CHAPTER VII
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7.1 Summary

7.1.1 CS-SnO$_2$-PANI hybrid composite

This chapter deals with a brief account of conclusions derived from analysis and interpretation of the experimental results of PANI, SnO$_2$, CS-SnO$_2$, CS-PANI and CS-SnO$_2$-PANI hybrid composite prepared by chemical precipitation and a chemical oxidative polymerization method. The structural, morphological and thermal features of all the composites are analyzed using FT-IR, XRD, UV-Vis, IIR-SEM, EDAX, TEM, BET and TG-DTA analysis.

The chemical bonding interactions of CS-SnO$_2$, CS-PANI and CS-SnO$_2$-PANI were established and confirmed by FT-IR spectroscopy. It reveals that amine and imine (N-H and N=) group nitrogen atom bonding with Sn$^{4+}$ either by protonation (or) coordination complexation. The results also indicated the interfacial interaction between chitosan, the inorganic counterpart of SnO$_2$ particles and PANI matrix.

XRD pattern imply that crystalline nature of CS-SnO$_2$ particles was successfully incorporated into the PANI matrix. The UV-Vis spectra of CS-SnO$_2$-PANI are found to red/blue shifted as compared to those of PANI and CS-PANI. The chitosan is an important biosurfactant material which alters the surface morphology of PANI and SnO$_2$ particles. The surface morphology of CS-SnO$_2$ composite has sphere-like particles covered on the biopolymer matrix. The CS-PANI composite shows a twist fibrous like structure and CS-SnO$_2$-PANI hybrid composite are observed as small bright particles of
CS-SnO$_2$ attached to the entangled structure of PANI which is in agglomerated form. The EDAX spectrum showed CS, SnO$_2$ and PANI hybrid composites are presented as per the elemental compositions.

The BET isotherm result indicates that the introduction of CS-SnO$_2$ on PANI matrix could obviously increase the surface area. TG-DTA analysis showed that residual weight and their weight derivatives of CS-SnO$_2$-PANI shows higher stability than CS-PANI and PANI. Overall, it is observed that introduction of SnO$_2$ particles on CS-PANI matrix has enhanced the thermal stability.

The photocatalytic performance of CS-SnO$_2$-PANI hybrid composite on cationic (MB) and anionic (RY) dyes were evaluated under the direct sunlight irradiation. The obtained result indicates that a CS-SnO$_2$-PANI composite has enhanced photocatalytic degradation efficiency than CS-SnO$_2$ and CS-PANI composite. 0.5 g/L of CS-SnO$_2$-PANI degrades 94.6 and 93.8 % of 10 mg/L concentration of MB and RY dye solutions respectively for about 210 min direct sunlight exposure at pH=6.5. Based on the results, it may be conclude that CS-SnO$_2$-PANI hybrid composite can be used as a promising biophotocatalyst material for degradation of textile effluent that contains the mixture of dyes.

Electrochemical properties of synthesized materials are studied by cyclic voltammetry, charge–discharge measurements and electrochemical impedance spectroscopy. Electrochemical measurements show that the mesoporous structure of CS-SnO$_2$-PANI electrode yields larger specific capacitance (383.15 Fg$^{-1}$) than CS-PANI electrode and the capacitance retention was 72% after 1000 charge/discharge cycles at
0.5 Ag\textsuperscript{-1} current density in the voltage range of 0 to 0.8 V. The results indicated that the CS-SnO\textsubscript{2}-PANI electrode has enhanced specific capacitance and cycling stability, which is due to the synergistic effect of three components. Thus, the resulting composite electrodes are promising materials for high-performance, environmentally friendly and low-cost electrical energy-storage device applications.

### 7.1.2 G-SnO\textsubscript{2}-PANI hybrid composite

The graphene, PANI, G-SnO\textsubscript{2}, G-PANI and G-SnO\textsubscript{2}-PANI hybrid composite are prepared by chemical precipitation and chemical oxidative polymerization methods. The structural, morphological and thermal features of all composites are analyzed using FT-IR, XRD, UV-Vis, HR-SEM, EDAX, TEM, BET and TG-DTA analysis.

The chemical bonding established in G-SnO\textsubscript{2}, G-PANI and G-SnO\textsubscript{2}-PANI are confirmed by FT-IR analysis. XRD patterns imply that the crystalline natures of G-SnO\textsubscript{2} particles were successfully incorporated into the PANI matrix. The UV-Vis spectrum of G-SnO\textsubscript{2}-PANI is found to red/blue shifted when compared to PANI and G-PANI.

The graphene is an important template material to alter the surface morphology of PANI and SnO\textsubscript{2} nanoparticles. The surface morphology of G-SnO\textsubscript{2} composite is observed as sphere-like particles covered with the graphene layer. The G-PANI composite shows a layer of fibrous like structure and G-SnO\textsubscript{2}-PANI hybrid composite are observed as small bright particles of G-SnO\textsubscript{2} attached to the layer-like structure in agglomerated form. The EDAX analysis showed a graphene, SnO\textsubscript{2} and PANI hybrid composites are present according to their elemental compositions.
The BET isotherm results indicate that introduction of G-SnO$_2$ and PANI matrix could obviously increase the surface area. Thermal property studied by TG-DTA analysis shows that the residual weight (TGA curves) and its weight derivative (DTA curves) of the G-SnO$_2$-PANI are more stable than G-PANI and PANI. Overall, the results show that the introduction of G-SnO$_2$ particles on PANI matrix enhanced the thermal stability.

The photocatalytic performance of G-SnO$_2$-PANI hybrid composite is evaluated by photodegradation of cationic (MB) and anionic (RY) dyes under direct sunlight irradiation. The obtained result indicates that G-SnO$_2$-PANI composite has enhanced the photocatalytic degradation efficiency than G-SnO$_2$ and G-PANI composites. With 0.5 g/L of G-SnO$_2$-PANI, the MB and RY dye solutions having 10 mg/L concentration can be degraded to 98.6 and 90.1% of its original dye concentration in 210 min direct sunlight exposure at pH=6.5. Based on the results, it may conclude that G-SnO$_2$-PANI hybrid composite can be used as a promising bio-photocatalytic material for degradation of textile effluent that contains the mixture of dyes.

Electrochemical properties of synthesized materials are studied by cyclic voltammetry, charge–discharge measurements and electrochemical impedance spectroscopy. Electrochemical measurements shows that the mesoporous structure of G-SnO$_2$-PANI electrode yields larger specific capacitance (539.06 Fg$^{-1}$) than the corresponding G-PANI electrode and the capacitance retention of 78% obtained after 1000 charge/discharge cycles at 0.5 Ag$^{-1}$ current density in the voltage range of 0 to 0.8 V. The results indicated that the G-SnO$_2$-PANI electrode has enhanced specific capacitance and cycling stability, due to the synergistic effect of three components. Thus,
the resulting composite electrodes are promising materials for high-performance, environmentally friendly and low-cost electrical energy-storage device applications.

7.1.3 CS-SnZnO hybrid composite

The SnO$_2$, ZnO, CS-SnO$_2$ and CS-SnZnO hybrid composites are prepared by chemical precipitation method. The structural, morphological and thermal features of all composites were analyzed using FT-IR, XRD, UV-Vis, HR-SEM, EDAX, TEM, BET and TG-DTA analysis.

The chemical bonding established between CS-SnO$_2$ and CS-SnZnO are confirmed by FT-IR analysis. XRD patterns imply that the crystalline nature of ZnO particles was successfully incorporated into the chitosan-SnO$_2$ matrix. The UV-Vis spectra of CS-SnZnO were found to red/blue shifted as compared to those ZnO and CS-SnO$_2$ molecular chains. The chitosan is an important biosurfactant material to alter the surface morphology of ZnO and SnO$_2$ particles. The CS-SnO$_2$ composite is sphere like particles covered on the biopolymer matrix. The morphology structure of CS-SnZnO hybrid composite is sphere particles of CS-SnO$_2$ attached to the hexagonal structure of ZnO and the whole structure in agglomerated form. The EDAX analysis showed CS, SnO$_2$ and ZnO hybrid composites were presented in the elemental compositions.

The BET isotherm results indicate that introduction of ZnO on CS-SnO$_2$ could obviously increase surface area. Thermal property studied by TG-DTA analysis showed that the residual weight (TGA curves) and their weight derivatives (DTA curves) of CS-SnZnO are higher stability than CS-SnO$_2$. Overall, the results show that the introduction of CS-SnO$_2$ particles on ZnO has enhanced the thermal stability.
The photocatalytic performance of CS-SnZnO hybrid composite is evaluated by photodegradation of cationic (MB) and anionic (RY) dyes under direct sunlight irradiation. The result indicates that a CS-SnZnO composite has enhanced the photocatalytic degradation efficiency than CS-SnO₂ composite. The CS-SnZnO photocatalyst (0.5 g/L) degrades 98.9 and 91.4% for MB and RY dyes respectively. Based on the results, it may conclude that CS-SnZnO hybrid composite can be used as a promising bio-photocatalyst material for degradation of textile effluent that contains the mixture of dyes.

7.2 Conclusions

The following conclusions are made from the foregoing discussion.

- The functional group interactions of CS-SnO₂-PANI, G-SnO₂-PANI and CS-SnZnO hybrid composites are confirmed by FT-IR analysis.

- The crystalline nature of hybrid composites is studied by X-ray diffraction analysis which confirms the successful incorporation of CS-SnO₂ and G-SnO₂ particles into the protonated amine group of PANI matrix. The crystalline nature of ZnO particles was incorporated onto the chitosan-SnO₂.

- Functional groups of CS-SnO₂-PANI, G-SnO₂-PANI and CS-SnZnO hybrid composites are confirmed by UV-Visible spectroscopy.

- Sphere like the structure of SnO₂ particles homogeneously distributed on the layered biopolymer matrix.
- CS-PANI composite consist of twist fibrous like morphology.

- CS-SnO$_2$ particles intercalated on PANI are in collapsed twist fibrous like structure.

- The sphere-like structure of SnO$_2$ particles homogeneously distributed evenly on the layered structure of graphene.

- Graphene layered structure is covered on the PANI matrix to form a multiple layer stacked state structure.

- G-SnO$_2$ particles intercalated on PANI are in flake like and layer form of structure.

- ZnO particles intercalated on CS-SnO$_2$ are in collapsed form sphere like structure.

- Elemental compositions of CS-SnO$_2$-PANI, G-SnO$_2$-PANI and CS-SnZnO hybrid composites are analyzed by EDAX analysis.

- CS-SnO$_2$ intercalated PANI, G-SnO$_2$ intercalated PANI and ZnO and SnO$_2$ intercalated CS can effectively increase the surface area and mesoporous structure compared to other composites.

- CS-SnO$_2$-PANI hybrid composite has higher thermal stability than CS-PANI and PANI.

- G-SnO$_2$-PANI hybrid composite has higher thermal stability than G-PANI and PANI.
CS-SnZnO hybrid composite has higher thermal stability than CS-SnO₂.

Photocatalytic degradation of dyes:

Order of the photocatalyst in methylene blue dye degradation (%) efficiency is as follows: CS-SnZnO > G-SnO₂-PANI > CS-SnO₂-PANI.

Order of the photocatalyst in reactive yellow dye degradation (%) efficiency is as follows: CS-SnO₂-PANI > CS-SnZnO > G-SnO₂-PANI.

Electrochemical supercapacitor:

The order of specific capacitance and cycle stability of electrodes are as follows:

G-SnO₂-PANI > CS-SnO₂-PANI.