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Water soluble polyaniline coated electrode: A simple and nimble electrochemical approach for ascorbic acid detection

Utpal Rana[a], Nanda D. Paul[b], Sanjoy Mondal[a], Chanchal Chakraborty[a], Sudip Malik[a,*]

[a] Polymer Science Unit, Indian Association for the Cultivation of Science, 2A & 2B Raja S. C. Mullick Road, Jadavpur, Kolkata 700032, India
[b] Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, 2A & 2B Raja S. C. Mullick Road, Jadavpur, Kolkata 700032, India

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ABSTRACT

We report the design, synthesis, electrochemical stability and electrocatalytic applications of a new kind of water soluble polyaniline (PANI) composite. These water soluble PANI composites are extremely important in electrochemical sensor, semiconducting devices, light-emitting diodes, ultra-thin and flexible display devices, photoconductive sensors, and new fluorescent bio-probes. In the present work, we have prepared water soluble PANI using our designed and synthesized perylene disulphonic acid (PRSA) dopant. This PRSA dopant is a new and superior doping acid for synthesis of water soluble PANI. The PRSA/PANI composite prepared with it exhibits good electrochemical stability and superior electrocatalytic activity. It can sense ascorbic acid, a very important biomolecule, in neutral pH up to mM concentration level at the low electrochemical oxidation potential. Additionally, the modified electrode prepared from aqueous medium of PANI on ITO glass, is reusable and requires only a water rinsing and drying cycle in between measurements. PRSA/PANI composites also show a good semiconducting behavior and follow 1D-VRH (variable range hopping) electron transportation mechanism. The importance and novelty of this method are (i) synthesis of water soluble PANI by 'in-situ' polymerization method, which overcome the major and common problem of PANI processability in water; (ii) high performance electrocatalytic activity and reusability of PANI coated electrode. It also overcomes the electrochemical drawback of PANI synthesis, i.e. low yield, cost effective, limited processabilty etc.

1. Introduction

L-Ascorbic acid (AA, vitamin C) is the major antioxidant found in many organisms. It is a necessary nutrient which is extensively used as an antioxidant negotiator in foods, beverages and pharmaceutical applications, due to its major participation in several human metabolic reactions [1–4]. So, it is very important to find a method for quantification of ascorbic acid. One possible way is the oxidation of ascorbate ion from ascorbic acid in an electrochemical set-up. However, high potentials are required for the initiation of this reaction using conventional electrodes. Several attempts have been also tried to find chemically and electrochemically modified electrodes showing better electrocatalytic activity and stability with respect to ascorbate oxidation [5].

Polyaniline (PANI), the most important conducting polymer among the conducting polymer family, is used as active component of microelectronics, OLED, optical display, for anticorrosive protection, in bioanalysis, etc. because of its good electrical and optical properties as well as high environmental stability [6]. Due to the poor solubility of PANI in common solvents, coveted technological applications are not seen. So making the water soluble PANI is tremendous interest during the recent years for good application [7,8], particularly in the biological environment.

Usually, acidic condition (pH > 4) is required for the formation of the highly conducting form of PANI (ES) and it seriously restricts its applications in bioelectrochemistry, which normally desires a neutral pH environment. The electroactivity and conductivity of the PANI films in neutral aqueous solutions make them appropriate for catalysis and biotechnology-purpose applications [9,10].

Use of conducting polymer (CP) coated electrode for the purpose of AA oxidation has been investigated since 1989. Conducting polymer and metal binded polymer prepared electrochemically are generally utilized for AA oxidation [11]. However, several problems in electrochemical synthesis of polyaniline are the (i) low yield, that is why it is difficult to characterize and it limits application (ii) costing of such electrodes and (iii) the charge transfer reaction that causes a change in the total number of π-electrons on the conjugated PANI chain and thereby renders its conductivity [12].

* Corresponding author. Tel.: +91 3324734971.
E-mail address: psusm2@iacs.res.in (S. Malik).

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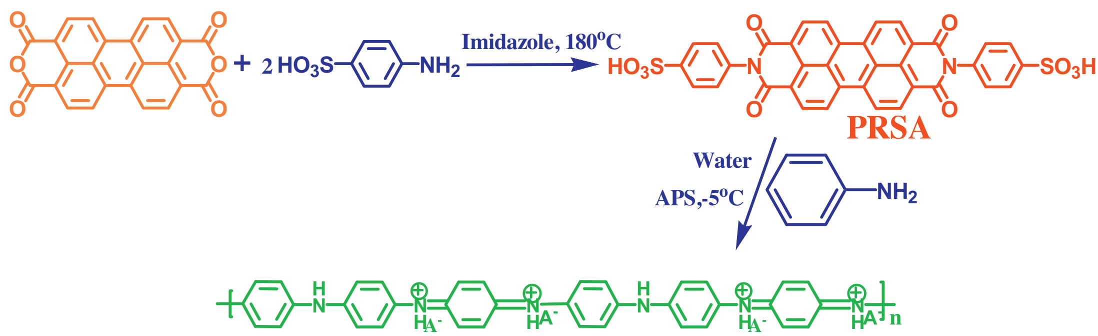

Fig. 1. Schematic presentation of PRSA/PANI synthesis.

In most cases, the PANI film is directly deposited onto the surface of the working electrode at the time of eletropolymerization. The resultant film is integrated and compacted with the surface of working electrode. So, it is very difficult to peel an integrated film off the working electrode. Externally prepared composite film may be helpful for overcoming it [13,14].

We report here a new as well as simple strategy for determination of ascorbic acid using modified PANI electrode prepared by a very quick and simple drop-coating method. Water soluble PRSA/PANI composites have been synthesized in water from the mixture of aniline, PRSA (1:100) and ammonium peroxydisulphate (1:1) by dilute polymerization method. The dilute polymerization is very important for *in-situ* preparation method because the dilute polymer solutions control nucleation and growths resulting good crystallization properties [15,16]. At the initial phase of polymerization, small amount of aniline will be protonated by dopant PRSA slowly to form anilinium ion that can interact with peroxodisulphate to form both monoanilinium peroxydisulphate and dianilinium peroxydisulphate. These anilinium peroxydisulphates convert to anilinium cation-radical to generate the H_2SO_4. As a result, in the reaction medium, the pH of the medium decreases and it proceeds the reaction faster [17–20].

The synthesized nanocomposites are easily dispersed in aqueous media. Aqueous solution (5 μL) has been drop casted on an indium tin oxide (ITO) coated glass slide to prepare PRSA/PANI/ITO electrode [21,22]. After drying in air at room temperature, it has been used as a working electrode for AA oxidation in neutral pH solution. The importance of dopant PRSA in the composite are (i) fluorescence due to the presence of fluorophoric aromatic perylene ring, (ii) the composite is water soluble due to the presence of $-SO_3H$ groups in dopant PRSA and (iii) enhancement of crystallinity, thermal stability etc.

2. Experimental

2.1. Materials

Aniline monomer (Merck Chemicals) was distilled under reduced pressure. Ammonium persulphate $(NH_4)_2S_2O_8$, (APS, Rankem chemicals) as a radical oxidant for PANI and Perylene tetracarboxylic acid-3,4,9,10-dianhydride (PDA) were purchased from Aldrich. Sulphanilic acid, phosphate buffer tablet were purchased from Merck Chemicals. All aqueous solutions were prepared in membrane filtered (Millipore Milli-Q system) water of resistivity 18 MΩ cm.

2.2. Synthesis

2.2.1. Synthesis of N,N′-bis(4-benzosulphonic acid)perylene-3,4,9,10-tetracarboxylbisimide (PRSA)

Perylene tetracarboxylic acid-3,4,9,10-dianhydride (2 g, 5.1 mmol), sulphanilic acid (2.6 g, 15.2 mmol), 350 mg of zinc acetate (2.2 mmol), and 15 g of imidazole were taken in round-bottom flask. The reaction mixture was refluxed at 170 °C for 4 h in inert atmosphere. After being cooled at room temperature, it was added to 50 mL of ethanol two times, refluxed and decanted at 80 °C to remove the imidazole from the mixture. The precipitate was collected by filtration. After drying in vacuum, it afforded 3.2 g

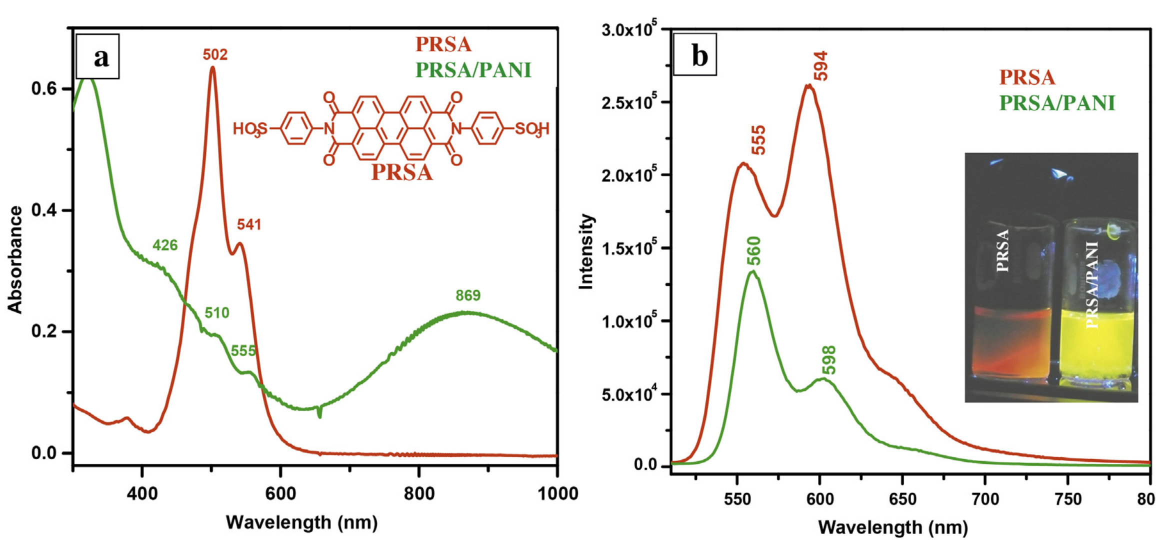

Fig. 2. (a) UV–Vis spectra, (b) fluorescence spectra of PRSA and PRSA/PANI composites from aqueous solution (path length = 1 cm, λ_{ex} = 502 nm).