Green synthesis of metal oxide nanocomposites and their photocatalytic activity

Abstract of

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Abstract

This thesis deals with the studies based on the synthesis and characterization of metal oxide nanocomposites such as CuO, Ag@AgCl-GO NCs, Mg doped WO_3@g-C_3N_4 and Sm_2O_3@g-C_3N_4@Bi_2O_3 using aqueous extracts of *Solanum nigrum* leaves, Mustard Pod, *Acacia nilotica* bark, *Tagetes erecta* flowers. The engineered nanocomposites were characterized using analytical techniques such as UV-visible spectroscopy, FT-IR spectroscopy, XRD, SEM@EDAX, FE-SEM, TEM, XPS and photocurrent response analyses. The photo-assisted catalytic property of the fabricated metal oxides and nanocomposites analysed against the degradation of toxic nitro compounds and dyes. The mineralization of toxic pollutants was analysed via LC-MS and COD analysis. The synthesized Sm_2O_3@g-C_3N_4@Bi_2O_3 nanocomposite employed in photoelectrochemical water splitting reaction for H_2 and O_2 generation.

The optical and electronic properties of synthesized metal oxide nanocomposites were examined using UV-visible spectra. The presence of phytochemical capping on the surface of synthesized nanocomposites was confirmed via FTIR analysis. The XRD analysis was used to assess the phase purity of the fabricated materials and in crystallite size determination using Debye-Scherrer equation. The shape, size and morphology of the nanomaterials were confirmed using SEM, FESEM and TEM analysis. EDAX and elemental mapping analysis was performed to confirm the elemental composition of fabricated materials. The SAED patterns were examined to understand the crystalline nature and phasic purity of synthesized materials. The chemical states of elements in fabricated metal oxide nanocomposites were confirmed from the XPS analysis. To investigate the light sensitivity of the materials, photocurrent response of the engineered metal oxide nanocomposites was analysed. The mineralization of toxic pollutants was investigated through LC-MS analysis, chemical oxygen demand (COD) measurement. Furthermore, the radical scavenging experiments were performed to assess the reactive radical species involved in photocatalytic processes. The recyclability of the synthesized materials was also assessed. The catalytic as well as photo-assisted catalytic activity of synthesized metal oxide nanocomposites were investigated in the deterioration of Congo red, Malachite green, 2-nitrophenol, Azure B under solar radiation. The reaction parameters like catalyst dose and pH of the medium was also investigated.

In chapter-3, we reported the green synthesis of *Solanum nigrum* extract capped copper oxide nanoparticles (SN@CuO NPs) at room temperature. UV-visible

spectroscopy confirmed the synthesis of SN@CuO NPs in reaction mixture while FTIR results revealed capping of phytochemicals of *Solanum nigrum* over spherical CuO NPs. The data obtained from spectroscopic analyses specified the formation of mesoporous, positively charged and highly stabilized CuO nanospheres due to adsorption of phytochemicals present in *Solanum nigrum* leaf extract on the nanosphere surface. SN@CuO NPs have shown promising catalytic activity towards reduction of highly carcinogenic dye Congo red making use of sodium borohydride. UV-visible, FTIR, ^{1}H NMR, ^{13}C NMR and mass spectrometric studies of the fractions of reaction mixture at different reaction stages have shown that the major degradation intermediates were benzidine and α-naphthol. The apparent rate constants for the products at intermediate and final degradation stages have been found to be 0.468 min^{-1} and 0.0189 min^{-1}, respectively. A plausible degradation mechanism for Congo red reduction has also been proposed in this study.

Chapter-4 represents the sonication assisted synthesis of Ag@AgCl-GO NC using mustard pod extract via sonochemical approach. HRTEM results revealed that the size of Ag@AgCl nanoparticles was reduced after conjugation with GO sheets. The photocatalytic efficacy of as synthesized Ag@AgCl-GO NCs was examined and compared with Ag@AgCl NPs in the visible light assisted degradation of 2-nitrophenol (2-NP), malachite green (MG) and Congo red (CR) under direct solar radiation as a model reaction. Rate of photocatalytic degradation of these pollutants was much higher in the presence of Ag@AgCl-GO NCs than that of bare Ag@AgCl NPs. Effective conjugation of Ag@AgCl NPs with GO sheets has been exemplified by FTIR, Raman, and XPS results. Conjugation of GO with Ag@AgCl NPs increased photogenerated electron-hole separation and facilitated transfer of electrons via delocalization to the graphene sheet, which resulted in increased photocatalytic activity. The major active radical species participating in the photocatalytic degradation of above pollutants are identified as the $^{\bullet}O_2^-$ and h^+. Electrons of the conduction band of AgCl react with O_2 to make superoxide radical $^{\bullet}O_2^-$, which oxidizes 2-NP, MG and CR molecules while the holes directly oxidized organic pollutants.

In the next chapter, we prepared Z-scheme type Mg-doped WO_3 supported onto g-C_3N_4 ternary photocatalyst by sonochemical intercalating Mg into WO_3@g-C_3N_4 binary composite in the *Acacia nilotica* bark extract medium. X-ray diffraction, SEM,

EDS, HR-TEM, photoluminescence and BET surface area analysis were used to explore the structural, morphological and surface characteristics. The findings indicated that the formation of highly crystalline with aggregated lump-based flakiness and various nano-sized crystals in stacked layers with smooth assemblies were taken place. The photoluminescence spectra illustrated that the annihilation of the plasmonic excitons was sufficiently suppressed in ternary composite. Under solar light irradiation, the designed Mg doped WO_3@g-C_3N_4 ternary nanocomposite shown better photocatalytic activity for Malachite green (MG) degradation than undoped g-C_3N_4 and WO_3@g-C_3N_4 binary composite. It was also investigated how physical parameters like pH, and catalyst dose affected the photo-degradation of MG as well as examined the recyclability up to 4 cycles. The radical scavenging studies suggested that the primary species responsible for the breakdown of MG by the Mg doped WO_3@g-C_3N_4 ternary nanophotocatalyst materials is the $^{\bullet}O_2^-$ radicals. Photodegradation of MG followed pseudo-first order kinetics with highest rate constant 0.090 min^{-1} using ternary composite. The superior visible radiation absorption, enhanced surface area, improved separation efficacy of excited e^--h^+ couples, and the photo-generated electron movement from g-C_3N_4 to WO_3 bands via Mg can all be contributed to the ternary WO_3@g-C_3N_4 nanocomposite's excellent photocatalytic performance as well as recyclability.

In chapter-6, we presented the synthesis of dual Z-scheme Sm_2O_3@g-C_3N_4@Bi_2O_3 ternary hybrid via co-calcination strategy. The created Sm_2O_3@g-C_3N_4@Bi_2O_3 hybrid displayed superior photocatalytic efficiency for Azure B (AzB) dye deterioration against visible light irradiation than pure g-C_3N_4, Sm_2O_3@g-C_3N_4 and Sm_2O_3@g-C_3N_4@Bi_2O_3 ternary hybrids. It is possible to attribute the better visible light absorption, higher surface area and improved separation efficiency of photo-generated electron-hole pairs to the increased photocatalytic activity of the Sm_2O_3@g-C_3N_4@Bi_2O_3 composite. The photodegradaton of AzB follow pseudo-first order degradation kinetics and the apparent rate constants are 0.0014, 0.0026 and 0.0316 min^{-1} for g-C_3N_4, Sm_2O_3@g-C_3N_4 and Sm_2O_3@g-C_3N_4@Bi_2O_3 ternary composite. The charges transfer of the Sm_2O_3@g-C_3N_4@Bi_2O_3 composite was shown to follow a direct solid-state dual Z-scheme rather than heterojunction by the mechanism analysis. The fabricated ternary hybrid shown efficient photoelectrochemical water splitting reaction for H_2 and O_2 generation.

In the last chapter-7 represents the brief summary of the research work performed and scope of further research work.

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