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# A simple and innovative route to electrosynthesis of $Eu_2O_3$ nanoparticles and its nanocomposite with p-type conductive polymer: Characterisation and electrochemical properties

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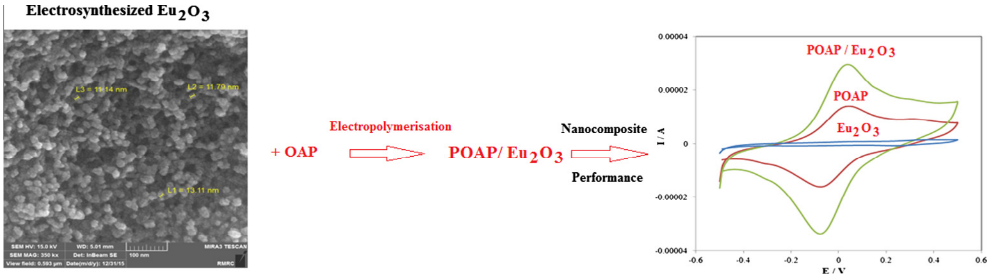
## GRAPHICAL ABSTRACT



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## ABSTRACT

Conductive polymers are usually used as an electrode in redox supercapacitor. However, due to accumulation of stress on polymer during repeating charge-discharge process, the cycle life of pure conductive polymer is poor, which needs to be further improved. For this purpose, combining conventional conductive polymers active material and nanomaterials to fabricate hybrid electrode has been considered to be one of the efficient avenues. In this paper, a simple and rapid electrochemical method has been carried out to prepare $Eu_2O_3$ nanoparticles and hybrid POAP/$Eu_2O_3$ to serve as the active electrode for electrochemical supercapacitor. Structural and morphological characterisations of $Eu_2O_3$ and composite film were carried out using powder X-ray diffraction, field emission scanning electron microscopy and energy dispersion of X-rays. Their electrochemical properties were also investigated using cyclic voltammetry, galvanostatic charge–discharge and electrochemical impedance spectroscopy. The as-prepared composites had excellent properties in the specific capacitance and a coulombic efficiency of 95%. The as-prepared composites had excellent properties in the capacitance, and its specific capacitance was up to 375 F $g^{-1}$ and a coulombic efficiency of 95%. This work introduces new nanocomposite materials for electrochemical redox capacitors with advantages including ease synthesis, high active surface area and stability in an aqueous electrolyte.

## 1. Introduction

Electrochemical capacitors (ECs), are known supercapacitor are charge-storage devices that capable of very fast charges and discharges, with a unique combination of high power, high energy and long lifetime. Supercapacitor electrodes and devices that utilise conducting polymers are envisaged to bridge the gap between existing carbon-based supercapacitors and batteries to form units of intermediate specific energy. The properties of conducting polymers can be greatly enhanced by forming composites between the

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conducting polymer and other materials such as carbon (including carbon nanotubes) [1], inorganic oxides and hydroxides [2,3], and other metal compounds [4–6]. The composite materials have improved conductivity (particularly at the more negative/reducing potentials) and better cycle ability, mechanical stability, specific capacitance and processability [5]. Some of the most famous CPs includes polyaniline, polypyrrole, polythiophene and their derivatives [7–10]. Polyaniline (PANI) is one of the most important p-type conducting polymers because of its unique electrical, optical, and optoelectrical properties, as well as its ease of preparation and its excellent environment stability. Aminophenols are interesting members of the class of substituted anilines. The hydroxyl group in the phenyl ring can be oxidized to quinine and quinine can be reduced again. POAP gives a surface film of interesting electrochemical and electrochromic properties when it is electropolymerised in acidic solution. This film is electroactive in aqueous and non-aqueous solutions containing protons but no response is observed at pH-value higher than pH 7. The variety of results for conductivity of the p-type conductive polymers and POAP films reported in the literature [11–16] show that the electrochemical response of them are strongly influenced by the experimental procedure used to produce the polymer film, dopant anions and the purity starting monomer [17–21]. A lot of attempts are going on to increase the capacitance values of the electrode with the minimum investment. As is highly expensive, alternative metal oxides are being explored. Most of the attempts are made with a small amount of ruthenium which served as an excellent metal oxide for supercapacitor, with other materials for better performance.

Our goals in this paper were increasing the capacitance of POAP electrode by using $Eu_2O_3$ nanoparticles to form a composite electrode and moreover increase the cycle ability of the electrode. The complementary properties of both components generate a synergistic effect to enhance the electrochemical performance. It is an aim of the present work to investigate POAP/$Eu_2O_3$ composite as supercapacitor electrode materials with several analytical tools such as X-ray diffractometry, field emission scanning electron microscopy, cyclic voltammetry, galvanostatic charge–discharge, and electrochemical impedance technique. The electrochemical tests demonstrate that the POAP/$Eu_2O_3$ composite is a promising material in the application of supercapacitors.

## 2. Experimental

### *2.1. Reagent and materials*

All the chemical materials used in this work, obtained from Merck Chemical Co., were of analytical grade and used without further purification. Double distilled water was used throughout the experiments.

### *2.2. Characterisation*

All electrochemical experiments were carried out by an Autolab General Purpose System PGSTAT 30 (Eco-chime, Netherlands). A conventional three electrode cell with an Ag/AgCl reference electrode (Argental, 3 M KCl) was used in order to carry out the electropolymerization of the POAP. A platinum wire and a carbon paste electrode was used as the counter and working electrodes respectively. A wide frequency range of 10 mHz to 100 kHz was used in EIS. Morphological investigations of the polymeric films were carried out by using SEM analysis. The microscope was a Philips XL 30 with a RONTEC X-ray energy dispersion detector (lithium doped silicon with a very thin beryllium window). The incident electron energy was 5 kV for recording the secondary electron images of different magnifications. The observed morphologies were microanalysed by energy dispersion of X-rays (EDX) at a working distance of 15 mm and 15 kV electron energy. Samples have been coated by Au before any analysis.

### *2.3. Preparation of $Eu_2O_3$ nanoparticles via cathodic pulse electrochemical deposition*

The reverse pulse voltammetry method was used for electrodeposition process. A stainless steel (316 L, SS) was used as the working electrode, a graphite plate and saturated calomel electrode (SCE) were utilized as counter and reference electrodes.

Aqueous bath electrolyte solution, containing $Eu(NO_3)_3$ (0.005 M) was used in electrodeposition process. Reverse pulse plating was performed via square wave potential, with utilization of $I_P = 10\ mA/cm^2$ and duty cycle 50 ($T_r = T_f = 10$ ms) at room temperature. Furthermore cathode potential respect to SCE was adjusted about −0.6 V and continuously was traced by multiscope in this value. Total time for an experience was selected 20 min.

Parameters of reverse pulse deposition are defined as follows:

$$\gamma(Duty\ \ cycle) = (T_{forward})/(T_{forward} + T_{reverse})$$

$$I_{average} = I_{peak} \times \gamma$$

After electrodeposition, the steel electrodes were rinsed several times with deionized water and then obtained powders were dried at room temperature for 48 h. The gel deposits were scraped by a non-metallic scraper, and subjected to heat-treatment. Heat-treatment of gels was conducted at temperature 780 °C. In dry air atmosphere for 3 h through electrical furnace equipped heating rate programmable for 10 °C/min.

### *2.4. Synthesis of POAP and POAP/$Eu_2O_3$ nanocomposite*

POAP/$Eu_2O_3$ composites were prepared by in a stirring solution containing 0.01 M monomer, 0.5 M $HClO_4$, 0.1 M $LiCO_4$, $5.0 \times 10^{-3}$ M Sodium Dodecyl Sulfate (SDS) and $Eu_2O_3$ (1% w/w) on the surface of the carbon paste electrode. The aggregation of nano $Eu_2O_3$ (1% w/w) reduced under ultrasonic irradiation and the nanoparticles redispersed in the aqueous solution. POAP electrode was synthesized in same solution without $Eu_2O_3$ nanoparticles in the carbon paste electrode. Electropolymerizations were conducted by 40 consecutive cycles at the sweep rate of 50 mV $s^{-1}$ in the potentials between −0.2 and 0.9 V. The mass of POAP films was approximated assuming a current efficiency for the electropolymerization process of 100%, using Faraday's law.

## 3. Results and discussion

$Eu_2O_3$ powder was characterized by means of X-ray diffraction (XRD) as shown in Fig. 1. In this figure, a strong and sharp peak at 2θ = 28, 33, 47 and 55° are characteristic of $Eu_2O_3$. SEM and EDX have been applied for analysis of the compound. EDX spectrum and SEM image of $Eu_2O_3$ have been shown in Figs. 2 and 3 respectively. As evident from SEM image and EDS spectrum, formation of $Eu_2O_3$ nanoparticles have been confirmed. The $Eu_2O_3$ particles are of spherical shape with diameter in the range from 10 to 20 nm.

Cyclic voltammetry (CV) was used to deposit POAP coatings from an electrolyte containing 0.01 M monomer, 0.5 M $HClO_4$, 0.1 M $LiCO_4$, $5.0 \times 10^{-3}$ M Sodium Dodecyl Sulfate (SDS) and dispersed $Eu_2O_3$ nanoparticles in the carbon paste electrode at a linear potential sweep rate of 50 mV $s^{-1}$ between −0.20 V and 1.0 V vs. Ag/AgCl during 40 cycles on working electrode. The solutions were stirred at 500 rpm with a magnetic stirred follower to disperse the $Eu_2O_3$. Fig. 4 shows the typical multi-sweep cyclic voltammograms during electropolymerization in the absence and presence of $Eu_2O_3$