

## Abstract

The massive industrialization has led to significant rise in dyes, phenols, pesticides and other organic pollutant with cancer-causing potential intermediates. Aromatic dyes, released from paper, plastic, food, cosmetics, leather and textile industries comprised of almost half of the total world dye market, can cause hypersensitivity and allergies. Generally, the dyes are classified as cationic, anionic, azo, insoluble dispersive and phthalocyanine dyes. Particularly, these dyes and their intermediates are considered as toxic, highly hazardous and carcinogenic. Moreover, these dyes are stable enough to retain in water and cause serious health deterioration to living organisms. The methods like chemical coagulation, sorption, electrolysis, oxidation, membrane separation and photocatalysis have used to tackle this problem. Among these method photo catalysis is low cost and environment friendly method, it combine catalysis and photochemical transformation of pollutants from toxic organic compound to non-toxic molecule. Metallic oxide nanoparticles have been widely used as photocatalyst for the degradation of organic dyes. From the fundamental point of view, metal oxide nanoparticles was considered as a semiconductor photocatalyst with wide band-gap. Among the various semiconductors, tin oxide ( $\text{SnO}_2$ ) has been considered as an excellent photocatalyst material due to its chemical and biological inertness, cost effectiveness, having strong oxidizing power, and highly resistant against chemical and photo corrosion. The photo catalytic ability is due to the generation of photo excited electron and hole pairs. The organic pollutant adsorbed on the surface of nanoparticles will react with these photo-generated electrons and holes to degrade organic dyes to  $\text{CO}_2$  and water. One of the most significant barrier in photo-catalysis is the charge separation, if there is not enough charge separation the electron-hole pairs will recombine to produce heat instead of dye degradation. Another hindrance is the wide bandgap ( $E_g \sim 3.6 \text{ eV}$ ),

which hampers its photodegradation efficacy and limits its response only to UV light (4% in solar energy as compared to visible light 43% in the solar spectrum). Most of investigation in the past was carried out to tailor the properties (mostly optical and structural) of metallic oxide by doping with transition metal ions. Quaternary metal oxide nanocomposite material was rarely investigated and its application related to degrade organic dyes have never been reported before to the best of our knowledge. So in present work we have successfully synthesized various quaternary metal oxide nanocomposite material using sol-gel, followed by hydrothermal method. Ethylene glycol was used as a directing agent to control surface morphology.

The nanocomposite material we have synthesized in present work consist of gadolinium (lanthanide series) transition metals and tin oxide. The variable in nanocomposite material was transition metal and we choose iron (Fe), cobalt (Co) and manganese (Mn) to prepare three different types of nanocomposite material. The influence of calcination temperature (500, 700, and 900 °C) for a given nanocomposite material have also been investigated. These nanocomposite material was characterized by various techniques like thermogravimetric analysis (TGA), fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), particle size analyzer (PSA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-Visible spectroscopy (UV-VIS). The nanocomposite material was successfully used as a visible light photocatalyst (for degradation of organic dyes), antifungal agent (against *Aspergillus niger*) as well as cathode material for fuel cell application.

In first batch, gadolinium doped tin oxide-iron oxide nanoparticles ( $\text{Gd/Fe}_{1.727}\text{Sn}_{0.205}\text{O}_3$ ) were synthesized. In FTIR spectra prominent peaks at 563, 418

and  $542\text{ cm}^{-1}$  were observed for Fe-O, Sn-O and Gd-O respectively. TGA-DSC curve exhibit that all inorganic metal precursor were physically absorbed. The uncalcined nanoparticles follows first order kinetics and Free-Man Carrol method was applied for calculating the activation energy. It was observed that nanoparticles calcined at  $700\text{ }^{\circ}\text{C}$  have  $8.9\text{ nm}$  particle size which is smallest among all and  $2.3\text{ eV}$  band gap. SEM micrographs shows hexagonal geometry. The dependence of electrical resistance on temperature shows that these nanoparticles possesses semiconducting behavior. These nanoparticles can be used as cathode material for solid oxides fuel cells (SOFCs) application. The nanoparticles calcined at  $700\text{ }^{\circ}\text{C}$  showed highest power density of  $83.27\text{ mWcm}^{-2}$  at  $650\text{ }^{\circ}\text{C}$  with open current voltage of  $0.793\text{ V}$ . The nanocomposite material calcined at  $700\text{ }^{\circ}\text{C}$  shows better photocatalytic activity against methylene blue ( $99.35\%$ ).

In second batch, gadolinium doped  $\text{CoSnO}_3$  nanocomposite was synthesized. FTIR spectra confirmed the presence of metallic oxygen bond. Crystallite size was extracted from XRD patterns using Williamson-Hall analysis. Enhancement in crystallite size was observed on increase in calcination temperature. Particle size determined from PSA also showed increasing trend with calcination temperature. The optical band gap calculated from UV-Visible spectroscopy widens with increase in calcination temperature. The nanocomposite material calcined at  $500\text{ }^{\circ}\text{C}$  shows better photocatalytic activity against methylene blue ( $94.7\%$ ) and methyl orange ( $91.9\%$ ) under sunlight. It was due to small particle size ( $21.3\text{ nm}$ ), large specific surface area ( $97.7\text{ m}^2/\text{g}$ ) and small band gap ( $1.7\text{ eV}$ ) as compared to the nanocomposite calcined at higher temperature.

In third batch, gadolinium doped  $\text{Mn}_2\text{SnO}_4$  nanocomposite were prepared. The FTIR spectra, the prominent peaks at 675, 597 and 542  $\text{cm}^{-1}$  were observed which corresponds to O-Mn-O, Sn-O and Gd-O respectively. The dependence of crystallite size on calcination temperature reveals that it is thermally activated because there is a linear increase in crystallite size with temperature. The optical band gap estimated from UV-Visible spectroscopy shows decreasing trend with increase in calcination temperature. The nanocomposite material calcined at 500 °C shows better photocatalytic activity against methylene blue (74.00 %) and methyl orange (54.96 %) under sunlight. It was due to small particle size (4.04 nm) and large specific surface area (26.48  $\text{m}^2/\text{g}$ ) as compared to the nanocomposite calcined at higher temperature.

Among various quaternary composite nanoparticles synthesized in the present work, Fe based nanocomposite material calcined at 700 °C showed highest photodegradation efficiency ( 99.9 %) against methylene blue under solar irradiation. The possible reasons for this remarkable achievement is large specific surface area and small optical bandgap that lies well in the visible region. Moreover, it shows potential ability to be used as cathode for fuel cell application. The Co based nanocomposite material showed ~ 92% photodegradation efficiency against methyl orange as compared to Mn based nanocomposite material. Manganese based nanocomposite have least photocatalytic activity against methylene blue as well as methyl orange due to wide band gap and least surface area. However, its antifungal activity against *Aspergillus niger* is notable.