNC electrode at different scan rates (from 0.1 V s⁻¹ to 100 V s⁻¹). GCD profile (d) at different current densities (from 0.1 A g⁻¹ to 137 A g⁻¹). (e) The change in faradaic capacitance (F g⁻¹) with increase in current density (A g⁻¹). (f) EIS spectra of G/PTCA/Capt-AgNC electrode, inset shows the Randles Equivalent Circuit, where Rs (ohm) is sheet resistance, CPE is constant phase element, Rct is charge-transfer resistance and W is Warburg constant.

A distinctive capacitive behaviour with quasi-rectangular CV curve was maintained throughout a good range of scan rates from 0.01 Vs⁻¹ to 100 Vs⁻¹ for G/PTCA/Capt-AgNC electrode as
shown in Fig. 7b and c; evaluating the power capability of the electrode material. It is noted that the nearly rectangular patterns were maintained up to a very high scan rate of 100 Vs\(^{-1}\), which demonstrates the high rate capability and quick dynamics of fast power delivery of the electrode material. This is due to the condensed aromatic rings, effective π-conjugated configurations with highly delocalized sp\(^2\)-hybridized electrons which possess ultrastability even at high scan rate. The quasi-isosceles triangular GCD profile (Fig. 7d) at different current densities further validates the perfect supercapacitive behaviour of the nanocomposite materials. The highest specific capacitance (\(C_m\)) of the electrode material calculated from GCD curve is 39.5 F g\(^{-1}\) at a current density of 0.1 Ag\(^{-1}\), retains a typical quasi-triangular shape with a specific capacitance value of 3.616 F g\(^{-1}\) even at ultrahigh current density of 137 Ag\(^{-1}\) shows appreciable charge-discharge reversibility as represented in Fig. 7e.

Electron impedance spectroscopy (EIS) was studied further at the open circuit potential (OCP) to ensure that the as-prepared GNS incorporated PTCA/Capt-AgNC nanocomposite is suitably equipped to promote fast charge-discharge as well as efficient charge storage. As demonstrated in Fig. 7f at lower frequency region, the imaginary part increases more sharply, indicating diffusion-limited electron transfer characteristic of the ideal capacitive behaviour of the material. The higher frequency region shows the real axis intercept, which provides negligible equivalent series resistance (ESR, \(R_s\)). The randles equivalent circuit is shown in inset of Fig. 7f and corresponding values are listed in Table S1 (see the supporting information), showing a very less sheet resistance of 5.809 Ω.

To explore the practical application of the electrode material, we also checked the cycling stability of the nanocomposite material with continuous charge-discharge cycles at a current density of 0.9A g\(^{-1}\) (Fig. 8a and b). Figure 8a display the cycling stability of the nanocomposite material which shows the capacitance retention 100% of its initial capacitance, showing an excellent electrochemical performance maintaining 107% columbic efficiency. Inset of Fig. 8a represents the corresponding galvanostatic charge-discharge cycles after 1000, 3000, 5000, 7000 and 9000 cycles which clearly shows the stable triangular GCD curve after each and every cycle. The cycling voltammetry curve (Fig. 8b) reveals that the capacitance values increases in initial few cycles and then, get stable in another 9000 cycles. It is found that the G/PTCA/Capt-AgNC nanocomposite electrode material is well suitable to make a highly durable energy storage device with excellent electrochemical performance.
4. Conclusions

In summary, a nanocomposite, PTCA/Capt-AgNCs decorated reduced graphene oxide nanosheet was prepared using a one-pot facile synthetic methodology. Higher dispersion stability and enhanced PL emission (QY ~ 0.32) were observed in the aqueous medium. The incorporation of nanocluster into graphene nanosheet effectively prevented its self-aggregation. The electrochemical capacitance behaviour of the nanocomposite is strikingly enhanced in comparison to the nanocomposite PTCA/capt-AgNC. Excellent charge-discharge discharge reversibility was observed in G/PTCA/Capt-AgNC nanocomposite. The improved electrochemical behaviour is due to the higher surface area and prevention of the stacking of nanosheets. The results obtained indicated that the material reported here has high potential applications in thin-film flexible electronics and energy storage devices.

Figure 8. (a) includes capacitance retention (%) versus cycle number and coulombic efficiency versus cycle number, showing the stability of as-prepared nanocomposite (G/PTCA/Capt-AgNC) {inset represents the galvanostatic charge-discharge profile after 1000, 3000, 5000, 7000 and 9000 cycles performed at 0.9 A g^{-1}}, (b) Cyclic voltammetry curve for initial cycles and after 5000, 10000 cycles at a scan rate of 0.1 V s^{-1} respectively.
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