Paper ID: 206

A Comprehensive Review on The Enhancement of Photocatalytic Activities of ZrO_2 Nanoparticle for Hydrogen Production and Dye Degradation by Introducing Doping, Co-doping and Composite Forming

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Abstract

An advanced exploration in nanoparticle technology has brought about a widespread photocatalytic application of ZrO_2 NPs owing to its intriguing physiochemical attributes especially strong antioxidant activities,a high redox potential.But their photocatalytic efficiency gets negatively affected due to their wide band gap (3.85 eV-5eV) and fast recombination of photogenerated species.An enormous number of approaches has been made by the researchers in past few decades to perceive a full potential of ZrO_2 NPs as an improved photocatalyst.This review offers a comprehensive analysis on the enhancement of ZrO_2 photocatalytic activities for hydrogen production and dye degradation through doping,co-doping and composite forming.This study has examined that doping and co-doping with metal and nonmetal effectively narrow the band gap by altering both recombination and separation of carriers.TiO_2,C_3N_4 etc.form composite with ZrO_2 exhibit superior interfacial surface activity leading to improvd hydrogen production under visible light.Finally, the article concludes with challenges and future outlook.

Keywords: ZrO_2 nanoparticle, photocatalytic, wide band gap,charge separation.

2.Introduction

One of the most important difficulties confronting humanity today is the poisoning of water by organic dyes and the complications that follow. Nanotechnology is one of the most effective remediation techniques when compared to other approaches as the nanoparticles can readily perforate the polluted system[1].Metal oxide NPs like CuO, TiO_2, ZnO have large band gaps and are present in the oxidized state which make them an advanced candidate as photocatalyst[2][3].

In current research ZrO_2 is garnering a lot of interest in the fields of photocatalysis and optoelectronics due to their strong ionic conductivity, biological and environmental compatibility, high valence band potential (VB,+4.0V) and low conduction band potential(-1.0 V vs.NHE),permitting it to manifest a large number of O vacancies together with a high capacity for ion exchange and redox activity on its surface[4][5].ZrO_2 has a number of beneficial properties, but one of its main drawbacks is that its limited activity only to the UV solar spectrum, due to its wide energy gap.[6]Also the visible portion of solar energy may not be used to its full potential since UV radiation makes up less than 5% of solar light[4][7].

In order to address these issues, doping is a useful tactic to modify the band gap, enhance efficiency of conversion of solar light, improve H_2 evolution and thereby regulating photocatalytic activity[5].For example[8]Ni[9][10]C[11] etc. Can be doped to elevate the valence bands of metal oxides to lower bandgaps[12].While impurity doping is taken into consideration for expanding the spectrum of light absorption, carrier separation is typically overlooked .Thus, it is imperative to clarify the carrier separation process by introducing Co-dopant (Mg/Mn)[13] ,(F/N)[14], (C,S)[9] in ZrO2.A number of ZrO2 based heterostructures have demonstrated improved photo catalytic activity, including TiO2/ZrO2[15],ZnO/ZrO2[16] etc.

Owing to NPs' wide range of uses and applications numerous techniques have been developed to create NPs with more control over their shape, size and other characteristics[3].Such methods are Sol gel[11],coprecipita-

tion[17][18],hydrothermal[19][20],chemical precipitation[21].Sol gel is the mostly used chemical technique owing to its being facile and low cost,yet it has drawbacks such toxicity,difficulty obtaining raw chemicals.Hydrothermal technique is simpler because it doesn't involve further grinding or high-temperature heating, which might reduce a catalyst's effectiveness[3].This review will further discuss how ZrO2 can be modified to improve photocatalytic efficiency.

3. Strategies to enhance photocatalytic activities

3.1. Introducing Mono-doping

3.1.1. Alkaline earth metal

To increase the PCD efficiency of ZrO2, a great deal of research has been done on the effect of doping different group IIA metals. Rajesh et al.[22] discovered an increased photocatalytic activity for 0.08 mol% Mg doped ZrO2,resulting in 94% and 90% degradation of MV and MB,respectively.They found that all the doped samples had a reduced bandgap of 5.03ev and an increase in crystallite size to 4.42 nm.Jeba et al.[23] reported crystalline structures with high combination of tetragonal and monoclinic phases by synthesized Sr doped ZrO2 NPs,utilizing the co-precipitation.A band gap range of 4.6 to 4.25 eV was discovered after studying the UV-Vis optical characteristics with an enhanced photocatalytic degradation of MB(92%) and antimicrobial activity.

3.1.2. Transition metal

Transition metals are frequently added in ZrO_2 NPs as dopants to alter and improve electron transfer mechanism and to reduce the recombination of charge.Waheed et al.[9] and Venkata et al. have confirmed a notable decrease in band gap energy in Ni doped ZrO_2 NPs owing to the formation of O vacancies.All the doped NPs prepared by co precipitation and thermal deposition had a remarkable degradation efficiency of MB,94.1% and 82.5%,respectively.Javed et al. have reported a high photocatalytic activity of Fe-ZrO_2 NPs and asserted that the synergistic interaction between the tetragonal phase and O vacancy have a effect on the degradation efficiency.Kisoo et al.[19] found 0.3 %-Y-ZrO_2 to be the most effective photocatalyst with a narrower band gap and a degradation efficiency of 98% toward Rhodamine B.10% Co doped ZrO_2 NPs by Waheed et al.[7],contributed significantly to the elimination of MB (96.5%),and this was attributed to the effective regulation of the recombination rate.Rajesh et al.[13][8]noticed an increased MV and MB degradation and PEC water splitting photocatalytic activity for 0.06% Cu-ZrO_2 NPs owing to improved size of pores and area of particular surface.

3.1.3. Non metal

With non metal doping,the catalyst's optical characteristics can be considerably changed.Shen et al.[10] investigated visible light driven photocatalytic processes utilizing N-ZrO_2 photocatalysts ZON and AZON,and had the greatest performance for degrading MO and the maximum rate of hydrogen generation (2.12 mmol g−1 h−1).Hiroshi et al.[11] produced N–ZrO_2 NPs with a high degree of crystallinity and obtained an effective degradation involving photolysis and adsorption,for MB and AM under a visible light intensity of 144.7 W/m2,are 96% and 67.2% respectively.When compared to P25 and pristine ZrO_2,Gamonpetch et al.'s[14]3D flower-like ZrO_2 photocatalyst doped with C demonstrated a high photoactivity efficiency.It was ascribed to the combined effects of higher C concentration and 3D mesoporous microflower architecture, which led to a narrower band gap(2.37 eV) and a lower likelihood of charge recombination for C-ZrO_2. By adding F ions to ZrO_2 powder, Hao et al.[20]were able to decrease the external band gap and also obtained a noteworthy MO degradation efficiency of 89.7%.

Table 1. Effect of different dopant and doping concentration on crystalline phase,morphology,size and bandgap on photocatalytic degradation of organic dyes.

Dopant	Author	year	Synthesis method	Doping (mol %)	Crystal size(nm)	Morphology/crystalline phase	Band gap (ev)	Dye used	Degradation (%)	Time (min)	Ref
N	Babel	2016	Thermal Decomposition	_	37.38	Spherical; m	3.8 5.0	MB AM	96 67.2	240	[11]

Ni	Waheed	2021	Co precipitation	3 5 7 10	18	Spherical; t	2.93 2.90 2.88 2.76	MB	78.4 87.7 90.7 94.1	120	[12]
Mn	Javed	2022	Co precipitation	3 10	15± 2.4	Quasi spherical; t	2.25 2.45	MB	85.6 96.2	160	[5]
C	Gamonpetch	2016	Solgel	0.1	_	agglomerate;m	2.37	MB	96	60	[14]
Fe	Waheed	2020	Co precipitation	3 5 7 10	17.13 18.82 21.55 24.01	Spherical; t	2.72 2.51 2.30 2.10	MB	78.5 82.2 85.2 94.2	120	[15]
Mg	Rajesh	2020	Precipitation	0.02 0.04 0.06 0.08	4.25 4.26 4.28 4.42	Quasi spherical; t	5.45 5.38 5.28 5.03	MV MB	92 89	70	[22]
Y	Reddy	2018	Hydrothermal	0.3	6.1	Spherical; t	3.66	Rh B	98	40	[17]
Cu	Rajesh	2020	Chemical precipitation	0.02 0.04 0.06 0.08	4.65 4.76 5.02 4.96	Spherical; t/m	5.30 5.21 4.65 4.44	MV	76 81 99 86	70	[18]

t (tetragonal),m (monoclinic).

3.2. Introducing co-doping

Recent research has examined simultaneous deformation of the lattice and band gap as potential pathways for enhanced activity with codopants compared to dopants.Shungao et al.[8]demonstrated an experimental and DFT research on the impact of N and F dopants on the H_2 evolution photocatalytic capabilities of m-ZrO_2 NPs .The electrical configurations and spatial arrangement of CBM and VBM revealed that the enhanced photocatalytic activity of FNZO NPs were associated with the impurity improved spatiotemporal carrier separation during transit and bulk carrier recombination. Rajesh et al.[13]looked at the increased photocatalytic capabilities of (Mg-Mn) co-doped ZrO_2 catalyst,ascribed to surface imperfections resulting in decreased band gaps.A stabilized monoclinic phase was attained by diminishing the size of NPs and augmenting the O vacancies with a remarkable 96% and 94% degradation efficiency for both MB and MV dye compounds in less than 70 minutes.[24]According to ODEH et al.wet impregnation of C and S into ZrO_2 NPs demonstrated superior photocatalytic performance with a highly mesoporous structure and removal efficiency of BOD,COD,TOC,Cl- and NO3- about 87.6%,77.3% ,97.7% 84.4% and 63.9% within 120 min respectivel.Cu/NiO doped ZrO photocatalyst was produced by Aneeqa et al.[23].They reported that the degradation efficiency of MB and MO dyes was increased by almost 99% and attributed this improvement to the synergistic influence of the solution's PH, starting dye concentration, catalyst dosage, and irradiation reaction duration.Agorku et al.[25]linked the enhanced activity of multi elements doped ZrO_2 photocatalysts to the concerted effect of the dopants.The outcome demonstrated the cooperative effects of doping C,N,S and Eu in the ZrO_2 NPs improved the degradation of indigo carmine and a critical role that Eu doping control played in S,C,N-ZrO_2 electron and hole recombination reduction.

Table 2. Influence of co-doping on morphology,band gap and photocatalytic efficiency of ZrO_2 NPs

Co-Dopant	Author	Year	Synthesis method	Morphology; crystalline phase	Band gap (ev)	Rate constant (k/min)	Dye/ Pollutant	Degradation(%)	Time (min)	Ref
Mg-Mn	Rajesh	2022	Co-precipitation	Spherical; t&m	2.65	_	MV MB	94 96	70	[13]

F-N	Yin	2020	Hydro-thermal	Aggre-gated; m	3.4	_	_	_	60	[14]
C-S	ODEH	2021	Wet impreg-nation	Spherical; t+r	3.4	$2.9x10^{-3}$ $3.4x10^{-3}$ $9.9x10^{-3}$	TOC COD BOD	97.7 77.3 87.6	120	[13]
Cu-NiO2	Aneeqa	2021	Hydro-thermal	Spherical; t	3.49	$8.8x10^{-1}$	MB MO	99	10 35	[23]
C-N-S	Agorku	2015	Co-pre-cipitation	Spherical; t+m	2.99	$1.09x10^{-2}$	IC	100	150	[25]
Cr,-SO42-	Shady	2017	Impreg-nation	Porous amop hous	2.82	$10.03x10^{-3}$	MB	95	69.11	[26]

t (tetragonal),m (monoclinic),r(rhombic).

3.3. Composite formation

The formation of composite with ZrO_2 NPs facilitate H_2 production by improve charge separation,increase active surface area and also modify band gap for better light absorption. Enhanced ROS generation facilitates dye degradation process. Absorbing capability of dye increases and leverages synergistic effects, resulting in more efficient breakdown of organic pollutants. The heterostructure and morphology of these composites play an important role to activate the surface area for generating •OH and HOO• radicals that take part in the process of H_2 production and dye degradation. The percentage of composite materials also effects the band gap and morphological properties. Like in 10% ZnO in ZnO/ZrO_2 composite gives the lowest bap gap of 3.2 eV but equal percentage of ZnO and ZrO_2 shows less agglomeration in morphology and that facilitate better photocatalytic performance. Where 6.9% TiO_2 gives best performance.In ZrO_2/ZnO composite the photocatalytic activity increases with decreasing crystalline size as it decreases the recombination of photogenerated charge carriers. In ZrO_2/g-C_3N_4 composite ZrO_2 content more than 5% can decrease the photocatalytic activity as excess amount of ZrO_2 results agglomeration in the surface, absorption of light decreases. Moreover composite with mono layer slap surface of WO_3 creates heterostructure. Due to interlayer spontaneous polarization, band gap decreases significantly. That's why these heterostructures can harvest more solar energy to enhance photocatalytic activity.The formation of heterojunction with composite allows electrons to move from the higher conduction band material to lower one and holes moves lower to higher one. This phenomenon improves photocatalytic efficiency.Further nanocomposite with two metal oxides is highly stable and have increased surface area to enhance better photocatalytic activity compared single nanoparticles.[27][28][29][30][31][32][33][32][34] [35][36]

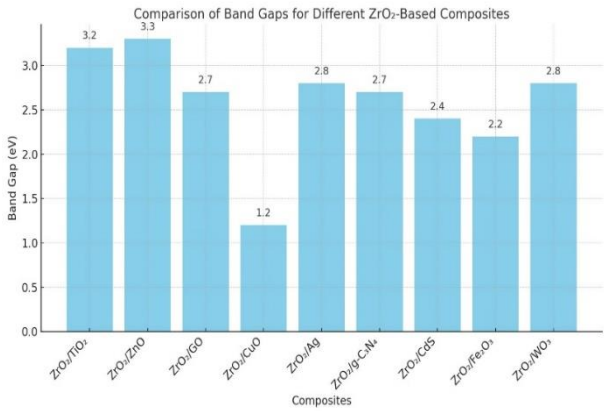


Fig.1. comparison of bandgap of different ZrO_2-based composite

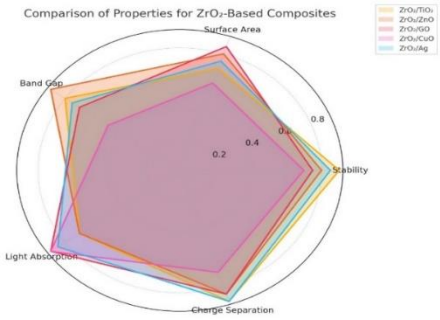


Fig.2. Comparison of properties for ZrO_2-based composite

4. Mechanism of Hydrogen production and Dye degradation

The solar photocatalytic hydrogenation of water using ZrO_2 NPs is responsible for the mechanism to obtain H_2 through a set of chains, promoting sunlight-driven splitting.In the presence of UV or sunlight, ZrO_2 will absorb photons with energy equal to or higher than its bandgap.When ZrO_2 absorb a photon, the electrons move from VB to CB leaving holes in valence positions.This produces electron-hole duos. Separation of these e^--hole pairs must

be done efficiently to avoid recombination, or else the energy caught by absorption is wasted. Particularly, the more stable crystal structure of ZrO_2 allows for charge separation to a greater degree.Electrons in the conduction band are available to decrease protons (H^+) from water, facilitate the production of H_2 gas.The holes in the valence band act as strong oxidizing agents and can oxidize water molecules to generate oxygen (O_2). Reduction reaction:

$2H^+ + 2e^- \rightarrow H_2$; Here the holes in the valence band migrate to the surface and participate in the oxidation of water (H_2O) to produce oxygen gas (O_2) and protons (H^+), which contribute to further hydrogen production.

For dye degradation hole reaction with water:

$h^+ + H_2O \rightarrow OH\cdot + H^+$; The generated ROS, particularly hydroxyl radicals (OH·), are highly reactive and can break down complex dye molecules. These radicals attack the dye molecules, leading to their degradation into simpler, less toxic compounds like CO_2, H_2O, and other smaller molecules.

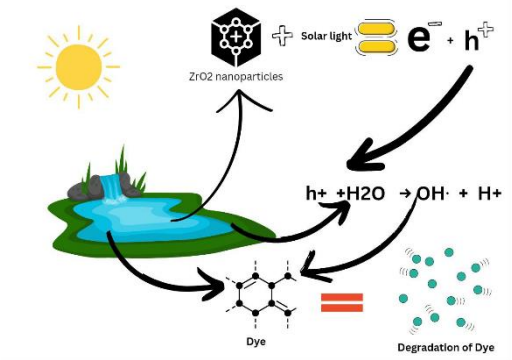


Fig.3. Mechanism for Dye degradation and Hydrogen production

5. Conclusion

In this review we have analyzed three different techniques that enhance the photocatalytic activity of ZrO_2 NPs for H_2 production and dye degradation application. Doping, co doping and composite forming techniques enhance the photocatalytic activity in terms of improved charge separation, enhanced surface area and active sites, improved light harvesting and band gap engineering .A peak percentage of these techniques have showed desired result. High band gap of ZrO_2 (~5 eV) nanoparticles comes to 1.2eV. In doping it comes to 2.1eV , in codoping it becomes 2.65eV and by forming composite it comes to 1.2eV. Low band gap facilitates the production of excited radicals for required application. For future work ,doping in composites can create a huge research scope in this field. By integrating principles from nanotechnology, chemistry and environmental science this study fostering innovation in the design of next generation materials for real world application..

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