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Chemical Catalytic Applications of Nanocomposites in Photo Reactors: Review

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ABSTRACT
Nanocomposites as a photocatalysts are chosen for the photocatalytic degradation of organic pollutant molecules. Noble metal decorated mixed metal oxides composite and reduced graphene oxide deposited metal oxide nanocomposites are of cost-effective photocatalysts. Nanocomposites are act as better photocatalysts due to their tunable surface characteristics as acidic and basic properties, advanced oxidation or reduction abilities makes them unique approach for heterogeneous photocatalysts. Development of cheaper semiconductor photocatalysts, which are highly effective and reusable photocatalytic applications of nanocomposites under visible light, is very challenging materials. We prepared cost-effective ternary mixed metal oxide nanocomposites chemical catalysts with rGO with heterojunctions of rGO-ZnO-TiO_2-Nb_2O_5 labelled as rGZTNb for efficient photo catalysis in photo reactor under visible light radiations for chemical catalysis. Author described about eh development effect of heterogeneous photocatalysts. Heterogeneous visible light photocatalysts of semiconductor mediated materials at the nanometer scale have paid much attention towards the past decade due to their beneficial strategies in the photocatalytic usage. ZnO and TiO_2 along with Nb_2O_5 nanocomposite combinations as solid powders can significantly enhance light absorption, then separation pairs of electron-hole by photogeneraton.

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Introduction
Mixed Metal oxides are highly crystalline for their enhanced catalytic efficacy [1, 2]. The combination of 2 or more metal oxide powders have tunable surface properties of the materials are opt for specific applications [3,4]. Hence, mixed metal oxide catalysts act as a photocalysts and their nanocomposites offers wide range of advantages including synthesis methods, nature of materials and their green applications [5, 6]. The selected nanocomposites are of high importance because of surface acidic and basic properties after modifications [7, 8].

Nanocomposite is combination of matrix, in which different materials combine to develop new properties of the nanomaterials ensuring that one of the materials have size range in 1-100 nm [9, 10].

Bi or tri-metallic mixed metal oxide nanocomposites as a photocatalysts are ideal nanomaterials in material science. In particular, silver (Ag^0) decorated zinc oxide (ZnO) along with cobalt oxide (CoO) and titania, TiO_2 (Ag-decorated Zn-Co/TiO_2, AZCT, K M Reddy et al., and reduced graphene oxide (rGO) deposited zinc oxide (ZnO) along with titania (TiO_2) and niobium pentoxide, Nb_2O_5 (rGO deposited Zn-Ti/Nb_2O_5, rGZTNb, ongoing work of K M Reddy et al., are of author anticipated in the present review [11,12].

Why Author Focused on the Titanium and Niobium Oxides as Better Photocatalysis?
Among several photocatalysts which are known to work, nano-sized TiO_2 is used mostly. TiO_2 is one of the most intensively studied catalysts in photocatalysis owing to its chemical and photo stability, nontoxicity and photosensitivity. A large number of studies have been reported using TiO_2 as a catalyst for water splitting and for removing the organic contaminants in waste water of textile industry. Similar to TiO_2 another nano-sized oxide that has been used for the purpose is Nb_2O_5. Recently Nb_2O_5 has become a promising alternative to replace the commercial TiO_2. The application of Nb_2O_5 as catalyst for the photo degradation of dyes in the textile industry is reported in the literature. However, the band gaps of these materials (TiO_2 and Nb_2O_5) are very high (> 3.2 eV), which allows the use of only UV light to activate in photo catalysis.

In the field of photocatalysis and materials research using various nanocomposites of energy and environmental applications [13-20]. As reported in traditional methods use of titania based photo electrode, lot of benefits in exploiting new semiconductor materials and its mixed derivatives, modifications includes oxide of various transition and rare earth metals sulfides oxy-nitrides sulfides semiconductors with no metals, surface plasmon resonance (SPR) materials metal oxides and Cl, F, N, C, like elemental photocatalysis have been reported for energy and environmental applications [13-64].

Nanocomposites are made by loading the rGO over the TiO_2-ZnO in Nb_2O_5 in a new method like making of semiconductor metal oxide by sol-gel method and in autoclave microwave technique followed by sonication with rGO to get rZTNb, the composition of the nanocomposite is to combine in a such way that the two transition metal oxides combine with the rare earth metals to form a stable nanocomposites (112-128).

Recent research on visible light photo catalysis is favourable, under visible light can induce a positive thermal effect and ternary composite photocatalysts have been emerged on the successive charge transfer occurs between three different components, such as ZnO-MoS2-rGO TiO_2-MnO_2-Pt and g-C3N4/Red P/MoS_2. These newly fabricated ternary composites and nanocomposites will act as photocatalysts and enhances the photocatalytic activity and stability as well [65-70].

Author presented in his previous work, novel nanocomposites, as they have been regarded as promising for decreasing bulk recombination in semiconductors [12, 71-76]. Photocatalytic degradation visible light multiphase crystal structure has paid much attractive results owing to success for the preparation of nanocomposites with ternary composite having various crystal phases [72-84]. The homojunctions may enhance the photocatalytic degradation performance of the pristine sulphite photocatalysts through a better separation efficiency of photogenerated electron-hole pairs without any further treatments [19-20, 31, 75-76].

In the authors previous studies Ag decorated nanocomposites or ternary composites could efficiently enhance the visible light photocatalysis of semiconductor catalysts in photoreactors [12, 85-86].

In the present review author described the enhanced chemical catalytic performance of rGZTNb and other nanocomposites of ternary composites, which attributes synergistic between homojunctions and heterojunctions with noble metal Ag and rGO as surface deposits over nanocomposites. rGZTNb is a promising nanocomposite for chemical catalysts in a photoreactors under visible light photocatalysis systems. In this present study is a innovative strategy for making heterojunction or homojunction novel nanocomposties for effective photocatalytic activity in a photo reactors. The heterojunctions may enhance the effective photoactivity of the use nanocomposites in this review are highly effective on acidic and anionic dye and cationic and basic dyes as well at optimal pH values at 5 [27-28,35, 38-41, 80-91].

Nanocomposites as a Photocatalysts

In our previous work, we synthesised with new modified photocatalyst The deposition of nanosized silver particles on the DP25 surface increases the photocatalytic activity of the semiconductor oxide, by increasing the efficiency of charge separation of the photogenerated electron-hole pairs. The presence of silver mainly enhances the photocatalytic oxidation of organic compounds that are predominately oxidized by holes. [92].

In our previous work, we mainly focus on the synthesis and characterization of two versatile metal nanocomposites AZCT and rGZTNb. These nanocomposites shows better action on the photocatalysis of MO dye solution under visible light source [12]. Figure 1 presented in our previous work, sharp and strong XRD lines are indicates the high crystallinity and high pure of nanocrystalline samples. The crystallite size can be calculated with Scherrer equation with the peak at 30.419°, combination of Zn-Co-TiO_2 along with Ag particles over the crystallite structure and when matrix formed the crystallization (Figure 1) deviated from the growth rate and slight variation in the observed angle is observed. similar work was carried for rGZTNb also and the same as shown in the Figure 2.

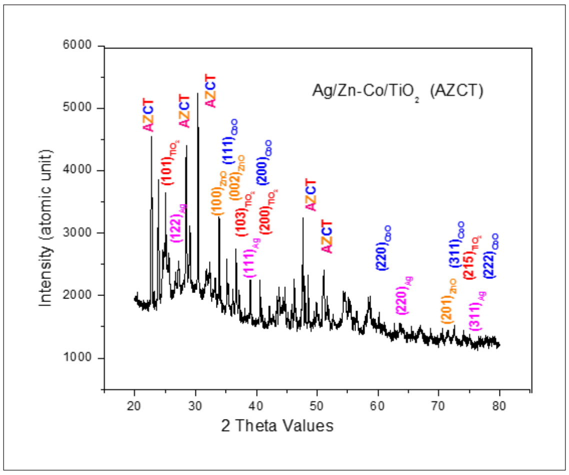

Figure 1: PXRD Pattern of AZCT Nanocomposite

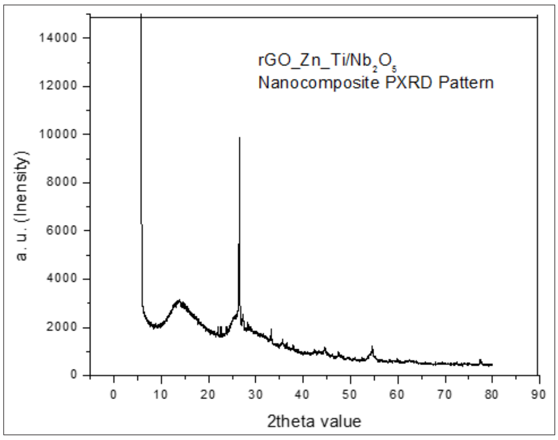

Figure 2: PXRD Pattern of rGZTNb Nanocomposite

In the present review, presented the new novel nanocomposite material with mixed phase which was tested for photocatalytic properties in the the environmental applications and as for the energy storage material. As prepared nanocomposite is show better results under visible light may be due to its unique photocatalytic properties [12].

In our previous work we also demonstrated the nano bio-composite with Ag nano clusters (AgNCs), We have successfully demonstrated a facile method of controlled synthesis of silver nanoclusters ligated with bio compatible glutathione for visible light photocatalytic and biosensing applications point of view. We have also reported control over experimental parameters to modulate the size and morphology of AgNCs [95].

Along with AgNCs we also proved our research work in nanocomposites we have demonstrated a facile low temperature synthesis of Ag-TiO_2 hybrid nanoclusters stabilized by a biocompatible ligand glutathione. Visible light induced photocatalytic activities of silver nanoclusters are found to be negligibly small, whereas functionalization of silver nanoclusters with TiO_2 NCs enhances the catalytic efficiency by an order of magnitude. [95].

Another nanocomposite we developed novel methodologies to prepare colloidal nanocomposite by anchoring ultra-small silver nanocluster with TiO_2/Nb_2O_5. Two synthetic strategies were employed to prepare hybrid nanocomposites with varying compositions and especially the niobium content [96].

Mechanism of Nanocomposites

From the authors previous articles visible light photocatalysis, mechanism over the anocomposites like AZCT, rGZTNb are presented as best photocatalysts. Under the visible light irradiations these type of nanocomposites are highly active, as electrons excited fastly from the valence band to the conduction band and further react with acidic hydrogen ions. When compared with AZCT with rGZTNb, the low-shift and up-shift of both conduction and valence band energy level in the AZCT and rGZTNb nanocomposites results as an efficient separation of both surface and mass recombination of photogenreated electron hole pairs. The intimate contact at the atomic level for the heterojunctions between two different nanocomposites with multiphase promote the separation and transfer of photogenerted charge carriers. Owing to the energy level difference of the AZCT and rGZTNb nanocomposites which having higher oxidation capacity can rapidly remove the pollutants in aqueous solutions. Thereby increase the photocatalytic activity and exhibit the excellent synergistic effects of the heterojunctions of different multiphase semiconductor metal oxide nanocomposite materials. Figure 1 illustrates about the two different nanocomposites under visible light source [97-129].

Quantum Efficiency

Figure 2 represents the quanturm efficiency (QE), is a measure under photocatalytic reactor, where nanocomposites are act as photocatalysts in the photocatalytic degradation studies was dispersed uniformly in the vessel of the photocatalytic reactor. The reaction mixture was mixed with constant stirring under visible light. The quantum efficiency was measured using 500 W halogen lamp and a 360 nm band pass filter. The results were calculated from the equation shown below:

$$QE\ (\%) = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} * 100\% = \frac{\text{Number of hydrogen molecules}}{\text{Number of incident photons}} * 100\% = (M * N_A * 2)/((I * A * t)/(E_g * J)),$$

Where, M is the quantity of dye degraded or converted to H_2O, I is intensity of visible light, NA is the Avogadro number, A is the area of incident light, t is the time, Eg and J are constants. The QE data is presented in the Table 1.

Figure 3, describes about the photogenerated electrons from the both TiO_2 and ZnO present in the rGZTNb nanocomposite with the deposits of rGO, is a typical mechanism illustrates about the electron-hole generation and separation of valence and conduction band. These two metal oxides (TiO_2, ZnO) will be transformed to the rGO over Nb2O5 because of its high photocatalytic activity, the photogenatrated charge carriers further increases. As the oxidation capacity can rapidly degrades the MO molecules by the AZCT and rGZTNb individually and mixed nanocomposites. Thereby further increases the photocatalytic activity of these nanocomposites as the nanocomposites are the evidence for the beautiful synergistic property of the heterojunctions of the rGO deposits can enhances the separation efficiency of the photogenerated electron-hole pairs and increases the activity in the visible region. Proposed nanocomposites property of charge transfer mechanism is depicted in the Figure 3 shown in the rGZTNb nanocomposite photocatalyst under visible light exposure.

Table 1: Different Photocatalysts Data Table

Photocatalyst	Modifier /deposits	Main matrix	Calcination temperature	Particle size (nm)	Characterizations	References
$Ag\text{-}TiO_2$	$AgNO_3$	Titanium (IV) iso propoxide	550 °C	13-20	XRF, XRD, EDX, TEM, XPS	[93]
AZCT	$AgNO_3$	Zinc acetate, Cobalt nitrate and TiO_2 prepared by sol-gel method	400 °C	7-10	XRD, FT-IR, UV-Vis	[12]
rGZTNb	Graphene	Zinc Acetate, TiO_2 and Nb_2O_5	500 °C	15-20	XRD, FT-IR, SEM	[12]
AgNCs	Bioligands	$AgNO_3$	120 °C	5-6	XRD, FT-IR, UV-Vis, SEM, TEM, EDAX, ESI-mass	[94]

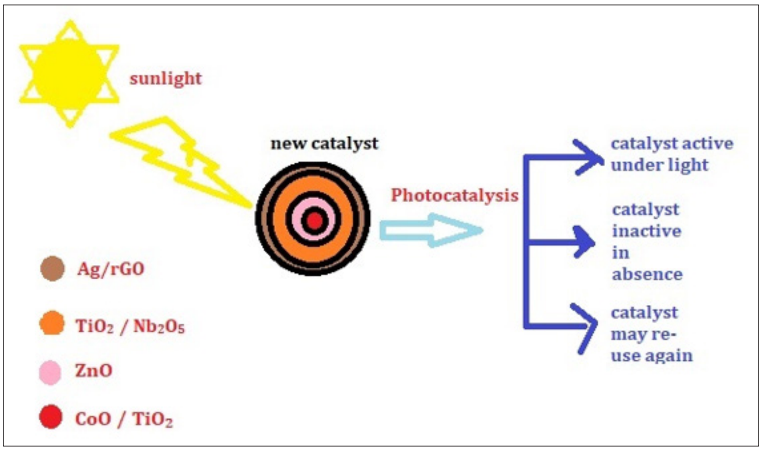

Figure 3: Scheme of AZCT / rGZTNb Metal Nanocomposites

DFT Calculations of Nanocomposites

The present work is a systematic study of nanocomposites, these photocatatalysts are shows better photocatalytic activity. Based on DFT (density functional theory) calculations for the nanocomposites include AZCT, rGZTNb are promising photocatalysts. The products from structural optimization can reveals the data about the interfaces, structures and optical properties of the nanocomposites. The optical and electronic properties by DFT calculations includes total and difference charge density, as well as charge population, demonstrate the polarity and polarization of material electron distribution and redistribution for the nanocomposites.

The Perdew, Burke, Ernzerhof (PBE), exchange correlation functional, and the ultrafast pseudopotential (129-130) in the calculations. The basis set cut off was 380-400 eV, and the k-space integration was done with a 3 x 3 x 1 k-mesh in the Monkhorst-Perk scheme. Further increase the cutoff and k-points show little difference in the results [128-133].

Conclusions

Nanocomposites plays vital role in the photocatalysis under UV, Visible and solar light. This is because of the their versatile crystallinity and surface properties like acidic and basic sites. With this review we compared our previous and present results for the synthesis and characterization of metal nano composites for the better applications in the photocatalysis. Present review demonstrates that the use of biocompatible ligands in the synthesis of hybrid nanocomposite allowed to selectively enhance the photocatalytic activity.

The same materials can also been used in the manufacturing of the energy storage devices. Metal oxide nanocomposites refer to materials consisting of mixture of two metal oxide nanoparticles. They show an extraordinary potential for application in many areas, such as aerospace and automotive industries and development of structural materials. Both metal oxides and nanocomposites with metal cluster deposited nanocomposites hold promise, but also pose challenges for real success.

In summary, rGZTNb or other nanocomposites that author highlighted in the review of nanocomposite applications as chemical catalysts in photoreactors as a semiconductor photocatalysts were successfully described about the synthesized methods and characterization and applications of these nanocomposites. These photocatalysts of ternary composites used for the water treatment and degradation studies under visible light with homo and hetero junctions between titania and zinc oxides over niobium oxides with rGO deposits are the future challenging emerging materials for the hydrogen evolution and visible light photocatalysis with heating effects. Nanocomposites formed by the mixtures of oxides of semiconductor in nature which act as photocatalysts. With the multi phase crystal structures significantly improve the separation of photogenerated electron-hole pairs, thereby increase the catalytic property and act as energy storage materials as hydrogen evolution performance activity. The surface of the mixed nanometal oxides can effectively enhances visible light absorption and promotes charge separation and also act as better energy and environmental applications. Owing to the energy level difference of the AZCT and rGZTNb nanocomposites which having higher oxidation capacity can rapidly remove the pollutants in aqueous solutions. Thereby increase the photocatalytic activity and exhibit the excellent synergistic effects of the heterojunctions of different multiphase semiconductor metal oxide nanocomposite materials.

The DFT calculations from C-2p is far lower than for Nb-3d. in particular, the Nb—O-Ti-O-Zn-O-G nanocomposite shows the strongest binding energy, and lowest excitation energy corresponding to its zero gap.

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