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Short communication

Ruthenium(II)-mediated synthesis of conducting polyaniline (PAni): A novel route for PAni–RuO₂ composite

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ABSTRACT

In this communication we describe the unprecedented ruthenium(II)-mediated synthesis of polyaniline. The synthesis enroute via formation of a simple ruthenium(II)-tetraaniline complex which on chemical oxidation with hydrogen peroxide in the presence of hydrochloric acid gives conducting polyaniline–RuO₂ composite. The reaction is novel in the way that both the metal center Ru(II) and the coordinated aniline molecules of the intermediate complex **1** take part in the oxidation reaction to yield polyaniline–ruthenium oxide hybrid.

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1. Introduction

Conducting polymers (CPs) [1] have attracted the scientific community ever since when polyacetylene was first synthesized by Shirakawa et al. in 1977 [2]. The greatest advantage of these 'organic metals' is their thin/thick film fabrication by simple electrochemical deposition. Particularly, attention on polyaniline (PAni) has been given due to its environmental stability, film-forming property with tunable conductivity and commercial viability. Polyanilines have been studied extensively due to the fundamental interest in reaction mechanisms and for their applications to practical devices for energy storage, electrochemical sensors, electrochromic devices, EMI shielding, corrosion protection and others [3–15]. Application of the CPs in energy storage devices is well known [16] and recent studies [17] in this area gave impetus to fundamental and applied research on CP-based new materials.

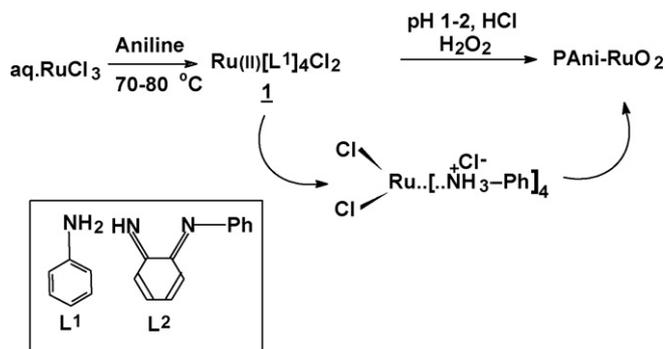
By compositing with metals such as Ru, Pd, Ag, Pt and Au (M-CPs), applications of conducting polymers are broadened [18–22]. In our efforts to synthesize such useful M-CP composites, we demonstrated a novel method to incorporate palladium particles into polypyrrole matrix (Pd-PPy), which oxidizes hydrazine efficiently even at low Pd loadings [23a] and a simple method to obtain surface modified PPy film with silver nanoparticles (Ag-PPy) [23b]. Ruthenium oxide (R.O) has been an attractive material

for electrochemical and photochemical processes [16,24]. Incorporation of this conducting material into PAni can give rise to organic–inorganic hybrid material with improved physical and chemical/electrochemical properties such as higher pseudocapacitance, gas-sensing behavior. For example, as both conducting polymers and R.O show high Faradaic pseudocapacitance, the composite electrodes of the two exhibit better specific capacitance as evident from recent studies [25]. The incorporation of R.O can impart conductivity to the CPs in undoped state. In this communication we describe ruthenium(II)-mediated synthesis of polyaniline. The synthesis enroute via formation of a simple ruthenium(II)-tetraaniline complex which on chemical oxidation with hydrogen peroxide in the presence of hydrochloric acid gives conducting polyaniline–RuO₂ composite. The reaction is novel in the way that both the metal center Ru(II) and the coordinated aniline molecules of the intermediate complex **1** (Scheme 1) take part in the oxidation reaction to yield polyaniline–ruthenium oxide hybrid. This type of metal-assisted synthesis of PAni routed through an aniline complex is unprecedented and we report, for the first time, the synthesis of RuO₂ embedded PAni.

2. Experimental

All chemicals are analytical grade. Aniline and ruthenium trichloride were obtained from MERCK chemicals (India). Electrochemical experiments were performed on Auto lab 302 potentiostat using three electrode assembly containing platinum foil working electrode (2.5 mm × 2 mm), platinum wire auxiliary electrode and

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Scheme 1. Synthetic approach for PANi-RuO₂ preparation.

saturated calomel (S.C.E.) reference electrode. FT-IR spectrum of the film was recorded on model no. Paragaon-500 of PerkinElmer. SEM images for film were taken on Hitachi 3000 H instrument. For obtaining better quality SEM pictures at high magnifications, samples were gold sputtered on JEOLFINE COAT ion sputter (model no. JFC-1100) for 3 min. X-ray diffraction (XRD) experiments were conducted on PANalytical's X'Pert PRO instrument.

2.1. Synthesis of the composite

To an aqueous solution of ruthenium trichloride (1 mM), aniline (5 mM) was added, stirred at 70–80 °C for about half-an-hour. The brownish precipitate was filtered and washed copiously with water and hexane to remove free ruthenium salt and aniline. The precipitate was taken into 100 ml water with 5 ml of HCl, stirred for 2 h and oxidized with 30% H₂O₂. The greenish-blue precipitate was filtered and washed with water.

3. Results and discussion

Methanol soluble PANi-RuO₂ composite is obtained when aniline and RuCl₃·H₂O (1:5 mM) are stirred in water for requisite period of time and oxidized with hydrogen peroxide in presence of hydrochloric acid. The formation of PANi-RuO₂ composite is evident from the cyclic voltammetry and UV-vis spectrum of the composite (Figs. 1 and 2). Cyclic voltammogram of PANi-RuO₂ (Fig. 1) showed two clear oxidation peaks at ca. 0.210 V and 0.72 V (vs. SCE) in the forward scan and prominent reduction peaks at 0.185 V and 0.650 V in the reverse scan. The overall CV can be visualized as rectangular shape suggesting pseudocapacitance property of the composite which also indicate the presence of immobile phase in the polymer [26]. In contrast, pure PANi doped with sulphuric acid shows oxidation peaks at 0.09 V and 0.625 V [3]. The shift in the oxidation potentials for the PANi-RuO₂ can be attributed

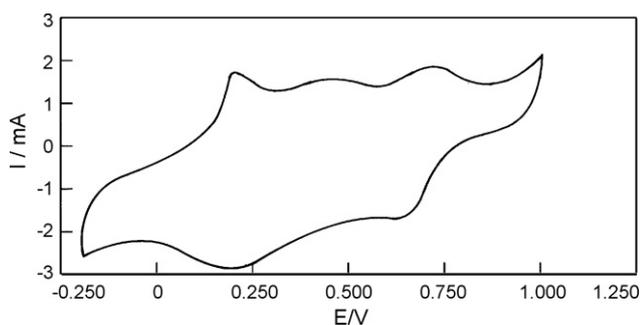


Fig. 1. Cyclic voltammogram of the composite on Pt electrode in 1 M sulfuric acid at 100 mV/s.

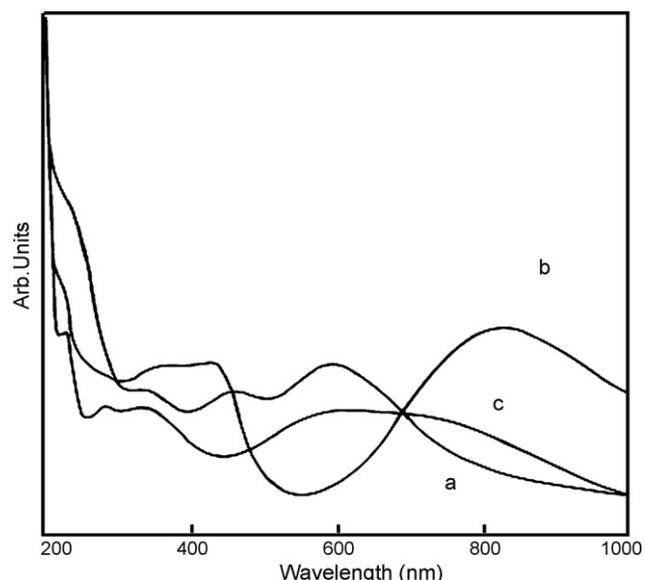


Fig. 2. UV-vis spectrum of the composite in methanol: (a) solid material, (b) colloidal material in doped state, and (c) colloidal material after dedoping with ammonium hydroxide solution.

to the possible interaction of polyaniline nitrogens with RuO₂ particles. The composite is soluble in methanol and can be dispersible in water. The UV-vis spectrum (Fig. 2) of the composite confirms the formation of PANi. The spectrum exhibited bands at 357 nm, 477 nm and 609 nm suggesting that PANi is partially doped (Fig. 2a). The second crop of fine material of PANi obtained by centrifugation of filtrate of the reaction mixture is also methanol soluble, water dispersible and gave UV-vis spectra similar to the colloidal PANi [27] in doped state with electronic bands at 350 nm [$\pi \rightarrow \pi^*$ of benzenoid

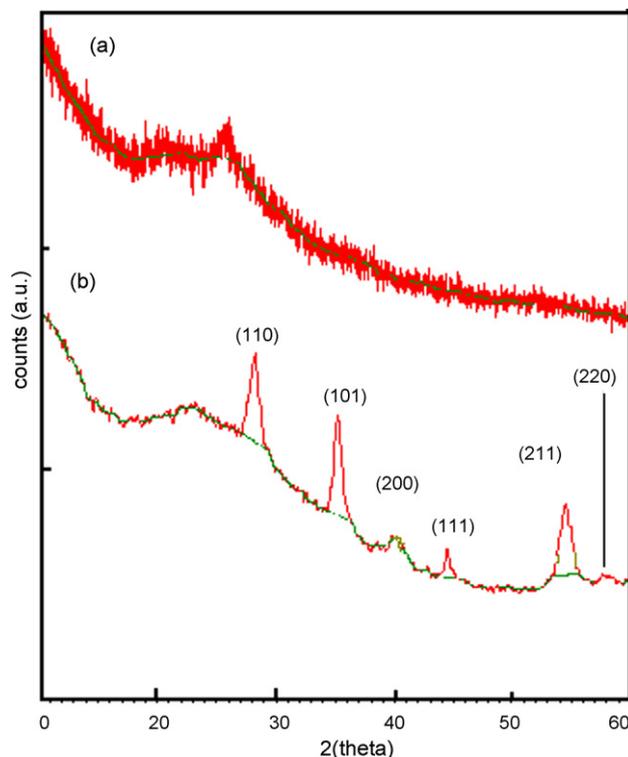


Fig. 3. XRD spectrum of the composite: (a) as prepared at RT and (b) after heated to 225 °C for 3 h.

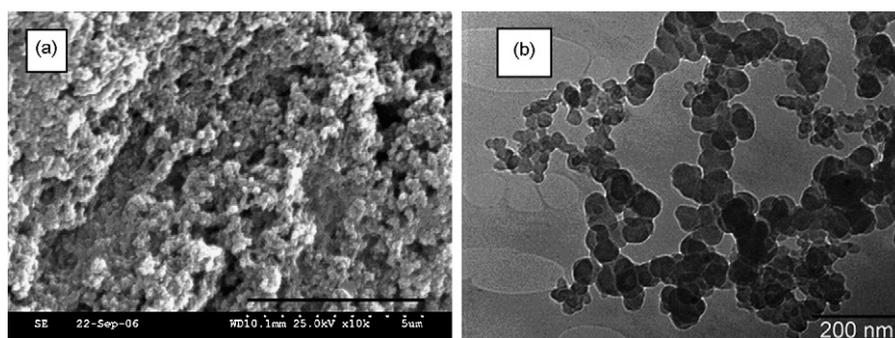


Fig. 4. (a) SEM and (b) TEM images of the composite.

structures]. The other two optical absorption peaks at 420 nm and 825 nm without the localized peak at 609 nm, are interpreted as excitations of valence electrons to the polaron band formed when emeraldine base is doped to the conducting emeraldine salt form (Fig. 2c). The FT-IR spectrum of the composite exhibited characteristic N–B–N and N=Q=N bands at 1495 cm^{-1} and 1135 cm^{-1} , 1635 cm^{-1} , respectively. The band observable for N–H stretching around 3350 cm^{-1} is broad, showed tendency to split and shifted to 3413 cm^{-1} suggesting possible interaction of the group with ruthenium oxide particles.

XRD (Fig. 3) analysis of the composite exhibited broad peaks due to PANi at $2\theta = 20.97$ and 25.3 . When the composite is heated for 3 h at 225°C , crystalline phase for RuO_2 is developed [28] with peaks at $2\theta = 28.12(1\ 1\ 0)$, $34.94(1\ 0\ 1)$, $40.14(2\ 0\ 0)$, $44.14(1\ 1\ 1)$, $54.26(2\ 1\ 1)$ and $57.65(2\ 2\ 0)$. The existence of Ru in (+IV) state, i.e., RuO_2 is confirmed by XPS analysis of the sample. Only the Ru $3p_{3/2}$ peak was available for the evaluation of the Ru species oxidation state, because the more intense Ru $3d_{(5/2+3/2)}$ peaks (BE = 280–284 eV) were totally masked by the C 1s peak of carbon. The spectrum showed a broad Ru $3p_{3/2}$ peak at $462 \pm 0.2\text{ eV}$ assignable to Ru in (IV) oxidation state [29]. The surface of the composite is amorphous and shows sponge-like morphology as seen by SEM. TEM analysis showed that it is composed of 18–50 nm size round platelets (Fig. 4). The pressed pellet of the as prepared composite exhibited a surface conductivity of 0.5 S/cm .

To gain more insight into the reaction pathway, we isolated the intermediate, complex **1** (Scheme 1) formed in the reaction of 1 mM of ruthenium trichloride with slight excess of aniline (5 mM). The brown complex **1** is soluble in polar organic solvents and the solution slowly changes into purple color probably due to oxidation of coordinated ligands/or metal center [30] through a complex mechanism. The NMR spectrum of fresh sample confirmed the formation of tetraaniline complex **1**. The proton NMR (DMSO) of the complex gave NH_2 resonance at $\delta = 5.01\text{ ppm}$, two triplets at $\delta = 7.01$, 6.47 ppm and a doublet at $\delta = 6.55$ similar to free aniline. It is known that when RuCl_3 is reacted with pure aniline (neat) at 130°C , the complex $\text{Ru}(\text{L}^1)_2(\text{L}^2)\text{Cl}_2$ (**2**) is formed [30] (where L^2 is the dimerized product of aniline, Scheme 1). Under our experimental conditions, as evident from the NMR analysis, we have not observed the formation complex **2**. However, we observed that Ru(III) is reduced to Ru(II) state during the course of reaction as a result of oxidation of some aniline molecules. The mechanism of formation of PANi– RuO_2 composite is expected to involve in withdrawal of coordination by aniline molecules from Ru(II) center as a result of protonation of NH_2 -group of aniline by HCl resulting in the formation of free anilinium and Ru(II) ions (Scheme 1) which on oxidation concomitantly give polyaniline and ruthenium oxide.

In conclusion, we have synthesized conducting polyaniline mediated through Ru(II) which enroute through the formation of

aniline complex **1** as suggested by NMR. The advantages of the synthesis of PANi by this method is that (i) there is a control of molecular weight of the polymer; hence soluble polymer is obtained; (ii) novel method to incorporate ruthenium oxide into the polymer matrix. The stoichiometry of PANi: RuO_2 can be varied just by addition of free aniline to the complex **1** reaction mixture just before oxidation by peroxide.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.synthmet.2008.03.015.

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