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Rekha
Department of Chemistry, College of Basic Sciences and Humanities, G.B. Pant University of Agriculture and Technology, Pantnagar, Uttarakhand (U.K.), India

Anjali Bisht
Department of Chemistry, College of Basic Sciences and Humanities, G.B. Pant University of Agriculture and Technology, Pantnagar, Uttarakhand (U.K.), India

Ila Joshi
Department of Chemistry, College of Basic Sciences and Humanities, G.B. Pant University of Agriculture and Technology, Pantnagar, Uttarakhand (U.K.), India

Shubham Sharma
Department of Chemistry, College of Basic Sciences and Humanities, G.B. Pant University of Agriculture and Technology, Pantnagar, Uttarakhand (U.K.), India

Sameena Mehtab
Department of Chemistry, College of Basic Sciences and Humanities, G.B. Pant University of Agriculture and Technology, Pantnagar, Uttarakhand (U.K.), India

NK Sand
Department of Chemistry, College of Basic Sciences and Humanities, G.B. Pant University of Agriculture and Technology, Pantnagar, Uttarakhand (U.K.), India

MGH Zaidi
Department of Chemistry, College of Basic Sciences and Humanities, G.B. Pant University of Agriculture and Technology, Pantnagar, Uttarakhand (U.K.), India

Correspondence
Rekha
Department of Chemistry, College of Basic Sciences and Humanities, G.B. Pant University of Agriculture and Technology, Pantnagar, Uttarakhand (U.K.), India

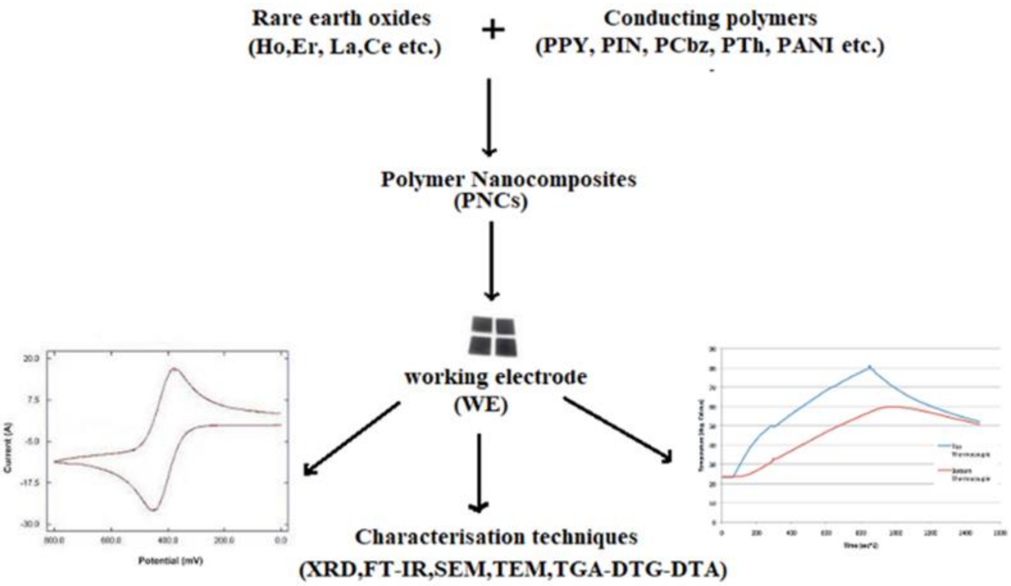
Rare earth based conducting polymers: A review

Rekha, Anjali Bisht, Ila Joshi, Shubham Sharma, Sameena Mehtab, NK Sand and MGH Zaidi

Abstract
This paper present recent advances in the field of composites of rare earths with conducting polymers. The synthesized composites were characterized by some common techniques viz; scanning electron microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X- Ray Diffraction spectra (XRD), UV-visible and simultaneous TG-DTA-DTG. The semiconducting and electrochemical behavior of rare earth based composites were investigated using four probe conductivity meter and cyclic voltammetry (CV) respectively. An overview of different techniques of synthesis and their application in various fields of electronics and communication is presented.

Keywords: Rare earth oxide, conductivity, supercapacitance, conducting polymer

Introduction
Constraint in availability of power due to continuous depletion in the reservoirs of fossil fuel has affected the performance and functioning of electronic and energy storage appliances [1,2] ·For such reasons, efforts on modification in the performance of such appliances are under way through blending design engineering with organic electronics [3, 4]. Unlike conventional inorganic semiconductors, organic electronic materials are developed from conducting polymers (CPs), dyes and charge transfer complexes [5]. CPs are synthesized either through chemical oxidation of the monomer or electrochemical oxidation of the monomer. Conjugated bond system along with polymer backbone is responsible for conducting nature of CPs [6] The major technical challenge in the performance of CPs based electronic and energy storage systems are the loss in material integrity under prolonged exposure of temperature, time and electrolyte media [7,8] . The morphology of polymer and related composite materials are altered due to segmental movement of macromolecules under exposure of temperature and electrolyte media with time, that imparts reduction in their conductivity and charge storage performance.



Electrical conductivity of electrodes is routinely recorded at variable temperatures without taking the cognizance variations in their microstructure under exposure of temperature and electrolyte media with time [9-11].

The electronic and electrochemical significance of CPs has been well documented since decades [12-15]. Common CPs employed for semiconducting and charge storage applications are PPY, PIN, PCbz, PAc, PANI and PTh [16] (Fig.1). Among all of them, PPY due to ease of preparation, environmental stability, electrical conductivity and charge storage has received increasing attention as electrode material for semiconducting and electrochemical energy storage devices [17-19]. The high energy valence band and low energy conduction band determines the electrical conductivity of PPY that increases with voltage and temperature [20, 21] .

Rare earth elements are the group of “lanthanoids” having 15 elements with atomic number from 57 (lanthanum) to 71 (lutetium) in modern periodic table. The demand of rare earth elements and their compounds has been raised since decades for advancements in low-carbon technologies. REOs are the chalcogenoides derived through oxidation of the set of seventeen chemical elements specifically fifteen lanthanides, as well as scandium and yttrium from d-block of modern periodic table. Blends of REOs with conducting or insulating polymer substrates make them useful for semiconducting, dielectric, optoelectronic and electrochemical applications [22-24]. Rare-earth elements are used for production and fabrication of glasses [25-27], optical communication electro-optic and photonic devices [28], magnets, catalysts, alloys, and semiconductors. Common rare earth element derived devices under application are electric motors of hybrid vehicles, wind turbines, hard disc drives, portable electronics, microphones, speakers, LCD , plasma screens.

Fillers contribute pivotal role towards modification in semiconducting and electrochemical performance of CPs. Since past decades, a wide range of chalcogenoides derived from transition metals (Table 1) has been employed as fillers for modification in semiconducting [29] and electrochemical performance of CPs [30]. The product derived through blending of such fillers with CPs are defined as PNCs. The electrochemical supercapacitance of such PNCs are well documented, whereas, limited search has been made on implication of REOs as fillers (Table 2) for semiconducting and electrochemical applications.

Electrical and electrochemical characteristics of REOs vary in size dependent manner PNCs derived through blending REOs with CPs offer wide spectrum of applications as solid polymer electrolytes [31, semiconductors [29], windows in dye-sensitized cells [32], electrochemical behavior and charge storage [33-35] .

Common CPs involved in synthesis of REOs based PNCs are PPY [36], PTh [37], PANI [12] and PIN [38]. Among such CPs, PPY has received increasing attention as polymer substrate due to ease of synthesis, thermal, chemical, electrochemical stability and semiconducting nature.

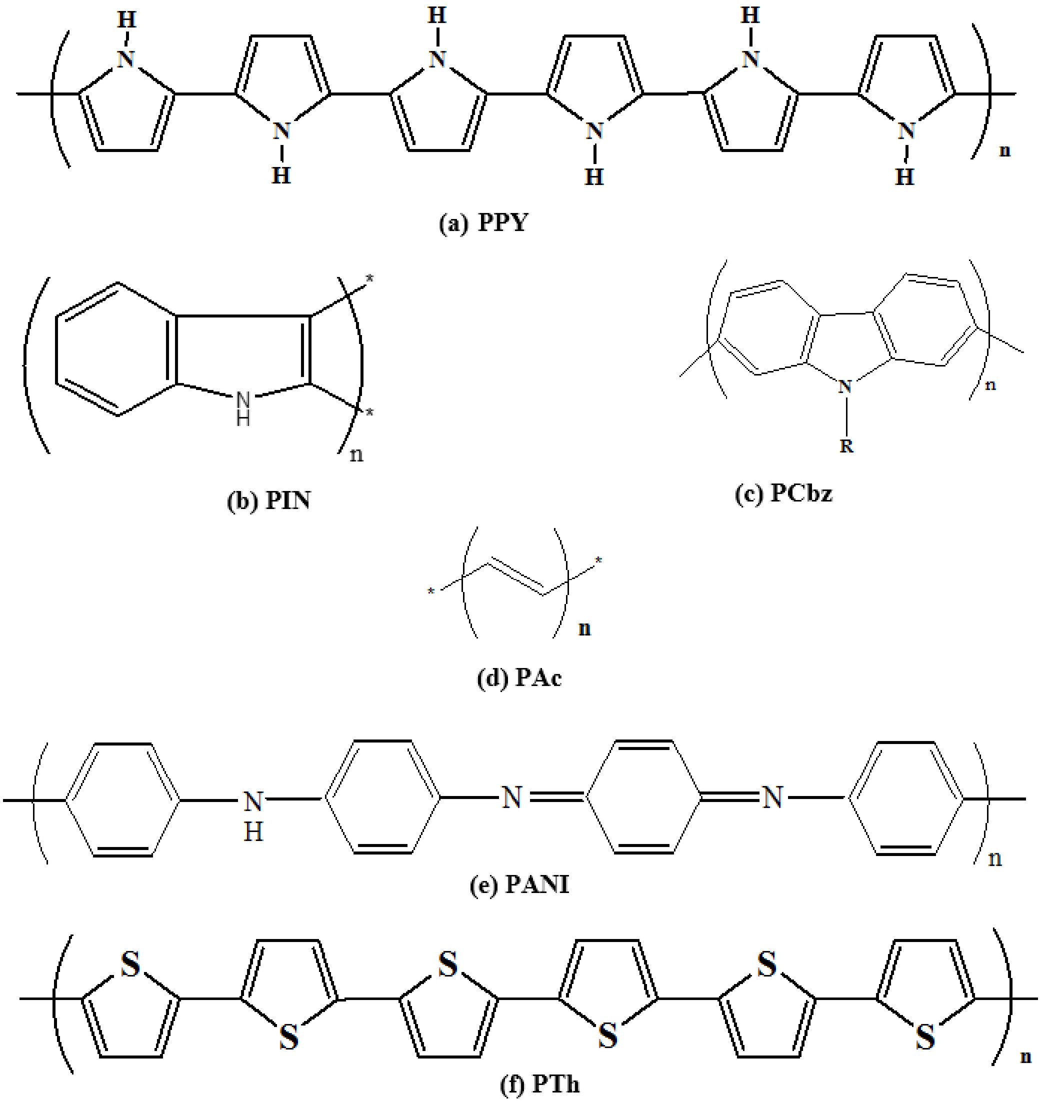


Fig 1(a-f): CPs used for semiconducting and electrochemical applications

Semiconducting and electrochemical performance of PNCs are evaluated in as their working electrode (WE) that are fabricated through coating a composition of carbonaceous material with CPs and a polymeric binder. Common carbonaceous materials employed for fabrication of WE are graphite and its tubular nanostructures. CPs used are either synthesized or commercially procured. Common conduction mechanism in REOs (polar) has been explained through polaron theory (Fig. 2).

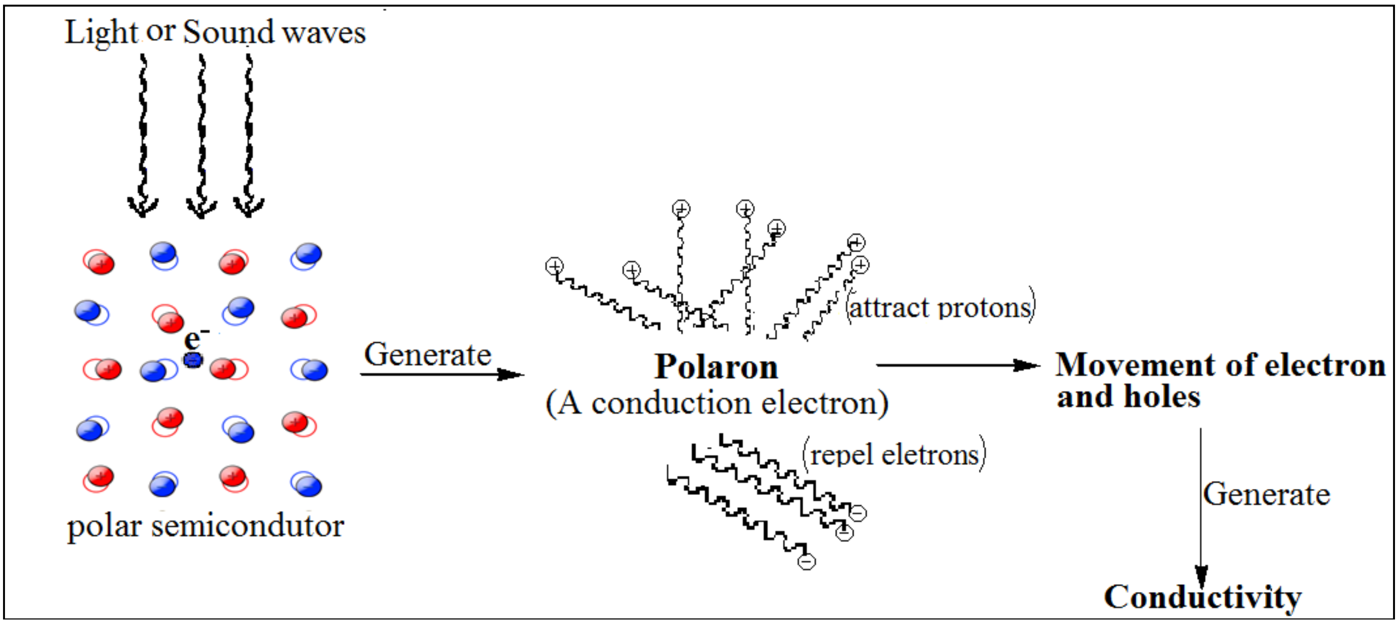
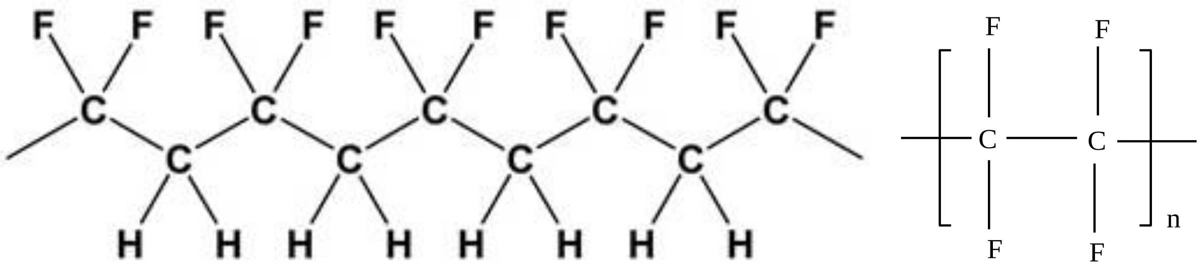


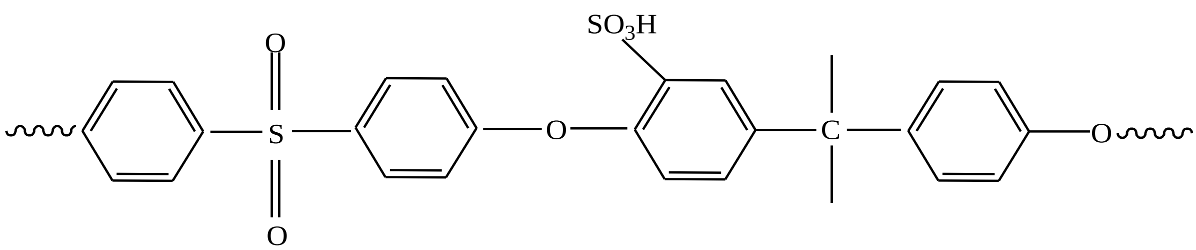
Fig 2: Conduction mechanism through polaron theory

Doping with acidic functionalities reduces the band gap that enhances the conductivity of PPY [39]. Semiconducting components and electrodes for charge storage devices are routinely developed through either of chemical or physical vapor deposition over semiconducting wafers. Alternatively, PPY electrodes are produced through electrode position over metals or by hand laying of a composition of PPY over metallic substrates in presence of graphite, dopants and polymeric binders [12-14].

Common polymeric binders employed for development of WE are polyvinylidene fluoride (PVDF), polytetrafloroethylene (PTFE) and sulphonated polysulphone (SPS) (Fig.3).



(a) PVDF (b) PTFE



(c) SPS

Fig 3: Binders used for electrode fabrication

Table 1: Applications of various REOs based PNCs

Polymer	REO	Applications	Ref.
PEO	La_2O_3	Semiconductor & spe	Kumar *et al*., 2011
PANI	La0.67Sr0.33MnO_3	Sensor	Gupta *et al*.,2010
PANI	Sm_2O_3, La_2O_3	Thermally stable material	Huang, Z *et al* ., 2014
PANI	CeO_2	Thermally stable material	Wang *et al*., 2012
PANI	CeO_2	Semiconductor and supercapacitor	Wang *et al*.,2012
PANI	La-Nd	EMI	Wang *et al*.,2017
PANI	Ce–TiO_2	Sensor	Sampreeth *et al*.,2017
PANI	CeO_2, Dy_2O_3	Thermally stable material	Zhang *et al*., 2015
PANI	Sm_2O_3, La_2O_3	Thermally stable material	Huang *et al*., 2014
PANI	Terbium(iii)	LED	Rafiqi *et al*.,2015
PANI	WO_3	Sensing	Parvatikar *et al*.,2006
PANI	Tb_3, Nd_3, Ce_3	Semiconductor	Chai *et al*., 1997
PANI	Nd_2O_3:Al_2O_3	Dielectric constant	Ansari *et al*., 2016
PCz		Semiconductor	Hoshino *et al*.,2010
PIN	TiO_2	Semiconductor	Unal *et al*., 2014
PIN	Y_2O_3	Dielectric constant	Maji *et al*., 2017
PPY	CeO_2	Semiconductor	Galemback eta l.,1997
PPY	CeO_2	Sensor	Karimi *et al*., 2018
PPY	Nb_2O_5	Semiconductor	Seemaa *et al*.,2014
PPY	Y_2O_3	Semiconductor	Cheng *et al*.,2006
PPY	Sm_2O_3	Supercapacitor	Liu *et al*.,2012
PPY	Y_2O_3	Batteries, sensors and actuators	Vishnuvardhan *et al*.,2006
PPY	La^{3+},Sm^{3+}, Tb^{3+}, Eu^{3+}	Supercapacitor	Sun *et al*., 2013
PPY	RuO_2	Supercapacitor	Xang *et al*., 2008
PPY	Eu_2O_3	Supercapacitor	Thakur *et al*., 2017
PPY	Y_2O_3	Dielectric constant	Vishnuvardhan *et al*., 2006
PVA	Ho^{3+}, Gd^{3+}	Optical display	Reddy *et al*.,2015
PVC/PPY		Dielectric	Mohanapriya *et al*., 2016
PVDF	La_2O_3	Thermally stable material	Song *et al*., *2010*

Conclusion

Now a days, great advances of rare earth oxides have been achieved in electrochemical and conductors by modifying surface of working electrode. This review, addresses the important examples of rare earth metals and conducting polymers with their synthesis, characterization and application. An improved thermal and cyclic stability, with low internal resistance of the composites was observed with application as dielectric, semiconductor and energy storage devices.

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