A Review On Various Doped Tio_2using Metallic And Non-Metallic Nanocrystals

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Abstract: In this study, various approaches for producing doped TiO_2 using metallic and non-metallic nanocrystals are examined. Due of a number of characteristics, including great physicochemical stability, low cost, and non-toxicity. In photocatalytic, photovoltaic and dye dye-sensitized solar cells applications; TiO_2 is one of the most often used semiconductors. TiO_2 has differing bang gaps in its rutile and anatase crystalline phases, respectively, of 3.0 eV and 3.2 eV.

Keywords: Co-precipitation method, Sol-gel method, hydrothermal method, doped components,

1.1 Introduction:

Fujishima et al. [1] reported that the Platinum electrodes are replaced with p-type semiconductor electrodes so that water can be electrochemically photolysis more effectively. Frank and Bard [2] have said that when compared to the doped or rutile forms, the high indensity radiation of CN^- disappearance was essentially at an ignition rate. The importance of physicochemical qualities in electronic devices including water splitting devices, solar cells, gas sensors, and dye sensitised photocatalyst [3-7]. The crystalline forms of this mineral are rutile, anatase, and brookite, which are all well-known. At ambient temperature, anatase is a common and stable phase in nanomaterial's [8–10].

TiO_2 has additional advantages such as non-toxicity, ease of production, and chemical stability [11].The n-type semiconductor titanium dioxide (TiO_2) is well-known. Under UV light (387 nm) with an energy greater than the band gap of 3.3 eV in the anatase crystalline phase, TiO_2 exhibits comparatively high reactivity and chemical stability. The development of photocatalyst with high reactivity under visible light (> 400 nm) could allow the use of the majority of the solar spectrum, even in low-light environments. Metal-ion implanted TiO_2 (using transition metals: Cu, Co, Ni, Cr, Mn, Mo, Nb, V, Fe, Ru, Au, Ag, Pt) [12-14], reduced TiO_2 photocatalyst [15-16], and non-metal doped-TiO_2 (N, S, C, B, P, I, F) [17-20] have all been presented as methods for TiO_2 modification.

TiO_2 is a low-cost, easy-to-handle substance that is non-toxic and non-hazardous. In recent years, ceramic tiles have gotten a lot of attention for new uses and production processes, such as reduced thickness products, digital decoration, and antimicrobial activity, all of which add value to the construction materials. The method of doping TiO_2 with metallic and non-metallic species is described in this study. Including a variety of dopant techniques that are now accessible.

1.2 The metaland non-metal ions nanocrystalsdoped TiO_2using co-precipitation method:

TiO_2 has been doping with a many different metals such as Co, Nb_2O_5, Zn, $ZnFe_2O^{4+}$and $ZnFe_2O^{4-}$, Li ,Al,Cu,SnO_2, Ni, Ag, Fe and Ce. Because the Fermi levels of these metals are lower than that of TiO_2, photo excited electrons can be transferred from the conduction band of TiO_2 to metal particles deposited on the surface of TiO_2, while photo generated holes in the valence band remain on TiO_2. This greatly reduces the possibility of electron-hole recombination, resulting in efficient separation and higher photocatalytic activity [25]. To enhance the photocatalytic effect in the visible light region, many producing methods were, there are many techniques such as sol-gel, hydrothermal, spinning, co-precipitation, chemical vapour deposition, and pyrolysis and biosynthesis methods [26-27]. Among these, the co-precipitation method has several advantages such as cheap, better homogeneity, fine particle size, and time-saving.Detailed information about doped TiO_2 co-precipitations is shown in Table1 [28-44].

Doped Element	Preparation method	Characterization and its applications	Reference
Co	Co-precipitation method.	1. XRD results confirm the crystal structure and presence of anatase, brookite and rutile phase with particle size in the range of 43.63nmto 38.81nm. 2. UV spectroscopies studies band gap of cobalt doped TiO_2 nanoparticles was 2.59ev, 2.0ev, 1.68ev and 1.5evrespectively. 3. Wavelength was increased, bandgap shifted towards small values that`s mean photocatalyst activity can be increased.	[28]
Co^{3+}	Co-precipitation method.	According to the X-ray diffraction and Raman spectroscopy analysis, the substitution of Ti^{4+} by Co^{3+} creates oxygen vacancies and promotes the anatase-to-rutile transformation. The enhancement of high temperature NO_2 sensing performance is related to the alteration in electronic structure as well as the formation of rutile polymorph in the Co-doped TiO_2 sample.	[29]
Co	Co-precipitation method.	The XRD results of t the crystallite size of Co-doped TiO_2 nanoparticles decreases from 18 to 12 nm with the increase of doping concentration. The scanning electron microscopy was used to detect the morphology of	[30]

		synthesized nanoparticles which sizes changed with the altitude in the doping concentration to 6%. FTIR spectra exhibit broad peaks where anatase phases of TiO_2 demonstrate very sharp UV–Vis band gap results showed the reduction in band gap from 3.21 eV, for undoped TiO_2, to 2.74 eV, for Co doped 6% TiO_2 a good photocatalyst activity.	
Nb_2O_5	Co-precipitation	The powders containing 5 mol% Nb_2O_5 -doped TiO_2 presented similar photo activity under UV-light and higher photoactivity than P25 under visible light, with the benefit of having very small crystallite sizes, making it more suitable for glazed ceramic coatings.	[31]
Zn	Co-precipitation	The results show that the solar cell assembled with the $Zn_{0.1}Ti_{0.9}$ O_{2s}film exhibits a short circuit current density of 12.32 mA/cm^2,open-circuit voltage of 0.604 V, and a power conversion efficiency of 3.03%. Its power conversion efficiency is 1.5-fold higher than that of the cell assembled with the pure TiO_2 film.	[32]
$ZnFe_2O_{4+}$ and $ZnFe_2O_{4-}$	Co-precipitation	1. TEM images demonstrate that $ZnFe_2O_{4-}$ nanoparticles are spherical in shape (9 ± 2 nm) a $ZnFe_2O_{4+}$ TiO_2 nanocomposite exhibits spherical-like morphology (11 ± 3 nm). 2. HRTEM and SAED studies further confirm the phase purity of the samples and reveal the formation of core-shell in case of the composite. 3. The direct band gap of $ZnFe_2O_{4+}$ nanoparticles (2.11 eV) and $ZnFe_2O_{4-}$ TiO_2nanocomposite (2.30 eV). 4. Such results provide new prospects for optimizing and improving the properties and performance of semiconductor nanocomposite in photocatalyst degradation of dyes and water splitting.	[33]
Fe	Co-precipitation	1. XRD study shows the size of crystallite is attributed towards Fe^{3+} (0.64 Å) a large ionic radius than TiO_2 (0.60 Å). 2. Calculated band gap energy from the UV Visible spectra analysis is 3.35 and 3.25 eV. 3. SEM analysis reveals the average grain size is spherical in shape and porous in nature. 4. Solar cell applications.	[34]
Li	Co-precipitation	1. The XRD analysis of crystallite size of all the samples were in a range of 42 to 52nm.TiO_2 nanocrystals are predominantly in the rutile crystal phase with some traces of brookite phases. 2. The FESEM image has shown rectangular and hexagonal morphology in the form of nano particles. 3. The synthesized nanoparticles are good linearity property between the irradiation doses of 1 kGy to 10 kGy. The photocatalyst glow curves of gamma irradiated TiO_2 samples have shown increase in the photocatalystintensity with dose, annealing temperature and doping.	[35]
Al	Co-precipitation	1. According to the UV analysis band gab energies are 1.944 eV, 2.431 eV, 1.525 eV, 1.395 eV and 1.893 eV. 2. In UV result, Al doped TiO_2 wavelength is between 378 nm to 889 nm. 3.The main advantages of the proposed synthesis are its simplicity and further work on the optimization of pure TiO_2 and Al doped TiO_2 tetragonal particles growth for electronic and optoelectronic applications in progress.	[36]
Cu	Co-precipitation	1. The calculated band gap energy for 'pure' TiO_2 is also found to be 3.2 eV from the extrapolation of the corresponding plot. 2. Scanning electron micrographs of the catalyst samples depict the particle structures like irregular spherical of size around 20–100 nm. The size range of the dopant particles varied between 20 and 110 nm.	[37]
Sn	Co-precipitation	1. Crystallite sizes from 22.5 nm, 24.0 nm, 17.4nm, 18.9 nm and 19.8nm. 2.Band gap is 388nm	[39]
Ni	Co-precipitation	1. Crystallite size of Ni doped TiO_2 (Ni = 0.0, 0.1, 0.5, 1, 5 and 10 % wt) are 17.82 nm, 16.03nm, 13.84nm, 17.30nm, 17.47nm and 18.47nm. 2. Band gap is 448 and 840 nm.	[40]
Ni	Co-precipitation	1.The crystalline size was found to decrease significantly from 24.7 nm to 9.7 nm 2. FTIR confirmed the formation of Ti-O-Ni bonding due to sharpened and enhanced intensity of the bands in the range of 500-1000 cm^{-1} and 910-1030 cm^{-1}.	[41]

Ni	Co-precipitation	1. Decrease in the TiO_2-lattice parameter due to increased Ni-addition. For the anatase polymorph, the lattice parameter a is found as 3.7874, 3.7839 and 3.7836 Å respectively. 2. The Raman spectra of the samples were obtained between the wave numbers of 175–800 cm^{-1}. 3. XRD results, a mixture of anatase and rutile polymorphs were obtained with the amount of rutile increasing with increasing nickel concentration.	[42]
Ag	Co-precipitation	**S**ilver-deposited TiO_2 photocatalyst enhanced the inactivation of E. coli by visible irradiation when compared to that by using TiO_2. The similar 100% of high antibactericidal efficiencies and six times of rate of reaction compared to the usage of TiO_2 were obtained for either using visible light or UV light or even no light irradiation by the application of Ag-TiO_2.	[43]
Ag	Co-precipitation	1. Band-gap energy (2.24 eV vs. 3.20 eV) and lower electron-hole pair recombination rate due to the presence of silver. 2. Resulting in formation of a composite with high photocatalytic capacity.	[44]
Fe	Co-precipitation	1. XRD Crystallite size is decreases due to 17.82nm, 15.87nm, 15.13nm, 14.43nm, 13.78nm and 13.24nm. 2. The Fe-doped TiO_2 powders possess flat band potentials suitable for artificial photosynthesis reactions. Though, Fe_2O_3 is a p-type semi-conducting material, the Fe-doped TiO_2 materials exhibit n-type semi-conducting.	[45]
Ce	Co-precipitation	1. Crystallite size is decreases due 11.21nm, 10.32nm, 9.19nm, 7.38nm and 7.25nm. Anatase Crystal phase. 2. Ce-doped TiO_2 microspheres achieved an efficient visible light photoactivity in the photo degradation when reused, they might hold a good potential for application in wastewater treatment.	[46]
CeO_2	Co-precipitation	1. The particle sizes are 23.628nm,22.143nm, 22.005nm,21.349nm and 17.839nm. 2. The TEM images reveal that with the increase in the concentration of titanium, the shapes of the particles changed from angular to a spherical form, also indicating the average crystallite size was decreased. A small amount of weight loss was observed.	[47]

Table 1.The nano doped $TiO_2$by co-precipitation method of characterization and its applications

1.3 metal and non-metal ions doped TiO_2nanocrystals using sol-gel and hydrothermal method:

Reghvendra et al reported the doping in TiO_2 with various metal ions such as Hereafter, the samples are named as PT for pure TiO_2, AgT for Ag-TiO_2, BT for Ba-TiO_2, CoT for Co-TiO_2, CrT for CrTiO_2, CuNT for CuN-TiO_2, FeT for Fe-TiO_2, SnT for Sn-TiO_2, ZT for Zn-TiO_2, VT for V-TiO_2, ZMT for Zn + Mg-TiO_2, and ST for S-TiO_2 and investigated the DSSCs.The DSSCs with photo anodes made from different doped TiO_2 nanoparticles demonstrated increased short-circuit current density and efficiency. In comparison to the DSSCs based on FeT and ZT samples, the DSSCs based on FeT and ZT samples performed better, with conversion efficiencies of around 27 and 34 percent, respectively [48].Yuan et al. reported the doping in TiO_2 with various metal ions such as Ag^{2+}, Al^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, V^{5+}, and Zn^{2+} and investigated the photocatalytic activity. Depending on the ionic radii, valence state, and arrangement of the dopants, a significant influence of doping was seen. Among the several doped samples, Fe^{3+} doping at 1% concentration shown exceptional photocatalytic activity and increased toluene removal efficiency by up to 71% [49].Yu et al. synthesized the Zn-TiO_2 nanoparticles based on different Zn-doping concentrations and sintering temperatures. The role of sintering temperature and the dopant concentration demonstrated the phase transformation of TiO_2 from anatase to rutile. Further, this study explored the doping mechanism of Zn^{2+} ions in Zn-TiO_2 nanoparticles [50]. Sacco et al. discussed the importance of catalysts during the sol–gel synthesis of nanoparticles and evaluated the photocatalytic activity. They experimented with different V doping concentrations and photocatalytic activity for the removal of caffeine in water. Under UV radiation, nearly 96 percent of caffeine degradation was seen after 360 minutes of exposure [51].Moradi et al. prepared the Fe-doped TiO_2 nanoparticles by changing the doping concentration of Fe. Among the various Fe-TiO_2 samples, the sample prepared with the 1 wt % doping concentration demonstrated the extraordinary photo degradation of reactive red 198 [52].Senthil Kumar et al. synthesized and presented the study of Ag-TiO_2 nanoparticles for the photo-treatment application. The Ag-TiO_2 nanoparticles showed the redshift of the absorption edge, whereas the estimated band gap of 2.74 eV was reported[53].Gaidau et al. reported the electrochemical preparation of Ag- and N-TiO_2 nanoparticles by using an electrochemical process. They studied the self-cleaning capability of these nanoparticles; however, co-doped Ag-N-TiO_2 nanoparticles strengthened the self-cleaning capability [54].Gu et al. preferred the hydrothermal route to prepare the $BaTiO_3$ nanoparticles with the controlled diameter of the nanoparticles. They explored the promising application of the prepared nanoparticles for energy storage device application [55].Liu et al. investigated the hydrothermal synthesis of zinc magnesium co-doped TiO_2 (ZnMg-TiO_2) nanoparticles and evaluated the performance of a dye-sensitized solar cell. The As a result, conversion efficiency has increased to 27%.compared to a solar cell based on TiO_2 nanoparticles that are not doped this result was attributed to doping, which was shown to be present. Could result in positive flat-band shifting and, as a result, the quick transport carriers [56].The Zn-Mn-TiO_2 nanoparticles were made by Wattanawikkam and Pecharapa using a sonochemical method. The produced sample showed single-phase anatase-TiO_2 with spherical and homogeneous nanoparticle production. When compared to pure TiO_2 nanoparticles, the utilisation of the co-doped sample demonstrated remarkable photo degradation of Rhoda mine B dye, with a 10 times quicker degradation rate [57].Duane et al. investigated the

properties of tin-doped TiO_2 (Sn-TiO_2) nanocrystals synthesised using a hydrothermal technique, as well as the performance of a dye-sensitized solar cell based on Sn-TiO_2 nanocrystals. The crystallinity was unaffected by doping different Sn concentrations in TiO_2. However, the solar cell demonstrated enhanced conversion efficiency after the XRD peak shifted, indicating Sn-ion doping [58].

1.4Conclusion:

Titanium dioxide represents an effective photocatalyst for water and air purification and for self-cleaning surfaces. Additionally, it can be used as antibacterial agent because of strong oxidation activity and superhydrophilicity. TiO_2 shows relatively high reactivity and chemical stability under ultraviolet light should allow the main part of the solar spectrum, even under poor illumination of interior lighting, to be used. Visible light-activated TiO_2 could be prepared by metal-ion implantation, reducing of TiO_2, non-metal doping or sensitizing of TiO_2 with dyes. This paper reviews preparation methods of doped-TiO_2 with metallic and non-metallic species, including various types of dopants methods currently available. TiO_2 is one of the most commonly used semiconductors in photocatalytic and photovoltaic applications because of its different properties, such as low cost, low toxicity, chemical stability, and so on. It is used in photovoltaic application as a semiconductor in dye-sensitized solar cells (DSSCs). Doping TiO_2 is an interesting strategy used to improve its properties as a semiconductor and, thus, its efficiency in many applications.

1.5 Reference:

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