

Full length article

Charge storage ability of the gold nanoparticles: Towards the performance of a supercapacitor



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ABSTRACT

Polymer supported gold nanoparticles has been synthesized using a single-step route, from the corresponding monomer and metal salt precursors, and was analysed by means of optical, microscopic and surface characterization techniques. The metal-polymer supramolecular complex in combination with reduced graphene oxide form a 'hybrid architecture' and display the property of an electrochemical supercapacitor where the gold nanoparticles have a prevailing role as the charge storage component within the system.

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1. Introduction

Due to the rapid depletion of fossil fuel and increasing awareness for pollution control, the scientists around the world are searching for the viable replacement to the development of alternative energy production which can play the competitive role with all available technologies. Electrochemical capacitors, also known as supercapacitors have drawn an increasing attention, as the most promising candidates, for next-generation energy storage devices due to their high power densities, fast charge–discharge processes, long cycling life, and have enormous utilization in satellites, computers, electronics, mobile communications, and electrical vehicles [1,2]. Depending on the energy storage performance, two different categories of supercapacitors are reported, such as, electrical double layer capacitor, based on carbonaceous materials and pseudo-capacitor, based on conducting polymers [3]. Pseudo-capacitive materials have higher charge storing capacity but has limitation due to their lower cycle life in charging–discharging processes compared to carbon based materials. The scientists have been aimed for the development of the various carbon-based materials with novel functionalities for different applications.

Electrochemical properties of Nb_2O_5 in combination with mesoporous carbon showed an increase of capacitance with good cycling stability as compared with Nb_2O_5 alone [4]. In a similar way, the composite of polyaniline and carbon nanotube also

showed improved specific capacitances as compared with pure polyaniline [5]. Reports has been published on polyaniline grafted carbon nanofiber composite with the enhancement of both specific capacitance and capacity retention property [6]. Graphene is considered to be a superior material, as compared with other carbon-based material, for supercapacitor application due to its excellent electrical, surface and mechanical properties [7]. Reduced graphene oxide-polyaniline composites showed improved electrochemical performance in terms of specific capacitance and the capacity retention rate over polyaniline alone [8]. A facile production of graphene through the electro-exfoliation from graphite has been reported for the direct fabrication of supercapacitor with an impressive capacitance retention property [9]. A sandpaper-based supercapacitor was also reported through the assembling of graphene and carbon nanotube and showed the performance with long lifetime and good cycling stability [10].

Metal nanoparticles have been created enormous interest for the fabrication of electronic devices. The optical behaviour of metal nanoparticles in combination with the electronic property of the semiconductor nanoparticles have useful applications for photovoltaic [11] and electroluminescence [12] devices. Metal nanoparticles also have various applications, such as, rectifiers [13], transistors [14], non-volatile memory device [15] and also in fuel cell and chemical and biological sensors [16–20]. Among the nanoparticles, the polymer capped metal nanoparticles synthesized by *in-situ* polymerization and composite formation (IPCF) method [21–26] has been particularly attractive due to the functionalization of the nanoparticles by the polymer chain [27].

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In this current article, we report the fabrication of polymer stabilized gold nanoparticles, gold-poly [4-(thiophen-3-yl)-aniline] (Au-*pTA*), using the IPCF synthesis method from the precursors of auric acid and 4-(thiophen-3-yl)-aniline, respectively. We paid special attention to characterize the composite product by using optical, microscopic and surface analysis techniques.

To enhance the electrochemical property of the Au-*pTA*, reduced graphene oxide (RG) was added to the gold-polymer composite through a milling process (formation of Au-*pTA*-RG system) for supercapacitor application. For the control experiment, poly [4-(thiophen-3-yl)-aniline] (*pTA*), Au-*pTA*, RG and *pTA*-RG (the composite of *pTA* and RG) were also tested for electrochemical charge/discharge characterization. The results show that the Au-*pTA*-RG composite system display an excellent supercapacitive performance as compared with other tested materials.

2. Experimental details

2.1. Materials

Ammonium persulfate (APS), hydrogen tetrachloroaurate (III) hydrate (auric acid), 4-(thiophen-3-yl)-aniline were purchased from Sigma-Aldrich. Methanol was obtained from Merck and ultrapure water (specific resistivity: >17 M Ω cm) was used in this experiment wherever required.

2.2. Synthesis of *pTA* and Au-*pTA*

In a typical experiment, 0.05 g of 4-(thiophen-3-yl)-aniline was dissolved in 10 mL of methanol in a 25 mL conical flask. To this solution, 5 mL of freshly prepared APS (0.5×10^{-2} mol dm $^{-3}$) was added drop wise. The appearance of brown precipitation with time indicating the formation of the polymer (*pTA*). A solid dark green precipitation of Au-*pTA* was obtained due to the reaction between auric acid (5 mL of 0.5×10^{-2} mol dm $^{-3}$) and 4-(thiophen-3-yl)-aniline (0.05 g in 10 mL of methanol). The entire procedure was carried out at room temperature under continuous stirring condition.

2.3. Synthesis of *pTA*-RG and Au-*pTA*-RG

The reduced graphene oxide was synthesized using a modified Hummers protocol followed by the reduction with hydrazine. The incorporation of reduced graphene to the polymeric materials (*pTA* and Au-*pTA*) were done through a milling process for the period of 6 h by maintaining the carbon and polymer ratio 1:10. The electrochemical properties show the evidences in favour of the successful incorporation and the polymer-graphene composite formation.

2.4. Material characterization

The UV-vis spectra were measured using a Shimadzu UV-1800 spectrophotometer with a quartz cuvette. The JEOL (JEM-2100), 200 keV, transmission electron microscope (TEM) with LaB $_6$ electron source was used for the microscopic analysis of the sample. An ultra-thin windowed energy dispersive X-ray spectrometer (EDS) attached to the TEM was used to determine the chemical composition of the samples. TEM specimens were deposited onto a carbon coated copper TEM grids. The X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-3A X-ray diffractometer operating at 20 kV using Cu-K α radiation ($k=0.1542$ nm). The measurements were performed over a diffraction angle range of $2\theta=20^\circ$ to 90° . X-ray photoelectron spectra (XPS) were collected in a UHV chamber attached to a Physical Electronics 560 ESCA/SAM instrument. Electrochemical measurements were carried out with a BioLogic SP-300, attached with EC-Lab software connected to a computer. A

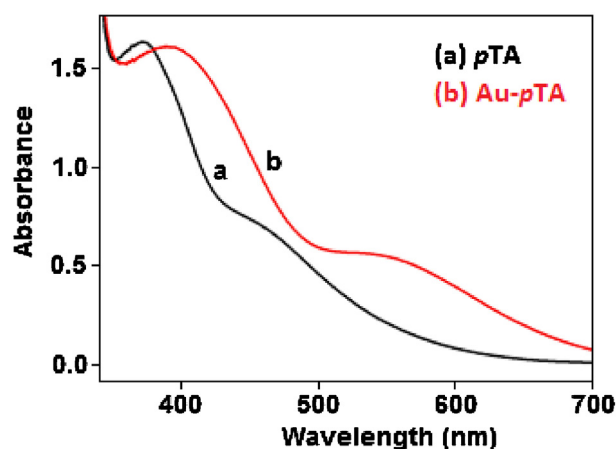


Fig. 1. UV-visible spectra for (a) poly [4-(thiophen-3-yl)-aniline] and (b) Au-poly [4-(thiophen-3-yl)-aniline] samples. For the gold-polymer sample, the absorption band with in the range from 500 to 650 nm is due to the combination of polaron-bipolaron transition effect and the surface plasmon absorption band for gold nanoparticle.

three-electrode system was used in the experiment where a glossy carbon electrode (GCE) was used as the working electrode and the Ag/AgCl electrode and a Pt wire electrode were used as the reference and counter electrodes, respectively.

3. Result and discussion

To synthesis the metal-polymer supramolecular composite system, we have chosen 4-(thiophen-3yl)-aniline and auric acid as the starting materials. Here, auric acid was used as an oxidizing agent and during the polymerization, of 4-(thiophen-3yl)-aniline, the released electrons reduced the gold ions to form gold atoms. The coalescence of these atoms forms nanoparticles, which are encapsulated and stabilized by the polymer and the method is known as 'in situ polymerization and composite formation (IPCF)' in which both the polymer and the nanoparticles are produced simultaneously that facilitate an intimate contact between them through functionalization [21–27].

We have first examined the optical behaviour of the synthesized metal-polymer composite material using UV-visible spectrophotometer (Fig. 1A). The spectrum for *pTA* (a) shows the absorption peak at 368 nm which is due to the $\pi-\pi^*$ transition of the benzenoid rings and the similar transition effect has also been observed for the Au-*pTA* (b) sample at 392 nm. The shifting of peak position of Au-*pTA* towards the higher wave length region, as compared with the *pTA*, indicates the formation of more density of states, due to the presence of gold nanoparticles, which facilitate the $\pi-\pi^*$ transition at the lower energy as reflected by the UV-visible spectra. Again, a shoulder-like appearance is observed for *pTA* sample within the range between 430–500 nm due to the polaron-bipolaron transition. For Au-*pTA* (b) sample, a prominent absorption band has been observed from 500 to 650 nm and that originates due to the combination of polaron-bipolaron transition effect and the surface plasmon absorption band for gold nanoparticle. The spectral nature indicate the formation of gold nanoparticles during the reaction between auric acid and 4-(thiophen-3yl)-aniline.

The presence of the gold nanoparticles in the sample was confirmed by transmission electron microscopy (TEM) technique. The TEM image of the Au-*pTA* sample, Fig. 2A, shows the uneven surface of the material with dark spots. A typical energy-dispersive X-ray spectroscopy analysis (Fig. 2B) obtained from the electron beam being focused onto the dark spots on the analysed material confirms that these spots are gold particles. The TEM image, with higher magnification, (Fig. 2C) shows that the gold particles, with in

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