

Synthesis of polyaniline–bismoclite composite and its function as recoverable and reusable catalyst

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Abstract

Polyaniline–bismoclite (PANI–BC) composite, which is effective in catalyzing the condensation of indole and carbonyl compounds, has been synthesized and characterized by spectral, physical and electrical methods.

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1. Introduction

Conducting polymer is a very important material for modern scientific world. Among the conducting polymers, polyaniline has been most extensively studied and it is an electrically conducting polymer with features that can be exploited in various applications such as light emitting diode (LED), organic field effect transistor (FET), electro magnetic interference (EMI) shielding, antistatic materials, sensing materials, secondary batteries [1] and catalyst [2].

The properties and the nature of conducting polymers mainly depend on dopants. In doping process of conducting polymers the accessibility of inorganic salts (Bi, Al, Sn-salt, etc.) is very low. As part of our systematic efforts to prepare novel polyaniline material, the considerable efforts have been made towards the synthesis of polyaniline based metal oxychloride material. To the best of our knowledge, there are few reports on conducting polymer based metal halide and metal oxyhalide material [3]. Metal oxyhalides might be utilized as ion conductors [4], catalyst [5,6] and superconductors [7].

Bismuth compounds are attractive since many of them are commercially available and have little or no toxicity [8]. With

increasing environmental concerns and the need for ‘green reagents’, the interest in bismuth and its compounds has increased tremendously in the last decade. Among the bismuth compounds bismoclite is having unique properties. Bismoclite is water insensitive material which, in addition, exhibits an extremely low toxicity (LD₅₀ ORL (rat): 22 g/kg). Due to the lack of insolubility and Lewis acidity of bismoclite the actual use of this material is limited. Here, we report the synthesis of polyaniline–bismoclite (PANI–BC) composite using polyaniline base and bismuth trichloride under room temperature in acetone solvent and evaluated the catalytic function of PANI–BC composite.

The replacement of the current chemical processing with more environmentally benign alternative is an increasing attractive subject [9]. The use of Bi(III) derivatives in catalytic transformations appears to be versatile and promising in their large-scale development. Very recently, we have reported the polyaniline based Bronsted and metal chloride salts as catalyst in synthetic organic transformations [2]. Indoles and their derivatives are used as antibiotics in the field of pharmaceuticals [10]. Bisindolylalkanes and their derivatives constitute an important group of bioactive metabolites of terrestrial and marine origin [11]. Protic acids [12] as well as Lewis acids [13,14] are known to promote these reactions. Recently, lanthanide triflates [15], montmorillonite clay K-10 [16], lithium

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perchlorate [17] and iodine [18] were also found to catalyze these reactions. However, among the above-mentioned catalysts, a few catalysts are more expensive and non-recoverable and have poor reactivity and non-eco-friendly nature. More recently, the catalytic activity of PANI–BC composite was checked in dihydropyrimidinones synthesis [19]. As a consequence of this activity, in this paper, we report the synthesis and characterization of PANI–BC composite and used as polymer based solid acid catalyst in bisindoles synthesis with desired features such as easy recovery, simple work-up procedure, reusable and eco-friendly.

2. Experimental

2.1. Materials

Aniline (reagent grade) from E. Merck was distilled prior to use. Reagent grade sodium persulfate, indole, benzaldehyde and derivatives, methanol, acetone, sulfuric acid, bismuth trichloride (BDH, India) were used without further purification.

2.2. Synthesis

2.2.1. Synthesis of PANI–BC catalyst

2.2.1.1. Preparation of polyaniline–bismoclite composite.

Polyaniline salt was prepared by the procedure reported earlier [20]. In a typical experiment, 10 ml of aniline was added to the 700 ml aqueous solution containing 30 ml H₂SO₄ taken in 2 l round bottomed flask. The solution was kept under constant stirring at 5–10 °C. To this solution, 23.8 g of sodium persulfate in 250 ml of water was added drop wise for 30 min. The reaction was allowed to continue for 4 h. The precipitated polyaniline-sulfate salt was recovered by filtration, and the precipitate was washed with 5 l of distilled water followed by 500 ml acetone. Thus obtained polyaniline-sulfate salt was kept in 1 l sodium hydroxide solution (1 N) and stirred for 12 h at ambient temperature. The solution was filtered, washed several times with water to remove excess NaOH. The product (polyaniline base) was dried at 100 °C until constant mass was reached. Polyaniline base (5 g) prepared by the above method was added to 500 ml acetone containing 0.1 M of BiCl₃. The solution was kept under stirring for 4 h at ambient temperature and filtered, washed with 1 l acetone. The powder was dried at 100 °C till a constant mass.

2.2.2. Synthesis of bis(indolyl)methane

For neat: In a 10 ml round-bottomed flask was placed indole (2 mmol), benzaldehyde (1 mmol) and 50 mg PANI–BC composite (20 wt.% with respect to indole) was allowed to react for 4 h at room temperature. The reaction mixture was washed with acetone to separate the catalyst and concentrated in vacuum. The crude mixture was treated with hexane and water affording the bis(indolyl)methane.

For solvent system: In a 25 ml round-bottomed flask was placed indole (2 mmol), benzaldehyde (1 mmol) and 50 mg activated PANI–BC composite (20 wt.% with respect to indole) in methanol solvent (10 ml) was stirred at room temperature for 4 h. The reaction mixture was washed with acetone to separate the catalyst and concentrated in vacuum. The crude mixture was treated with hexane and water affording the bis(indolyl)methane. All isolated products were characterized by ¹H NMR analysis.

2.3. Measurements

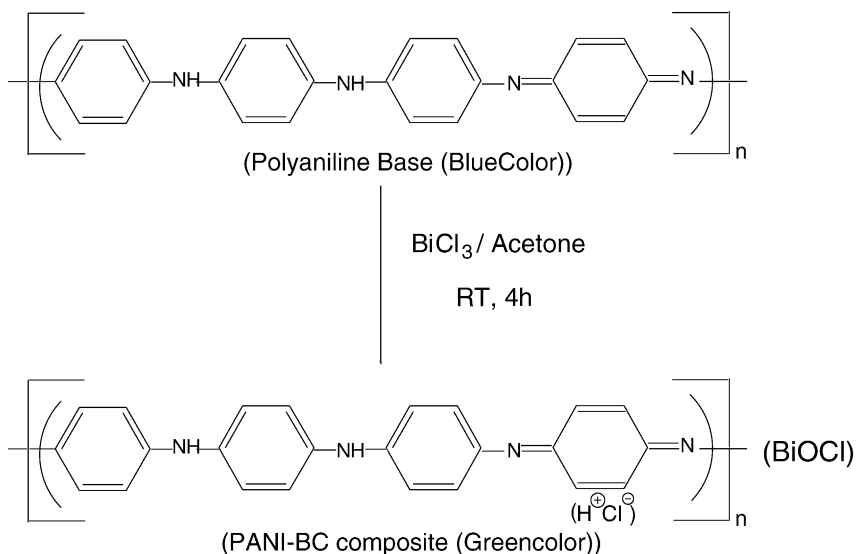
Resistance measurement of PANI–BC composite was carried out on a two probe connected to a Keithley digital multimeter (Model-2010). Pellet density was determined from the mass per unit volume of the pressed pellet. Fourier transform infrared spectra were recorded using GC-FTIR spectrometer (Model-740 Nicolet, USA). Wide angle X-ray diffraction spectra of powder samples were obtained using a Siemens/D-5000 X-ray diffractometer using Cu K α radiation of wave length 1.54×10^{-10} m and continuous scan speed of 0.045 °/min. Morphology studies of PANI–BC composite was carried out using Hitachi S520 scanning electron microscope instrument operating at 10 kV. Bisindoles were analysed by melting point and ¹H NMR (Gemini 200 MHz varian instrument) spectral techniques.

3. Results and discussion

Incorporation of bismoclite in polyaniline system through common processes like aqueous polymerization, emulsion polymerization, post doping techniques is not possible because, bismoclite is not soluble in water as well as in common organic solvents. In this report, PANI–BC composite is synthesized using BiCl₃ and polyaniline base. BiCl₃ is dissolved in distilled acetone and added polyaniline base and the mixture was stirred under nitrogen atmosphere. Upon addition of bismuth(III) chloride to polyaniline base, we have observed the color changes from blue color (PANI base) to green color indicated the protonation of polyaniline base (Scheme 1). During the reaction, BiCl₃ is hydrolyzed to give BiOCl and HCl. The evolution of HCl leads to the protonation of polyaniline base to PANI-HCl salt and BiOCl dispersed onto the protonated PANI-HCl salt. Conductivity and density of the PANI–BC composite were found to be 0.004 S/cm and 1.85 g/cm³, respectively.

3.1. Characterization of polyaniline–bismoclite composite

Infrared spectra of polyaniline-sulfate (PANI-H₂SO₄) salt, its corresponding polyaniline base and PANI–BC composite are shown in Fig. 1. The vibrational bands observed

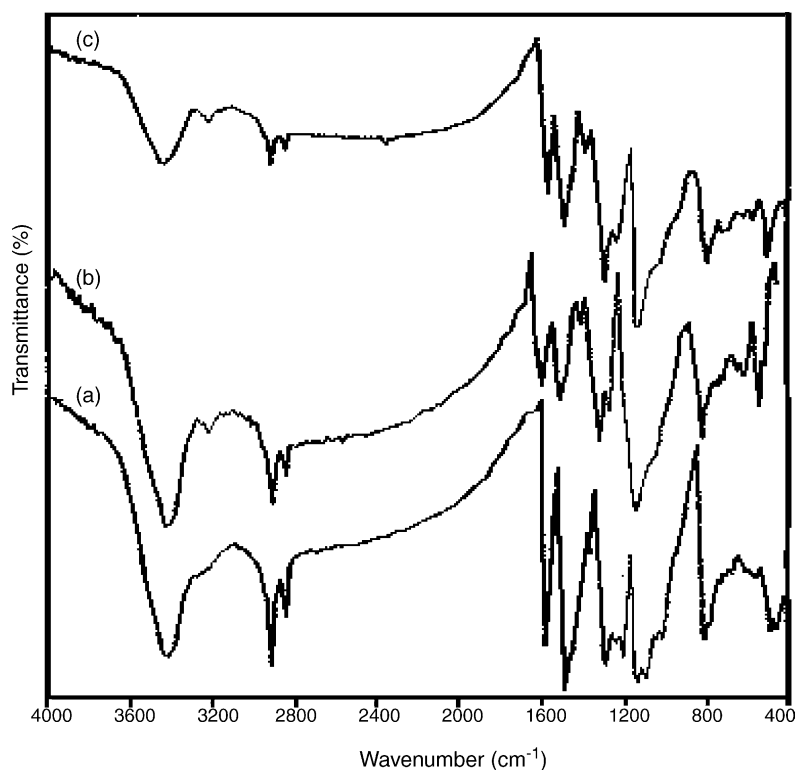


Scheme 1.

for the polyaniline base (Fig. 1a) are reasonably explained on the basis of the normal modes of aniline and benzene; a broad band at 3415–3460 cm^{-1} assigned to the N–H stretching vibration. The bands at 2920 and 2850 cm^{-1} are probably originate from a contamination of aliphatic nature or sum frequency and bands at 1565 and 1490 cm^{-1} are due to quinonoid ring (Q) and/or benzenoid ring (B).

The bands at 1370 and 1300 cm^{-1} are assigned to C–N stretching vibration in QBB, QBQ and BBQ, a 1240 cm^{-1}

band to the C–N stretch vibration of aromatic amine. In the region of 1020–1170 cm^{-1} , aromatic C–H in-plane-bending modes are usually observed. For polyaniline, a strong band characteristically appears at 1140 cm^{-1} , which has been explained as an electronic band or a vibrational band of nitrogen quinone. A band at 705 cm^{-1} is assigned to ring C–C bending vibration and the band at 580 cm^{-1} due to ring in plane deformation. The C–H out-of-plane bending mode has been used as a key to identifying the type of substituted benzene.

Fig. 1. Infrared spectra of (a) PANI base, (b) as-synthesized PANI-H₂SO₄ salt and (c) PANI-BC composite.

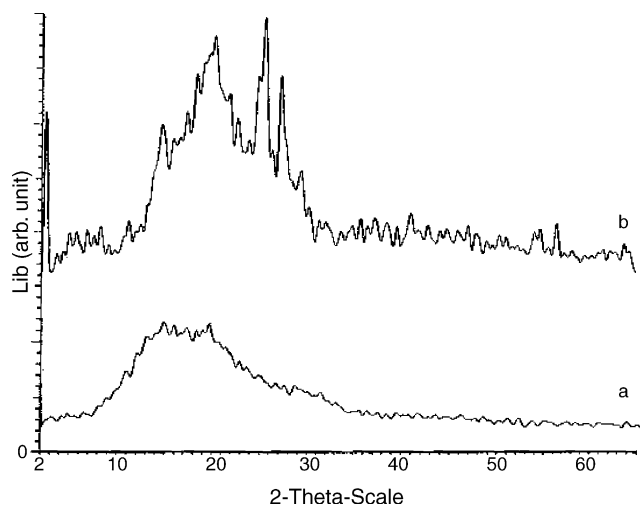


Fig. 2. X-ray diffraction pattern of (a) PANI base and (b) PANI-H₂SO₄ salt.

For the polyaniline base, this mode was observed as a single band at 825 cm⁻¹, which fell in the range 800–860 cm⁻¹ reported for 1,4-substituted benzene. The infrared spectrum of polyaniline base prepared is very close to the infrared spectrum of the polyaniline base system reported in the literature [21,22].

The infrared spectrum of PANI-H₂SO₄ salt is shown in Fig. 1b. The infrared spectrum of PANI-H₂SO₄ salt is similar to that of polyaniline base except a band around 3230 cm⁻¹ that is assigned to the NH₂⁺ group, which indicates the formation of protonated polyaniline salt. The doublet band at 1140 and 1110 cm⁻¹ in the polyaniline base which is assigned to mode of Q=N⁺H–B or Q–NH–B becomes a singlet in the salt spectrum. Infrared spectrum of PANI–BC composite (Fig. 1c) is very similar to that of PANI-H₂SO₄ salt (Fig. 1b) and this result indicates the formation of polyaniline in composite form.

XRD of polyaniline base indicate the amorphous nature of the polyaniline base Fig. 2a with peaks 2θ at 15.0° and 19.5° values corresponding to the interface distance $d=6.048$ and 4.546 Å, respectively. X-ray diffraction patterns of PANI-H₂SO₄ salt (Fig. 2b) show peaks at $2\theta=14.5^\circ$, 20° and 25° and these positions are in accordance with the earlier report [23]. XRD patterns of the PANI–BC composite shows peaks at $2\theta=26.0^\circ$, 32.5°, 33.5° and 46.5° values corresponding to the interface distance $d=3.448$, 2.756, 2.682 and 1.946 Å, respectively (Fig. 3a). The peak positions are in good agreement with those found for bismoclite (Fig. 3c) as well as reported results [24]. This result clearly indicates that bismoclite is present in polyaniline composite.

Morphology of PANI–BC composite (Fig. 4) shows core shell type morphology with relatively uniform diameter from 0.8 to 3 μm.

In polyaniline–bismoclite (PANI–BC) composite, HCl is acting as dopant. PANI–BC material is a novel polyaniline composite, which shows crystallinity of bismoclite, conduc-

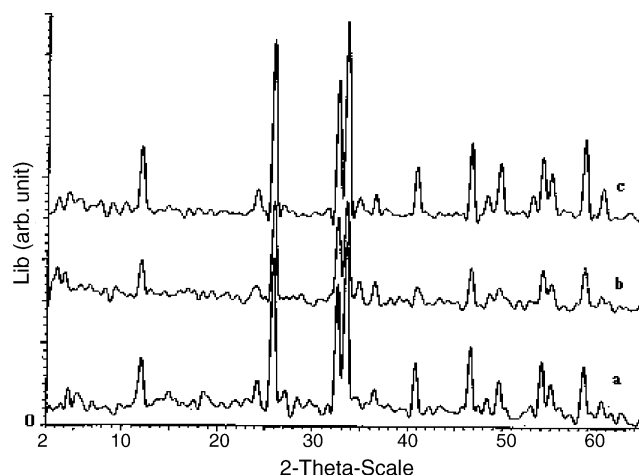


Fig. 3. X-ray diffraction pattern of (a) PANI–BC composite, (b) reused PANI–BC composite and (c) bismoclite.

tivity at room temperature and exhibiting catalytic property in organic transformation.

3.2. Catalytic function of PANI–BC composite in the synthesis of bis(indolyl)methanes

PANI–BC composite used as polyaniline based solid acid catalyst in bisindoles synthesis (Scheme 2) with desired features such as easy recovery, simple work-up procedure, reusable and eco-friendly.

There was no appreciable reaction when benzaldehyde allowed to react with indole in the absence of catalyst. A trace amount of product (2%) was observed with bismoclite (BiOCl) alone as catalyst. Synthesis of bisindole was also carried out in presence of PANI–HCl salt. The yield of the product was found to be less (62%). However, excellent yield (99%) was obtained with the use of PANI–BC composite as catalyst (Table 1, entry 1). This result indicates that, in PANI–BC composite, the present of BiOCl is enhancing the catalytic activity of PANI–HCl salt. The influence of the amount of PANI–BC composite catalyst was also investi-

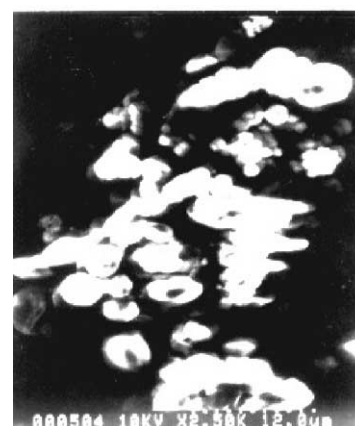
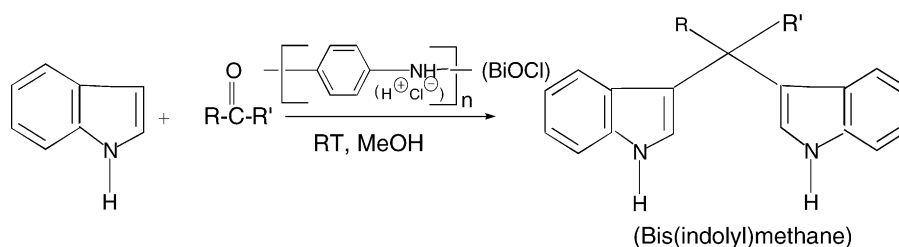


Fig. 4. Scanning electron micrograph of PANI–BC composite.



Scheme 2.

gated. Use of 10, 15 and 20 wt.% of catalyst (with respect to indole) gave the product 80, 88 and 99% yield, respectively.

Reusability of the catalyst was checked by the condensation of indole with benzaldehyde using PANI–BC composite in methanol medium, which results in 99% yield. The PANI–BC composite was recovered and reused for a further seven times and resulted in 99–97% yields. This result indicates that PANI–BC composite does not lose its activity and can be reused. Encouraged by this result, we carried out further investigations on several carbonyl compounds (Table 1, entries 2–14). Aromatic aldehyde containing electron-donating as well as electron-withdrawing groups (entries 2–10) gave good yields. 2,4-Dichloro benzaldehyde (entry 11) gave low yield (52%) than other aldehyde and this may be due to the effect of chlorine substitution in 2 and 4th position of the aldehyde. Furthermore, the catalytic performance of PANI–BC composite system was checked towards the α,β -unsaturated aldehyde such as cinnamaldehyde (entry 12). Catalytic application of the PANI–BC composite was extended to condensation of aliphatic aldehyde and ketone such as heptaldehyde and cyclohexanone (entries 13 and 14) which gave 47 and 52% respectively in 24 h.

The condensation reaction of indole with benzaldehyde, anisaldehyde and cinnamaldehyde was also carried out under solvent-free condition and obtained excellent yields 85, 99 and 82%, respectively. This result indicates that PANI–BC

composite acts as an efficient catalyst under solvent free condition also.

3.2.1. 3,3'-Bis(indolyl)-4-methylphenylmethane

Solid; mp, 96–97 °C; yield-95%; $^1\text{H NMR}$ (200 MHz, CDCl_3): δ 2.35 (s, 3H), 5.85 (s, 1H), 6.62 (s, 2H), 6.95 (t, 2H, $J = 8.0$ Hz), 7.05 (d, 2H, $J = 8.0$ Hz), 7.15–7.30 (m, 6H), 7.35 (d, 2H, $J = 8.0$ Hz), 7.85 (br s, 2H).

4. Conclusions

In summary, the present results demonstrate the chemistry of polyaniline-metal oxychloride material with experimental data and application as a convenient and facile catalyst for the electrophilic substitution reaction of indole with carbonyl compounds giving bis(indolyl)methanes in excellent yields. The use of this inexpensive, easily preparable, stable, recyclable catalyst with simple work-up and cleaner reaction make this protocol practically, economically and eco-friendly attractive. This development is likely to lead not only to refinements of the existing models, but also to greater depth of understanding of fundamental and technologically important phenomena of polyaniline-metal oxychloride material.

Table 1
Synthesis of bisindolylmethanes using PANI–BC composite as catalyst

Entry	Substituents		Time (h)	Yield (%)
	R	R'		
1	C_6H_5-	H	4	99
2	4-(Me)– C_6H_4-	H	4	95
3	4-(OMe)– C_6H_4-	H	4	99
4	3,4-di-(OMe)– C_6H_3-	H	4	98
5	2,3-di-(OH)– C_6H_3-	H	4	97
6	4-(Cl)– C_6H_4-	H	4	94 ^a
7	4-(OH)– C_6H_4-	H	4	98 ^a
8	3-(OMe)-4-(OH)– C_6H_3-	H	4	95 ^a
9	4-(NO ₂)– C_6H_4-	H	4	98 ^a
10	2-(NO ₂)– C_6H_4-	H	4	96 ^a
11	2,4-di-(Cl)– C_6H_3-	H	4	52
12	$\text{C}_6\text{H}_5\text{CH}=\text{CH}-$	H	4	87 ^a
13	$\text{CH}_3(\text{CH}_2)_5-$	H	24	47
14	$-(\text{CH}_2)_5-$	–	24	52

^a Products are isolated from preparative column (EtOAc–Hexane) chromatography.

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