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Inexpensive synthesis route of porous polyaniline–ruthenium oxide composite for supercapacitor application

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HIGHLIGHTS

- The PANI–RuO_2 composite thin films have been synthesized by simple and inexpensive SILAR method.
- The PANI–RuO_2 composite thin film electrode exhibited specific capacitance of 664 F g^{-1}.
- The PANI–RuO_2 composite thin film shows enhanced stability over 5000 cycles.

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ABSTRACT

Porous polyaniline–ruthenium oxide composite has been synthesized using a successive ionic layer adsorption and reaction (SILAR) method. The result of X-ray diffraction indicates the amorphous nature of polyaniline–ruthenium oxide (PANI–RuO_2) composite. Fourier transform infrared (FT-IR) and FT-Raman spectroscopy studies reveal the formation of composite material. The morphology of PANI–RuO_2 composite observed using scanning electron microscope (SEM) shows hierarchical nanofibers with small particles grown on the nanofibers. The electrochemical measurement shows that PANI–RuO_2 composite electrode material yields specific capacitance of 664 F/g and higher capacitance retention (89%) of its initial capacitance after 5000 cycles. The unique structure of PANI–RuO_2 composite and the coexistence of conducting PANI with RuO_2 are found to be responsible for the superior electrochemical properties.

1. Introduction

Supercapacitors have attracted great interest as a promising energy storage device due to their higher energy density and longer cycle performance than conventional dielectric capacitors. Supercapacitors are now widely used in hybrid electric vehicles along with the improvement in transportation field [1,2]. It is clear that the performance of capacitors mainly depends on the properties of the electrode materials. Current research has been centered mainly on conducting polymers such as polyaniline, polypyrrole, polythiophene with metal oxides [3,4]. Amongst conducting polymers, polyaniline has received a significant amount of attention due to its simple doping/dedoping chemistry promising electrical, electrochemical and optical properties [5].

The successive ionic layer adsorption and reaction (SILAR) method has become the prime choice for fabrication of nanostructured films in which synergy between distinct materials may be achieved in a straightforward and low-cost manner. SILAR method is inexpensive and it does not require sophisticated instruments. Any type of substrates can be used for deposition of thin films in SILAR method. A wide diversity of materials like chalcogenides, mixed metal chalcogenides and oxides may be employed and film fabrication is performed under mild conditions [6–11].

The present paper deals with the synthesis of PANI–RuO_2 composite film by SILAR method. The prepared PANI–RuO_2 composite thin films are characterized and studied for structural, morphological, and elemental bonding. Further, PANI–RuO_2 composite thin films have been studied for the supercapacitor application with cyclic voltammetry, charge–discharge and electrochemical impedance techniques. Finally, the stability of the PANI–RuO_2 composite electrode is studied and the comparison of supercapacitive

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properties between PANI and PANI–RuO_2 composite electrode has been made.

2. Experimental details

2.1. Synthesis of PANI

The synthesis process of polyaniline thin film by oxidative chemical polymerization is based on chronological reaction on the substrate surface by successive immersion of substrate into separately placed cationic (Beaker 1) and anionic (Beaker 2) precursor sources at room temperature (300 K). Fig. 1(a) shows the schematic presentation of SILAR method for deposition of PANI thin film. The first beaker contains 0.1 M aniline monomer dissolved in 1 M sulfuric acid which serves as the anilinium cations (anilinium salts) source, and the second beaker contains an oxidizing agent of 0.1 M ammonium persulphate dissolved in 1 M sulfuric acid. Both the beakers were placed at room temperature. The mirror polished stainless steel substrate was immersed in the first beaker to adsorb aniline monomers on the substrate surface for 15 s. After immersion of 15 s in the second beaker, the reaction occurred with ammonium persulphate oxidizing agent to form the greenish monolayer of polyaniline (emeraldine) on the substrate surface. Thus, it completes one SILAR cycle for the deposition of polyaniline thin film. This cycle was repeated for several times in order to increase the overall film thickness of polyaniline thin film.

2.2. Synthesis of PANI–RuO_2 composite thin films

In the present work, synthesis process of PANI–RuO_2 composite thin films by SILAR method is based on the immersion of substrates into cationic and anionic precursors. Fig. 1(b) shows the schematic presentation of SILAR method for deposition of PANI–RuO_2 composite thin film. Four beakers system is used for the deposition of PANI–RuO_2 composite thin films. The first beaker contains 0.1 M aniline monomer dissolved in 1 M sulfuric acid which gives the anilinium monomer cations (anilinium salts) source and the second beaker contains 0.1 M ammonium persulphate (APS) dissolved in the 1 M sulfuric acid provides oxidizing agent and hydrogen sulfate anions as an anionic precursor source. The third beaker contains aqueous $RuCl_3{:}xH_2O$ (0.01 M) kept at room temperature (300 K) and used as cationic precursor. The anionic precursor was double distilled water at 333 K temperature placed in fourth beaker. In this method, substrates were immersed alternatively in separately ion carrying precursor solutions with regular interval.

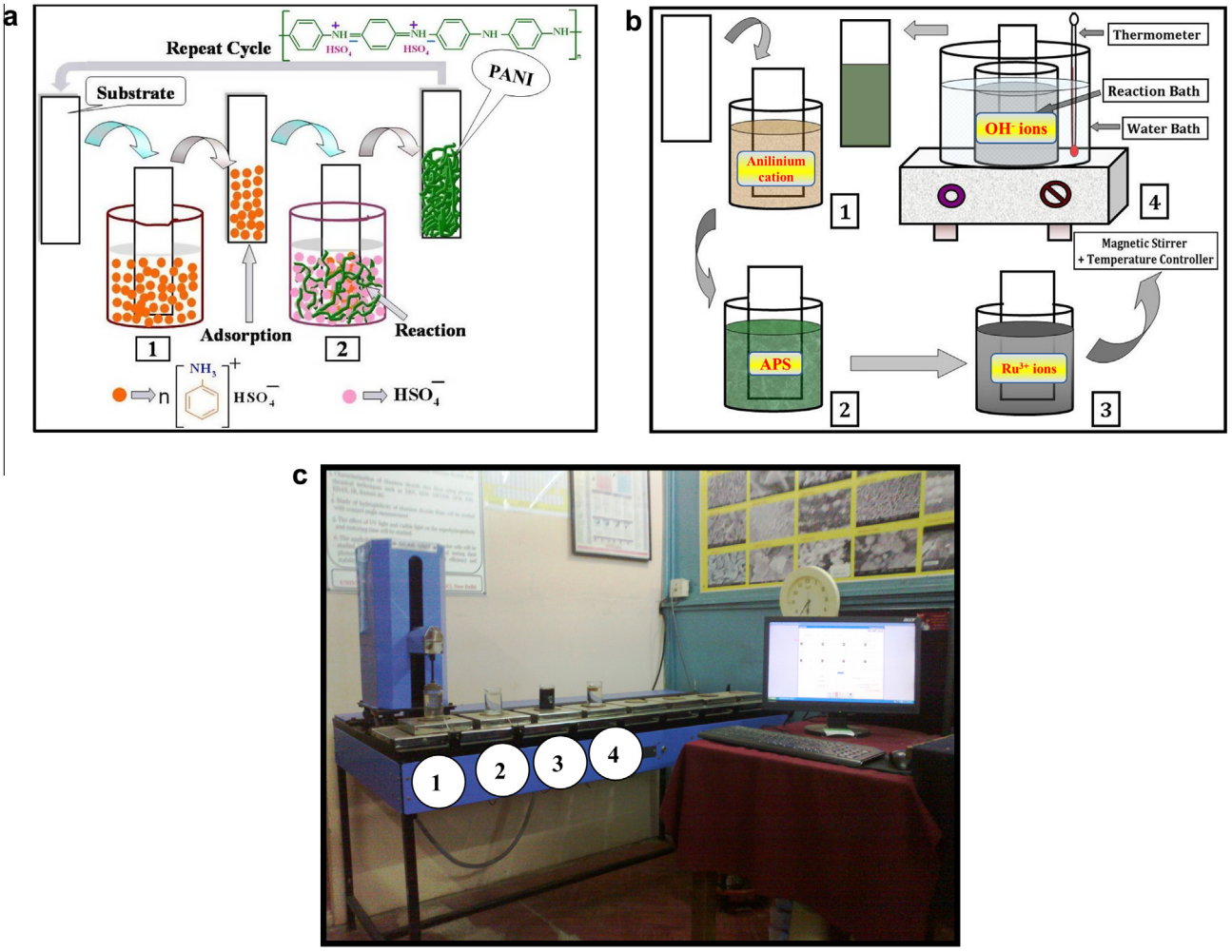

Fig. 1. (a) Schematic illustration of SILAR method for the preparation of polyaniline nanofiber [1st beaker – anilinium cation, 2nd beaker – APS], (b) schematic representation of the SILAR method for the PANI–RuO_2 composite thin films [1st beaker – anilinium cation, 2nd beaker – APS, 3rd beaker – Ru^{3+} ions, 4th beaker – OH^- ions], (c) photograph of computer interfaced SILAR unit for the deposition of PANI–RuO_2 composite thin films [1st and 3rd beakers contain cationic and 2nd and 4th beakers contain anionic solutions].