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Simultaneous use of dopant combination during synthesis of polyaniline: an approach towards synergistic improvement in different properties

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Abstract:

Polyaniline (PAni) is one of the most widely explored intrinsically conducting polymers which is conducting in nature in its partially doped form. The present investigation reveals the synergistic effect of simultaneous use of dopant combinations during synthesis of PAni on its different properties. Individually and dual doped PAni were synthesized via electrochemical and solid state route. Electrochemical synthesis was carried out in polar protic (aqueous) as well as aprotic (dimethyl formamide) solvent using sulfuric acid (H_2SO_4) and *p*-tuluenesulfonic acid (PTSA) as dopants. Solvent-free solid state synthesis of PAni involved the dopants citric acid monohydrate (CA) and camphorsulfonic acid (CSA). For all cases total dopant concentration was maintained at 1M and relative proportion of the dopant concentrations was varied at 1:3, 2:2 and 3:1. Simultaneously dual doped PAni exhibited synergistic improvement in electrical conductivity for all cases. Dopant ratios of [H_2SO_4]:[PTSA]=3:1 and [CA]:[CSA]=3:1 resulted in highest extent of synergy for respective synthesis processes. Dopant combination of H_2SO_4 and PTSA in protic and aprotic polar medium of synthesis exhibited maximum improvement of conductivity by 1.5 and 2.6 fold increase. However, the combination of CA and CSA in solid state synthesis exhibited a maximum of 8 fold increase of conductivity compared to individually doped samples which is even higher in comparison with 4% (w/w) addition of multiwalled carbon nanotube in CA doped PAni. Synergistic improvement was also observed for different dual doped PAni in supercapacitive behaviour as well as thermal degradation characteristics within certain range of temperature.

Experimental:

PTSA : *p*-toluenesulfonic acid
CA : Citric acid
CSA : Camphorsulfonic acid

Aniline + H_2SO_4 ⟶ Aniline sulphate (AS)

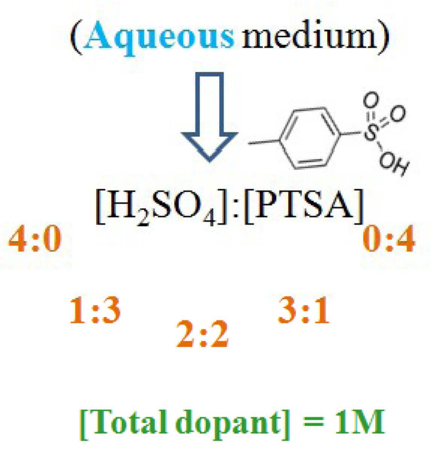
Electrochemical synthesis

Amount of reagents	Applied current	Reaction conditions
Water 100 ml Aniline sulphate Dopant	50 mA	Cu (-), C (+) 1 hr Cu (+), C (-) 30 min Total 1 or 3 cycles

Graphite plate (Working electrode) | Copper plate (Counter electrode)

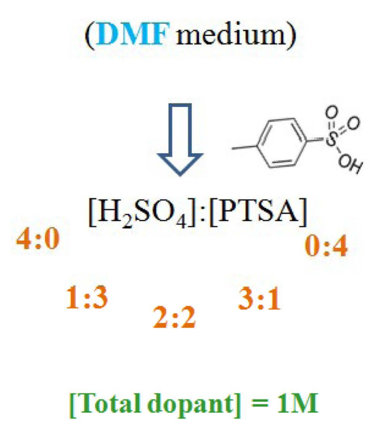
Solid-state synthesis AS + Oxidant + Dopant ⟶ Mixed together in mortar-pestle

Electrochemical synthesis in aprotic polar medium



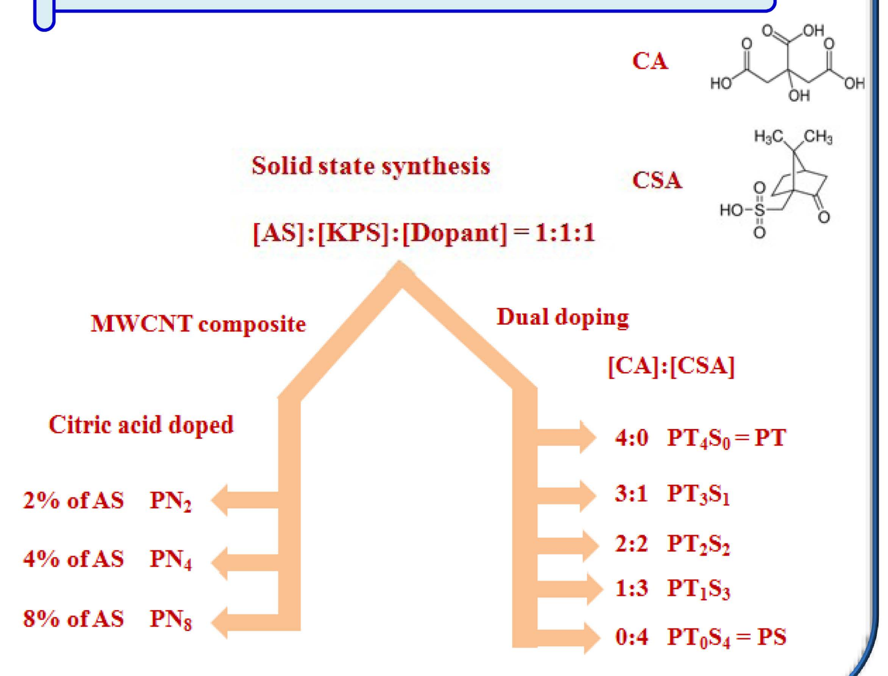
Sample code	Composition	
	Conc^n. of H_2SO_4 (M)	Conc^n. of PTSA (M)
P_0	0	0
P_{40}	1	0
P_{31}	0.75	0.25
P_{22}	0.5	0.5
P_{13}	0.25	0.75
P_{04}	0	1

Electrochemical synthesis in protic polar medium



Sample Code	Composition	
	Conc^n. of H_2SO_4 (M)	Conc^n. of PTSA (M)
PS_0T_4	0	1
PS_4T_0	1	0
PS_3T_1	0.75	0.25
PS_2T_2	0.5	0.5
PS_1T_3	0.25	0.75

Solid state synthesis (solvent-free route)



Results and discussion:

Electrochemical synthesis in aprotic polar medium

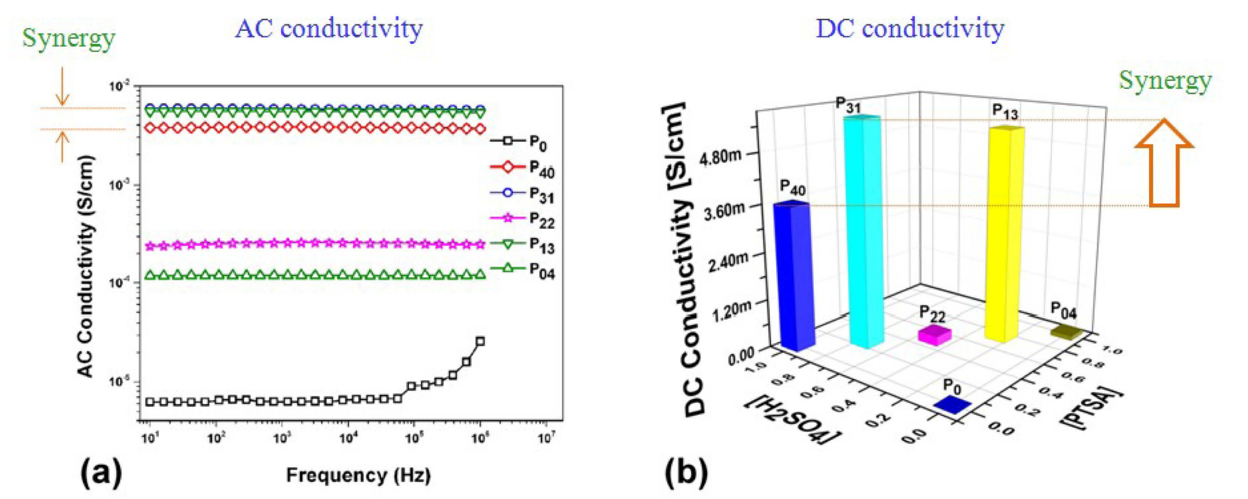


Fig. 1. Synergistic improvement in (a) AC and (b) DC conductivity for dual doped PAni compared to individually doped PAni.

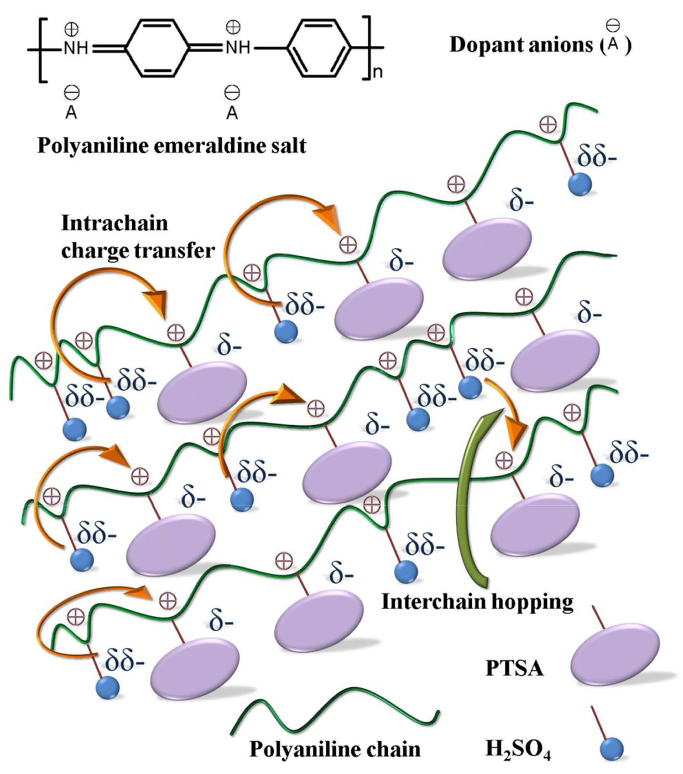


Fig. 2. Mechanism of synergistic effect of simultaneously dual doped PAni owing to improvement in inter- and intra-chain hopping, which is facilitated by the difference of the charge densities along the polymer chain.

Electrochemical synthesis in protic polar medium

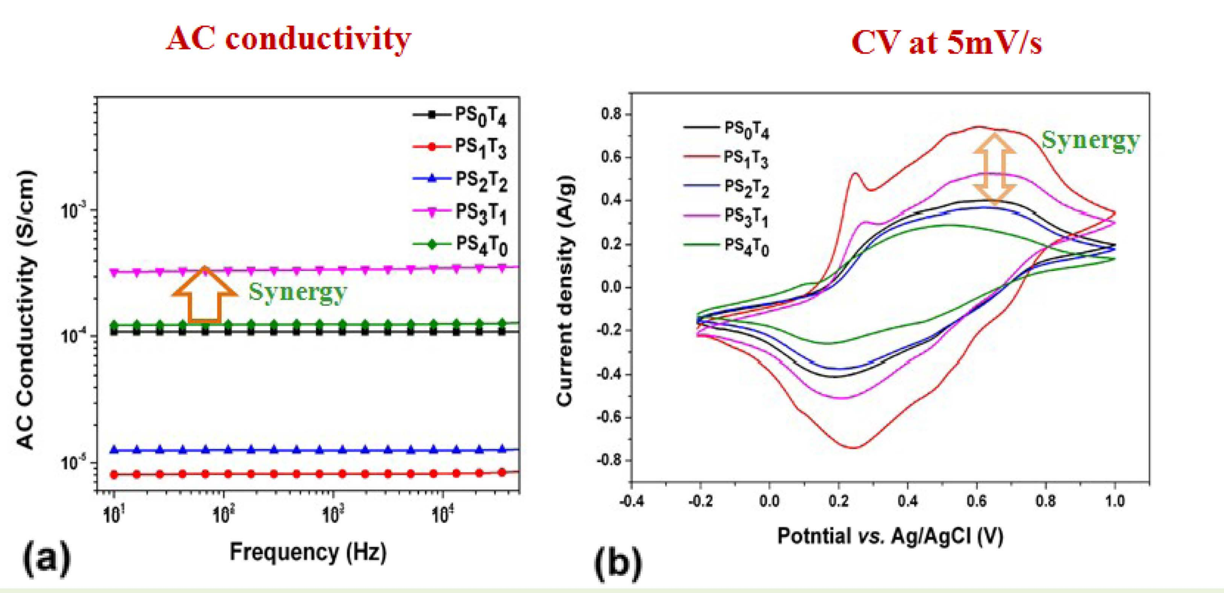


Fig.3. Synergistic improvement in (a) AC conductivity and (b) electrochemical capacitive behaviour. Increase of enclosed area under cyclic voltammogram indicates improvement of gravimetric capacitance.

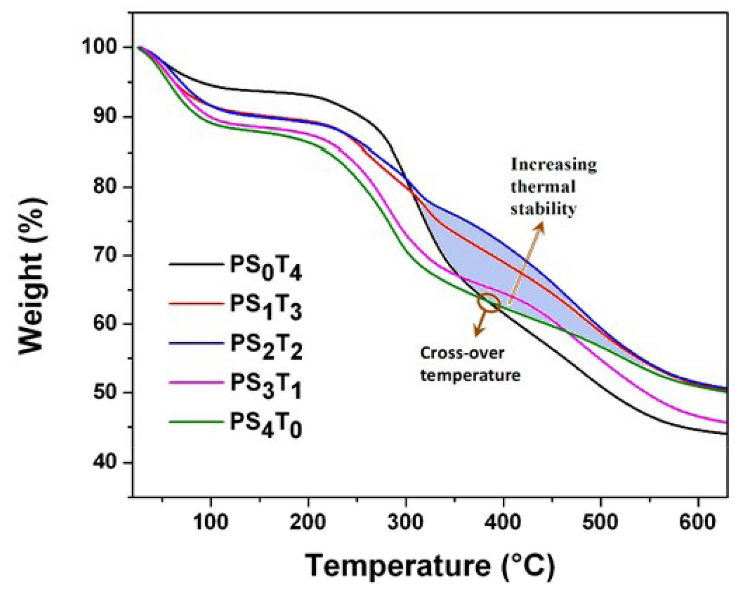


Fig. 4. Improvement of thermal degradation behaviour of dual doped PAni within certain range of temperature. Heat dissipation in the course of rearrangement of dopants improve degradation behaviour of PAni.

Solid state synthesis (solvent-free route)

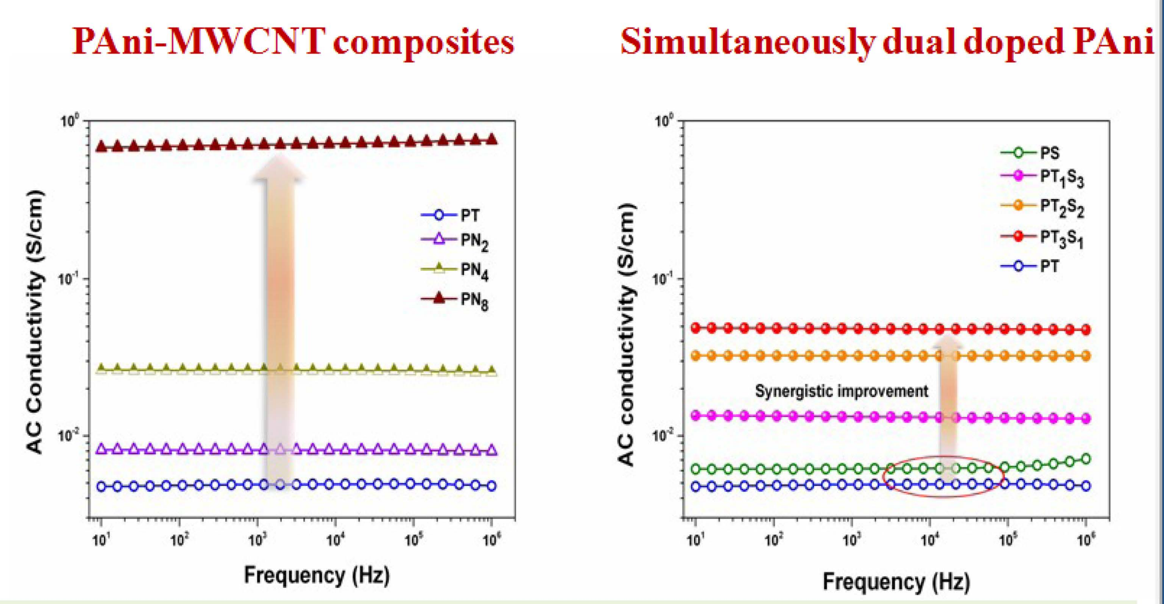


Fig. 5. Synergistic improvement in AC conductivity of dual doped PAni in comparison with PAni-MWCNT composites.

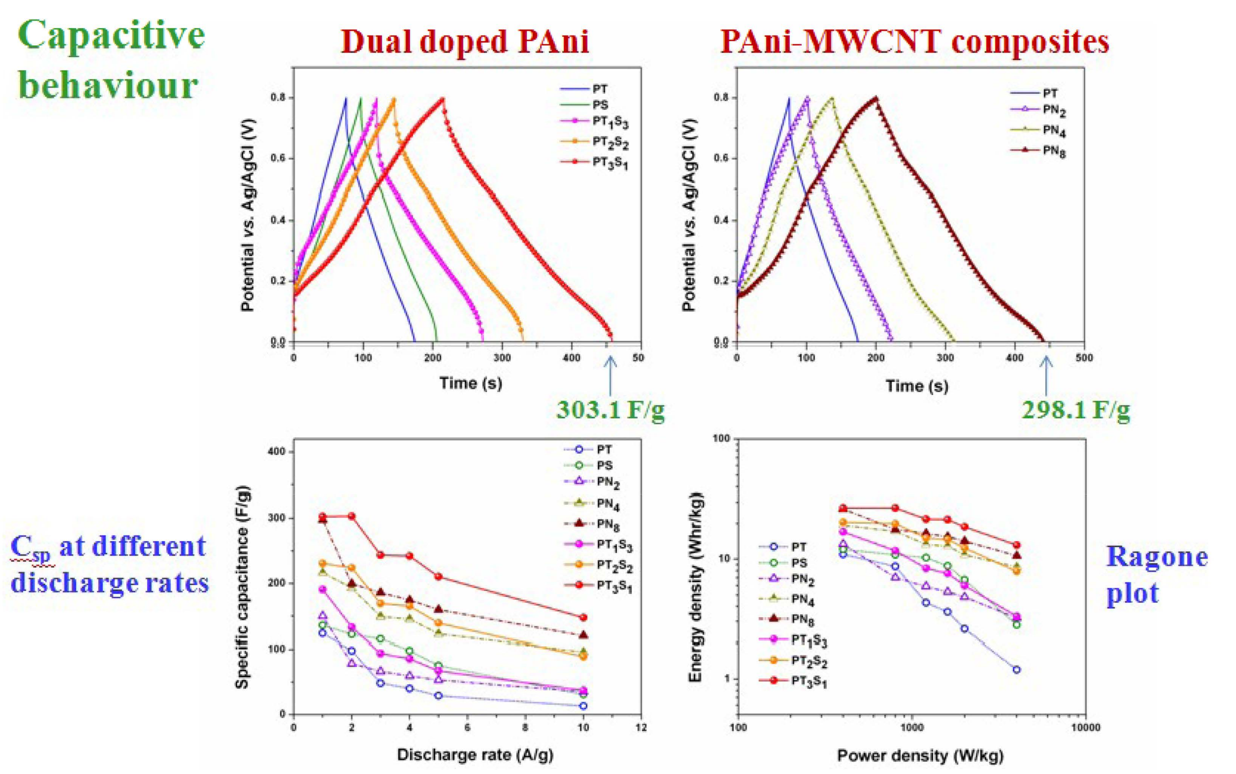


Fig.6. Galvanostatic charge-discharge study to compare capacitive performances of dual doped PAni with PAni-MWCNT composites.

Conclusions:

- Synergistic improvement in conductivity is observed for dual doped PAni in comparison with individually doped PAni.
- Synergistic effect is observed for electropolymerization in presence of polar protic or aprotic medium as well as for solvent-free solid state synthesis.
- Synergistic improvement of thermal degradation behaviour is observed within certain range of temperature.
- Synergistic improvement of electrochemical capacitance may be equivalent to 8% (w/w) addition of MWCNT.
- Synergistic improvement of AC conductivity has been achieved at the level equivalent to 4% (w/w) addition of MWCNT.

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