An evaluation of noble nanocomposites based on zinc oxide: synthesis, characterization, environmental, optical and biomedical applications

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Metal oxide nanocomposites have concerned an obvious agreement of consideration because of their enormous applications in numerous domains like photocatalyst, catalysis, biological and sensors. The conservational purification technology is getting advanced by the development of heterostructured semiconductor photocatalysts. In this paper, we documented a comparative analysis of synthesis process (Solution-based methods, High temperature-based methods and Electrical methods) and characterisation techniques such as Transmission electron microscopy, X-ray diffraction, Fourier-transform infrared spectroscopy and Scanning electron microscopy on various noble Nanocomposites (NCs) of metal (M) - zinc oxide (ZnO/ZO). This review inclines over multiple stat-of-the-art applications like photocatalytic, catalyst, sensor and biological activities. It could be concluded from this study that, the catalytic activity of noble M-ZO nanostructures depends not only on the noble metal species, but on the catalytic material architecture as well. The future research and development challenges together with future prospects are critically presented.

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1. Introduction

Recently, nanocomposites (NCs) of metal-oxide is one of the evolving research domain owing to its smaller size, unique structure, photocatalytic, thermal, electrical, antimicrobial, mechanical and optical properties [1],[2]. NCs of metal-oxide are mostly formed by the mixture of two or more metal oxides with specific concentrations [3]. NCs of metal oxide finds applicable in numerous applications like sensors, photocatalytic activity, catalytic activity, antimicrobial activity, Deoxy ribonucleic acid (DNA) binding property, anticancer activity, magnetic property,

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adsorption property, drugs, solar plate and reduction of Hydrogen peroxide (H_2O_2), battery materials, fuel cells, solar cells, gas sensors and Ultraviolet (UV) detectors [4-6]. The charge separation efficiency, charge transfer ability and life time carrier typically increases due to the presences of metal-oxygen-metal and metal-metal interfaces in nanocomposities [7],[8].

Zinc oxide (ZO) is a hexagonal, wurtzite type semi conducting oxide with energy band gap closer to TiO_2 (3.2 eV). For effective degradation of the dye molecules, the catalyst might have higher surface area as well as catalytically active surface sites. ZO is a typical photocatalyst in Group II-VI possessing specific advantages like higher electrical and environmental stability, increased photoelectric strength and lower cost [9-11]. In recent years, ZO has received more attention owing to its unique morphology and dimension dependent properties. ZO being a wide band gap semiconductor, it possesses a wide range of useful properties including electrical, chemical, optical and magnetic properties. Moreover, ZO can be applied in many evolving applications over gas sensing [12], catalysts [13], semiconductors [14], UV-shielding materials [15], nano generators [16], anticancer agents [17-28], antiviral and antibacterial agents [29-31]. Recent literatures revealed that undoped ZO and doped ZO find various interesting bio-applications [32-56]. A brief data of the synthesis method, precursors used in the synthesis of undoped/doped ZO and their applications is presented in Table 1. In this aspect, ZO is a well-known material for its characteristic features such as (i) wider scope for easy tuning of surface morphologies into variety of nanostructures [57], (ii) simpler processing at low temperatures for forming nano crystalline ZO, (iii) larger concentrations of lattice defects and oxygen vacancies in the crystal structures, (iv) lower temperature regenerative capacity and (v) reduced cost. The characteristics of ZO materials are largely dependent on their morphology, so that many ZOs are supplemented by certain shapes such as rods, tetrapods, belts, flowers, spheres, tubular whiskers and needles [58-63]. The non-toxicity, photo reactivity, commercial interest, and long term stability of ZOs are typically high thereby enables us to create photo-active nanoparticles (NPs) of ZO. Processing techniques ranging from simple reflux to hydrothermal or no chemical reactions with or without surfactants and templates are reported for obtaining high surface area nano-ZO photocatalysts.

Moreover, in recent years, drinking water is a major problem over whole world due to rapid increase in population density and by mixing of wastewater drainage from different dye industries such as textiles, manufacturing industries, etc [64-67]. The majority of waste water from dye industries typically contains dissimilar natural azo colour which is toxic and these colours are exceptionally harmful in nature and unsafe to sea animals, human beings as well [68],[69]. Azo dyes, for example, naphthol orange, methyl orange, rhodamine B, conga red, etc., were the principal materials of dye industries [70-72]. However, these synthetic colour dyes are pretty cheap. Therefore, the drained water released from industries must be carefully purified so as to be reused by human beings.

Presently, numerous researchers around the world are working on this domain so as to resolve the issues pertaining through expelling of unsafe dyes from polluted water by using typical transition metal based NPs before discharging them to rivers or oceans [73-75]. To reverse this issue, photocatalytic degradation technique is an emphasised technique amid other techniques in removing organic pollutants from colour dyestuffs for producing safe water [76]. The use of nano-composites (palladium, silver, platinum and gold) over ZO is a challenging technique for improving the nanophotocatalytical characteristics of ZO materials. NC products palladium (Pd), silver (Ag), platinum (Pt), and gold (Au) over ZO have decreased the recombination volumes for the electron-hole pairs, as these ZO-based NCs have accumulated metallic and photocatalistic holes [77]. The improved properties of noble NCs of M-ZO show that they can be used instead of traditional ZO materials for application in converters, sensors, photocatalysts and energy generators [78]. A number of noble M-ZO nanocomposite structures have also been recently investigated, which indicates that this noble M-ZO shall be conveniently used in nanotechnology. The properties and uses of noble M-ZO NPs as catalysts are determined by their structures. Therefore, in common, it is important to investigate the advancements in this domain. This paper aims in highlighting the latest state-of–the-art scientific advances and identifying the key research problems so as to formulate potential research in forming noble metal (M)-ZO NCs for wider applications.

In this article, the synthesis process of various noble M-ZO NCs were documented. Moreover, the characterise techniques such as Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Scanning electron microscopy (SEM) of various noble M-ZO NCs were discussed. Furthermore, the evolving applications such as photocatalytic activities, catalytic activities, sensing properties and biological activities were elaborated in detail. Finally, concerns were made for future scientific studies and other future prospects.

This paper is summarized as follows. Section 1 gives a detailed introduction on NCs of metal-oxides highlighting the features of zinc oxide and how these nanocomposites finds applicable in environmental, biological and medical applications etc., were discussed. Section 2 enumerates the methods of synthesis of zinc oxide NCs encompassing conventional methods like Solution based methods, High temperature based methods, Electrical synthesis methods etc., with detailed consideration towards recent literatures. Section 3 enumerates the characterization of NCs including techniques like Transmission electron microscopy, X-ray powder diffraction, Scanning electron microscope and Fourier-transform infrared spectroscopy. Section 4 discusses the enduring applications of NCs inclined over sensors, photocatalytic activity and biological properties. The future challenges and perspectives of this present study are discussed in Section 5. Finally, Section 6 concludes the paper.

Table 1. Applications of undoped and doped ZO.

Host precursor	**Dopant precursor**	**Synthesis method**	**Applications**	**Ref.**
$Zn(NO_3)_2.6H_2O$	-	Hydrothermal	Gas sensing	12
$Zn(NO_3)_2.6H_2O$		Wet chemical	Catalyst	13
$Zn(NO_3)_2.6H_2O$		Chemical spray pyrolysis	Semi-conductor	14
$Zn(NO_3)_2.6H_2O$		Dipping-hydrothermal	UV shielding	15
$Zn(NO_3)_2.6H_2O$		Chemical vapour deposition	Nano generator	16
$Zn(NO_3)_2.6H_2O$		SCS	Anticancer: DU-145, Calu-6, L929, 3T3-L1, Antioxidant: In vivo acute toxicity, Antitubercular: Mycobacterium tuberculosis H37Ra, *In-vivo* acute toxicity.	17
$Zn(NO_3)_2.6H_2O$		SCS	Anticancer: PC-3, HCT116, A549 and MDA-MB-231, Antioxidant, Antimicrobial: *Clostridium perfringens (C. perfringens), Salmonella enterica (S. enterica), Candida albicans (C. albicans), Fusarium oxysporum (F. oxysporum).*	18
$Zn(NO_3)_2.6H_2O$		Hydrothermal	Antibacterial: *Pseudomonas aeruginosa, Escherichia coli, Staphylococcus aureus and Bacillus subtilis,* Anticancer: PC-3, HCT116, A549 and MDA-MB-231, Antioxidant, Blood haemolysis, *In-vivo* acute toxicity.	19
$Zn(NO_3)_2.6H_2O$		SCS	Antibacterial: *C. perfringens), (S. enterica),* Anticancer: MCF-7.	20
$Zn(NO_3)_2.6H_2O$		Precipitation	Antimicrobial: *P. aeruginosa, E. coli, S. aureus, B. subtilis, C. albicans and Candida tropicalis,* Anticancer: PC-3, HCT116, A549	21

Host precursor	Dopant precursor	Synthesis method	Applications	Ref.
			and MDA-MB-231, Antioxidant, Blood haemolysis.	
$Zn(NO_3)_2.6H_2O$		Hydrothermal	Antibacterial: *C. perfringens, S. enterica,* Anticancer: *HeLa.*	22
$Zn(NO_3)_2.6H_2O$		SCS	Anticancer: DU-145 & Calu6,	23
$Zn(NO_3)_2.6H_2O$		SCS	Antibacterial*: E. coli, P. aeruginosa,* Anticancer: MCF-7.	24
$Zn(NO_3)_2.6H_2O$		SCS	Antibacterial: *C. perfringens, S. enterica,* Anticancer: *HeLa.*	25
$Zn(NO_3)_2.6H_2O$		SCS	Antibacterial: *C. perfringens, S. enterica,* Anticancer: HeLa, MCF-7.	26
$Zn(NO_3)_2.6H_2O$		SCS	Antifungal: *F. oxysporum, C. albicans.*	27
Zn $(CH_3COO)_2{\cdot}2H_2O$		SCS	Antibacterial: *P. aeruginosa, Salmonella typhi, E. coli, S. aureus* and *B. subtilis,* Antioxidant activity, Anticancer: HT-29, HeLa.	28
-	-	-	Antiviral	29
-	-	-	Herpes simplex virus (HSV)	30
-	-	-	HSV	31
$Zn(NO_3)_2.6H_2O$	-	Precipitation	Antibacterial: *E. coli, P. aeruginosa* and *S. aureus,* Anticancer: HL60 and Peripheral blood monobuclear cells.	32
$ZnCl_2$	-	Hydrothermal	Antibacterial: *E. coli*	33
$Zn(NO_3)_2.6H_2O$	-	SCS	Antioxidant	34
$Zn(CH_3COO)_2.2H_2O$	-	Hydrothermal	Antibacterial*: E. coli, P. aeruginosa, S. aureus*	35
$Zn(CH_3COO)_2.2H_2O$	-	Hydrothermal	-	36
$Zn(NO_3)_2.6H_2O$	-	Solvothermal	Antibacterial: *S. aureus*	37
Zinc target		Laser ablation	Antibacterial: *E. coli,* Psuedomonas spp, *S. aureus* and *E. faecalis.*	38
$Zn(CH_3COO)_2.4H_2O$	-	Precipitation	Antibacterial: *L. monocytogens*	39
$Zn(NO_3)_2.6H_2O$	-	Solvothermal	Antibacterial: E. *coli, S. aureus*	40
$Zn(NO_3)_2.6H_2O$	-	Precipitation	Antibacterial: E. *coli, S. aureus, P. vulgaris, Psuedomonas* and *P. acnes, Kiebslella.*	41
$Zn(CH_3COO)_2.2H_2O$		Thermal decomposition	Antioxidant	42
Metallic Zn	-	Gas expansion	Antibacterial: *E. coli*	43
$Zn(NO_3)_2.6H_2O$		DNA assisted synthesis	Antibacterial: *E. coli, S. aureus*	44
$Zn(CH_3COO)_2.2H_2O$	Ag	Room temperature solution synthesis	Antibacterial: *B. subtilis* and *S. aureus.*	45
$Zn(CH_3COO)_2.2H_2O$	Mn	Microwave irradiation	Antibacterial: E. *coli, B. subtilis, P. vulgaris, P. vulgaris* and *S. marceseus.*	46
$Zn(CH_3COO)_2.2H_2O$	Se	Room temperature solution synthesis	Antibacterial: *E. coli*	47
$Zn(CH_3COO)_2.2H_2O$	-	Precipitation	Anticancer: HepG2 cell	48
$Zn(NO_3)_2.6H_2O$	-	Precipitation	Anticancer: Colo 320	49

Host precursor	Dopant precursor	Synthesis method	Applications	Ref.
$Zn(CH_3COO)_2.2H_2O$	-	Biosynthesis	Anticancer: WEHI-3B cells	50
$Zn(CH_3COO)_2.2H_2O$	-	Precipitation	Antibacterial: *E. coli, S. aureus, P. aeruginosa, B. subtilis* and *S. acidaminiphila.* Anticancer: HepG2 and MCF-7 cells.	51
$Zn(CH_3COO)_2.2H_2O$ $Zn(NO_3)_2.6H_2O$	-	Room temperature solution synthesis	Anticancer: U87 and HeLa cells	52
$Zn(NO_3)_2.6H_2O$		Precipitation	Anticancer: S91 melanoma cells	53
$Zn(NO_3)_2.6H_2O$	Li, Na, K	Solvothermal	Anticancer: neuro2A cells	54
$Zn(NO_3)_2.6H_2O$	Cu	Biosynthesis	Antibacterial: *E. coli, S. aureus* and *S. pyogenes.*	55
$Zn(NO_3)_2.6H_2O$	Al	Precipitation	Anticancer: MCF-7 cells	56

2. Methods of Synthesis

For unveiling the characteristics and various applications of nanostructures of noble M-ZO NCs, distinctive analysis has been discussed in this study. These noble NCs of M-ZO that were synthesised by different processes with different structural characteristics and applications has also been summarized. The synthesis methods include UV-irradiation, solution based method, hydrothermal method, annealing, calcination, coating, sputtering, flame spray, etc. One or more of these approaches have been used in traditional synthesis.

2.1. Solution-based methods

Concerning lower cost, reproductivity and relatively mild synthetic circumstances, which include the deposing of the noble metal (M) on the ZO surface via selected noble metal ions, the production of noble M-ZO NC by means of solution based synthetic method is of considerable attention. Liu et al., synthesised the Pd-ZO by using a simple solution-based method and amine route was typically employed for oxidation [79]. Zhang et al., synthesised yttrium-zinc NPs by using simple solution method and ammonia hydroxide was employed for precipitation of NCs. The silver-ZO nanosheets were also obtained at normal temperature by depositing the solution of silver NPs on ZO nanosheets [80]. Liqiang et al., synthesised the modified Pd-ZO NC by using the mixture of ZO and $PdCl_2$ with specific ratio, and the synthesised process was monitored for six hours using UV-visible (UV-vis) spectroscopy [81].

2.2. High temperature-based methods

The organic pollute solvents were not used in this high temperature method, therefore, it favours green chemistry and eco-friendliness. Ag-ZO NC was synthesised by Whang et al., by using specific mixture of silver and ZO with 10 Hz laser beam for 30 minutes and at 500°C for 2 hours [82]. Moreover, the Pd-ZO nancomposite was developed by Baruwati et al., by mixing $PdCl_2$ and ZO, and by subsequent calcination process at 250°C [83]. Majhi et al., synthesised Au@ZO nancomposite by mixing gold and ZO at 500°C for 2 hours [84]. Certain NPs in 'Pd – ZO' were synthesised through pyrolysis 'flame spray'. In general, the flammable spray pyrolysis vaporized and burned the precursor ZO and palladium (Pd) (toluene and acetonitrile mixture solution), and further Pd deposition on ZO. This synthetic process, which expended much energy at high temperature, achieved noble M-ZO NCs [85].

2.3. Electrical Synthesis Methods

The electrical synthesis method is an electrochemical cell synthesis of chemical compounds. An electrical synthesis has a major advantage over a normal redox reaction; the ability to precisely change the necessary potentials and to avoid unnecessary half reactions [86]. 'Pt-ZO' NCs were synthesised by electro chemical method at 200°C with 10 hours annealing process [87]. Another Pt-ZO nanoparticle synthesis was reported by Li et al., [88]. However, Pd based ZO NC was synthesised by using electro chemical method at 600°C for 3 hours [89].

3. Characterization

In nanotechnology, characterisations of the NCs are very important. In this paper, we have documented dissimilar characterisation techniques like Transmission electron microscopy (TEM), X-ray powder diffraction (XRD), Scanning electron microscope (SEM) and Fourier-transform infrared spectroscopy (FTIR). The characterisation techniques were summarized in subsequent sections.

3.1. X-ray powder diffraction (XRD)

The XRD method was generally employed to regulate and support the crystal arrangement of NC at 200°C. 'Scherer equation' was castoff for calculation of crystal dimensions. The Scherer equation was $D = K\lambda/\beta\cos\theta$; $K = 0.9$; D = Crystal size (Å); λ = Wavelength of Cu-Kα radiation; and β = Corrected half width of the diffraction peak. XRD spectra demonstrate efficient metal-ZO nanostructure synthesis and crystalline structures.

The noble metal M-ZO nanostructures can also be indexed in all XRD diffraction peaks as a combination of crystalline structure of noble metal (M) and ZO. For example, as illustrated in Fig.1a, Pd/ZO composite XRD spectra was indexed as an arrangement of a centre-cubic facing structure and the palladium (Pd) structure of ZO which resemble a stick like a flower, a star and a skin-like structure. Fig.1b represents the XRD peaks of the NCs. The '2θ' peaks of ZO compound were at 32°, 34°, 36°,48°, 57°, 63°, 66°, 32°, 68° and 69°, and the corresponding crystal index were (100), (002), (101), (102), (110), (103), (200), (112) and (201). The ZO-AgI synthesised XRD spectrum can be indexed as an arrangement of AgI's crystalline arrangement and ZO's seed structure. The XRD spectrums were used to show the noble metal - ZO composites' crystal structures.

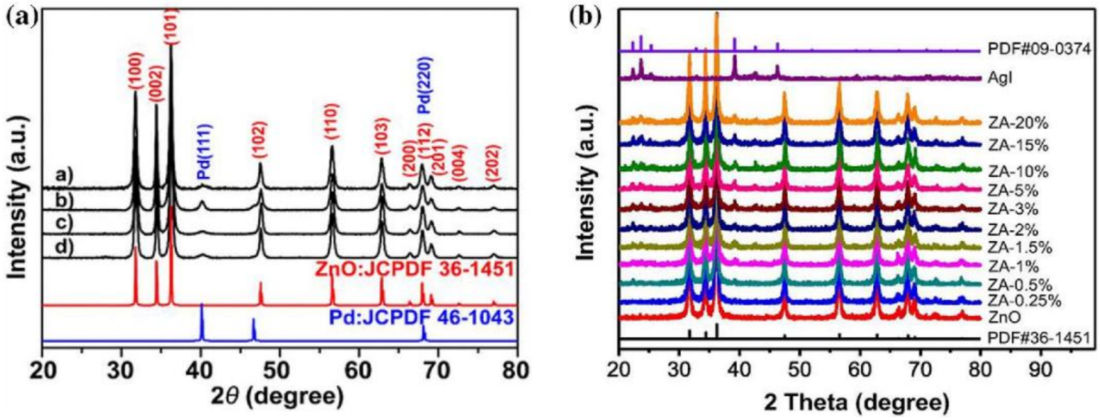

Fig. 1. XRD peaks of (a) Pd-ZO composites and skin needling-like structure, star-like structure, flower-like structure and tube-like structure [Reprinted (adapted) with permission from (Ref. 77). (b) ZO-AgI (Reprinted (adapted) with permission from (Ref. 77)].

3.2. Scanning electron microscope (SEM)

Field emission scanning electron microscopy (FESEM) was used to acquire the grain evidence and superficial morphology of NPs. The structures look like urchin, petal, sponge, comet and orange. Fig.2. (a-j) represents the SEM structure of yttrium (Y) based ZO NPs. The particles were rod-shaped, paddy-seed-like particles and that they are arranged in a well-ordered manner, with the average grain size of the NPs being 10 ± 2 nm. 3D nanoflower like structures of ZO fabricated through Palladium (Pd), Silver (Ag), Platinum (Pt) (Fig.2e) and Gold (Au) (Fig.2f); urchin like, and petal like, 'Au–ZO' nanoflowers; 'Au–ZO' nano-multipods, and nanopyramids; 'Ag–ZO' hollow microspheres (Fig.2g); sponge like ZO microcuboids (Fig.2h); Comet like (Fig.2i) and hexagonal rod aggregate (Fig.2j) 'Au–ZO' structure.

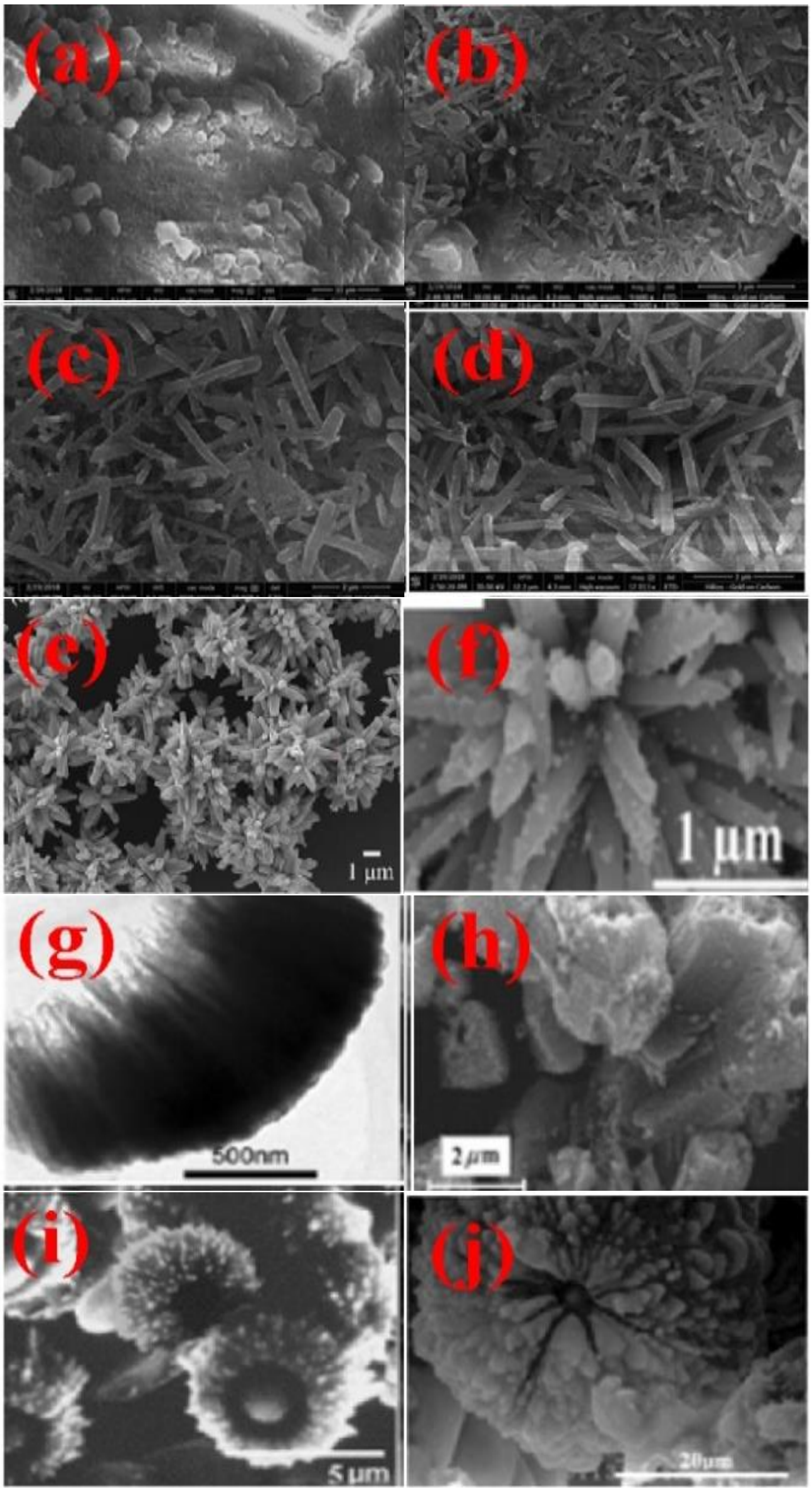

Fig. 2. Some examples of SEM images of the NPs (a-d) (Reprinted with permission from Ref. 90, https://pubs.acs.org/doi/10.1021/acsomega.9b03875, further permissions related to the material excerpted should be directed to the ACS). (e) Platinum (Pt) [Reprinted (adapted) with permission from (Ref. 91). Copyright (2010) American Chemical Society] and (f) Gold (Au) [Reprinted with permission from (Ref. 92)]; (g) 'Ag–ZO' hollow microspheres [Reprinted (adapted) with permission from (Ref. 93). Copyright (2008) American Chemical Society] (h) sponge like ZO microcuboids [Reprinted with permission from (Ref. 94)] (i) Comet like [Reprinted with permission from (Ref. 95)] and (j) hexagonal rod aggregate 'Au–ZO' structure [Reprinted (adapted) with permission from (Ref. 96). Copyright (2007) American Chemical Society].

3.3. Transmission electron microscopy (TEM)

Fig.3 represents the TEM structure of Pd based ZO NPs. The TEM images showed a simple design with the decoration of Pd NPs for ZO nanowires that indicated good transportability of electrons from ZO to Pd. Fig.4 represents the Synthesis process and Transmission Electron Microscopy (TEM) images of 'Au-ZO' nano-particles.

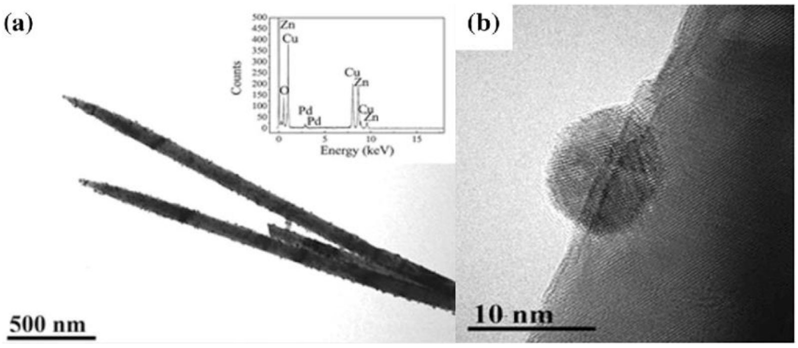

Fig. 3. Pd – ZO NPs (a) elemental identification and (b) TEM image with 10 nm magnification [Reprinted with permission from (Ref. 97)].

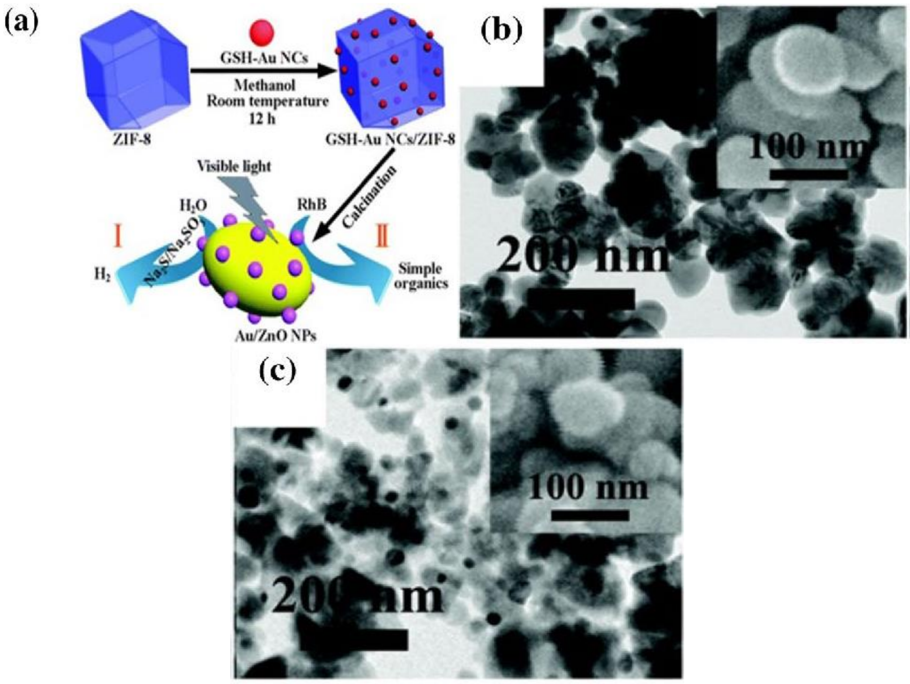

Fig. 4. (a) Construction method of 'Au-ZO' from ZIF8, (b) TEM image of ZO and (c) TEM image of 'Au-ZO'NPs [Reprinted with permission from (Ref. 98)].

4. Applications

NCs have several applications such as sensors, photocatalytic activities, catalytic activities, antimicrobial activities, DNA binding properties, anticancer activities, magnetic properties, adsorption properties, drugs, solar plate battery materials, fuel cells, solar cells, gas sensors, UV detectors and reduction of H_2O_2. In this paper, some important applications such as sensors, biological properties, photocatalytic and catalytic activities of M-ZO NCs were documented and elaborated in subsequent sections.

4.1. Sensors

NCs have excellent sensor property. It may be sensing of hydrogen gas, Liquefied petroleum gas (LPG), heavy metal ions, ethanol, acetone, carbon monoxide etc. Majhi et al., reported the sensing property of NCs with respect to hydrogen gas [99]. LPG and ethanol were sensed through Pd-ZO as reported by Baruwati et al., [100]. The hydrogen gas was sensed by the NC of Pt-ZO [101]. Jian et al., have reported the sensing property of Pd based ZO NC with respect to H_2S [102]. The Pd-ZO NPs were used for sensing the acetone organic solvent [103]. The Au/ZnO sensor manifests higher response, faster response–recovery time and good repeatability, resulting from the combination of 1D nanostructure with unique properties of Au NPs as reported by Guo et al., [104]. Ahmad Husain et al., reported the flower-like NC of Pt-ZO (Fig.5) which had gas sensing property. Flakes with tube-like polythiophene/ZO NC for LPG sensing application has also been reported [105].

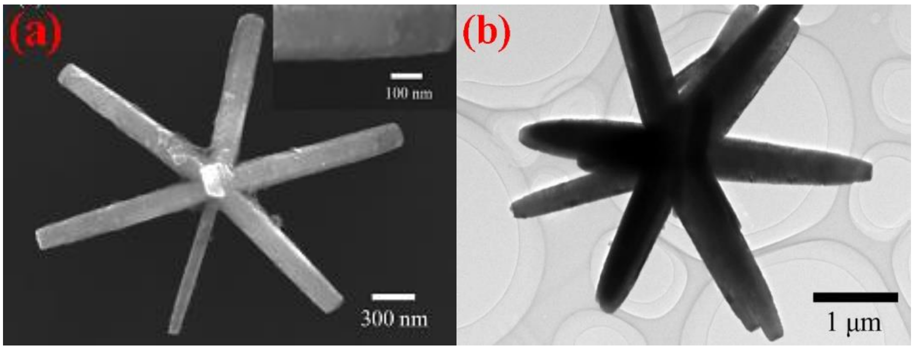

Fig. 5. (a-b): SEM and TEM images of flower-like NC of Pt-ZO [Reprinted (adapted) with permission from (Ref. 106). Copyright (2010) American Chemical Society].

4.2. Photocatalytic activity

Owing to the rise in population density, combining waste water runoff from various dye industries like pigment, textile, completing demands and photographic, drinking water is a serious concern in recent years over the globe. Majority of the waste water industries produce a range of natural azo colours that are poisonous and highly hazardous in nature, and are unhealthy for marine and humans. Azo Dye, for example, was the principal materials in dye industry; naphthol orange, methyl orange, rhodamine B, conga red, etc. Many scientists from across the globe are currently working on this field, using transitional NPs based on metal, to resolve the issue through the expulsion of unsafe colours [107-120].

To overcome this issue of a photocatalytic degradation technique, organic contaminants can be separated from colour dyestuffs into safe water, among other methods. Lee at el., investigated the photoctalytic activity of ZO/maghemite NCs against 2, 4-dichlorophenoxyacetic acid [121]. Lachheb et al., discovered the 'photocatalytic' degradation against methyl blue (MB) by using ZO–Fe_2O_3 NC [122]. Wu et al., reported the photocatalytic degradation over RhB [123]. Lei et al., synthesised NiO-Fe_2O_3-ZO and investigated the photocatalytic property against MO and 2-nitrophenol. They reported that, MO was found degrading 96.2% within 240 minutes and 2-nitrophenol was found degrading 93.1% within 240 minutes [124]. Sun et al., synthesised $ZnFe_2O_4$/ZO NC and investigated their corresponding photocatalytic properties [125].

4.3. Biological Properties

NCs have biological applications such as antibacterial activity, antifungal activity, anti-cancer activity, DNA binding etc. Bacteria is external cell wall structure used for labelling, both classified as 'gram positive' or 'gram negative'. Gram positive bacteria are heavier than gram-negative bacteria, with an outside membrane of the gram-negative bacteria, with peptidoglycan in their cell walls [126].

This reveals that, gram negative bacteria are packed in between the plasma membrane and outer layer, in the extra layer (periplasmic) as seen in Fig.6a. This layer is however, as described earlier, thinner than that of gram positive bacteria, and hence capable of diffusion and eventually damaging of cells owing to 'antimicrobial' nanocomposition [127-129].

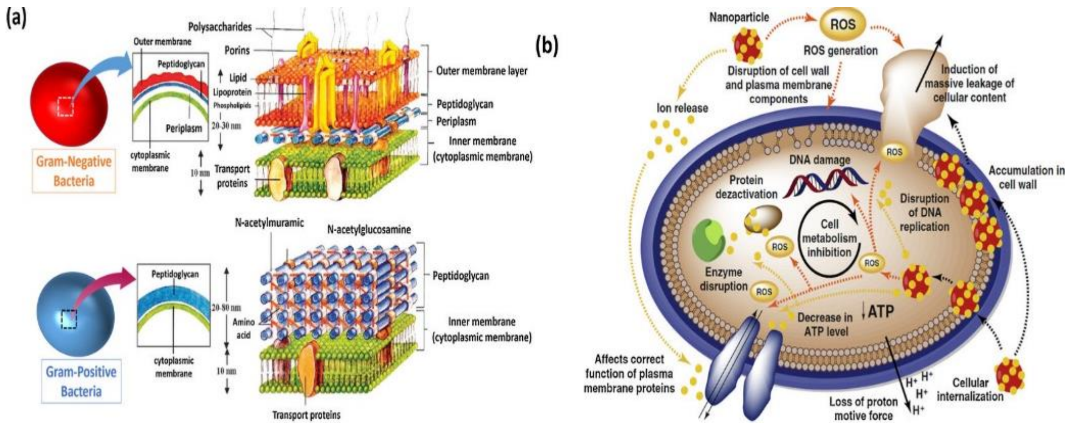

Fig. 6. (a) Evaluation among 'gram positive' and 'gram negative' bacteria's cell wall structures [Reprinted with permission from (Ref. 130)] (b) Schematic representation of antimicrobial mechanisms of metal ions [Reprinted with permission from (Ref. 131)].

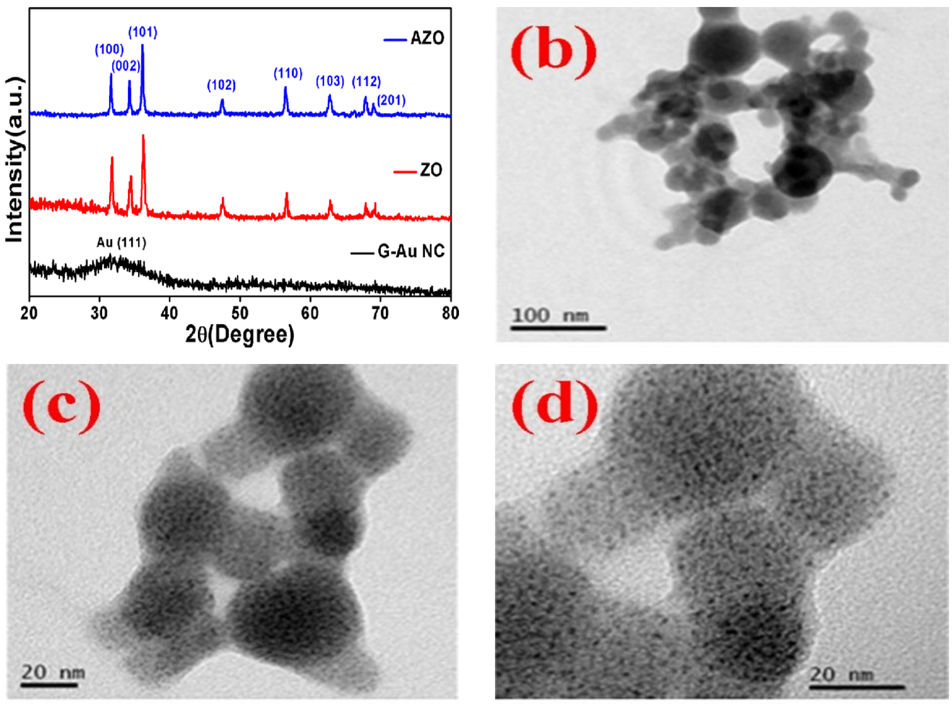

Fig. 7. (a) FTIR study of pure glutathione (G), Gold nanocluster (GAu NC), ZO−Au nanocomposite (AZO), and instinctive ZO, (b-d) TEM bright field images of ZO−Au NCs [Reprinted with permission from (Ref. 137), further permissions related to the material excerpted should be directed to the ACS].

K. A. Mohammed et al., synthesised Au-ZO and Ag-ZO NPs and subsequently characterised by UV-vis, XRD, electron microscopy (FESEM, TEM), and EDS. They investigated the antimicrobial activity by using fluorescence microscope and colony forming assay. They used gram positive bacteria such as *Escherichia coli* (*E. coli*) and gram negative bacteria such as *Staphylococcus aureus* (*S. aureus*) [132]. Ogunsona et al., documented the conventional antimicrobial activity of NPs [133]. Pandimurugan et al., synthesised ZO NCs and studied their antimicrobial activity [134]. Feng et al., synthesised NPs and investigated the antimicrobial activities [135]. Sun et al., reported the antimicrobial activity on synthesised NPs [136]. Fluorescence titrations of ZO-Au NC with the different DNAs carried out by Das et al., revealed the favorable binding interactions of NC towards calf thymus DNA with a maximum blue shift of the surface-related spectra of the NC [137]. The studies concerning ZO−Au NC was synthesized by fixing a glutathione-protected gold nanocluster on the surface of egg-shell-membrane based ZO NPs. Chakra et al., reported the enhanced antimicrobial and anticancer response of ZO/TiO_2 NCs [138].

Zamani et al., synthesized TiO_2@ZO NPs core–shell nanostructured and TiO_2@ mesoporous ZO–graphene oxide (TiO_2@ZO–GO) by sonochemical method. The SEM and TEM results indicated that, these NCs had a diameter about 190 nm and hexagonal in shape. The TiO_2@ZO–GO showed pH-dependent drug release behaviour due to the presence of large amount of carboxylic acid group. It was seen that, the release of curcumin from TiO_2@ZO–GO was dependent on pH of the medium [139].

4.4. Other Applications

Apart from aforementioned applications, ZO NCs find applicable in several other applications too. Few applications include magnetic property, adsorption property, solar panel, battery materials, fuel cells, solar cells, gas sensors, UV detectors and reduction of H_2O_2. Typek et al., reported the magnetometric studies of ZO/CoO NCs prepared by hydrothermal technique [140]. Ag-ZO/graphene oxide (Ag-ZO/GO) NC was produced by Tran Thi et al., and it was characterized by distinctive techniques such as XRD, SEM, Energy dispersive spectroscopy (EDS), HRTEM, X-ray photoelectron spectroscopy (XPS) and Brunauer–emmett–teller (BET) surface area techniques. They have reported the adsorption and photocatalytic activities of Ag-ZO/GO NC [141].

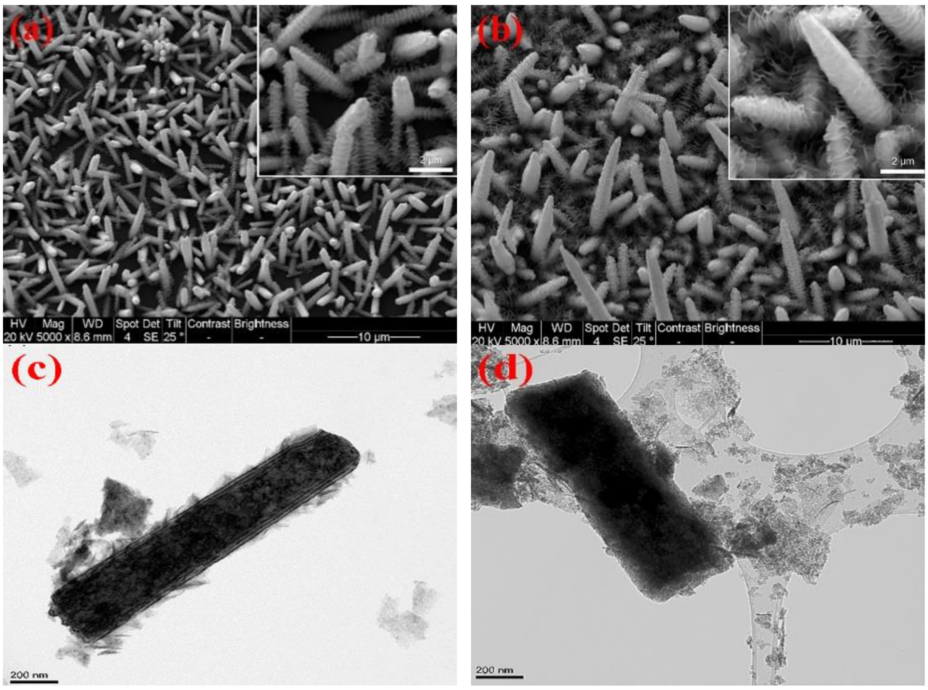

Fig. 8. SEM images of Co_3O_4@ZO nanorods with (a) 120 s of deposition time, (b) 360 s of deposition time, TEM images of Co_3O_4@ZO nanorods with (c) 120 s of deposition time, (d) 360 s of deposition time [Reprinted with permission from (Ref. 144)].

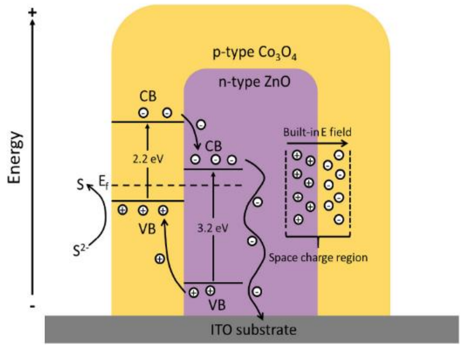

Fig. 9. Schematic representation of the p-n junction at Co_3O_4/ZO interface and the energy band structure of Co_3O_4@ZO NC photoelectrodes [Reprinted with permission from (Ref. 144)].

Co_3O_4@ZO NCs with core shell structure were produced by electrodeposition method by Yang et al., [142]. They characterized the material by XRD, SEM, EDS, Raman spectra and UV-vis, and subsequently analyzed the photoelectrochemical response under visible light. Ammonia gas sensor based on carbon nanotubes/reduced grapheme oxide/ZO NC was reported by Mohammed et al, [143]. Pandimurugan et al., reported the Ag modified ZO NC derived from Ag@ZIF-8 precursor for anode in Zn/Ni batteries [145]. Raza et al., developed ZO/NiO NC using a cost effective method using electrodes for low-temperature solid oxide fuel cells at 300°C-600°C [146]. Solvothermal and spin-spray coating methods were adopted by Mokhtar et al., to produce grapheme oxide-ZO NC for UV detection application [147]. Photochemical synthesis of Ag, Pd, Au, Pton Graphene/ZO Multihybrid nanoarchitectures as electrocatalysis for H_2O_2 reduction was anayzed by Das et al., [148]. The SEM and TEM images of Co_3O_4@ZO nanorods produced at different deposition times are displayed in Fig.8. Illustration of the p-n junction formed at Co_3O_4/ZO interface and the energy band structure of the photoelectrodes is given in Fig.9. Some examples of ZO based NCs with structure, synthesis and applications are shown in Table 2.

Table 2. Some examples of ZO based NCs with structure, synthesis and applications.

Structure of material	**Method of synthesis**	**Uses**	**Ref.**
Y-Zn NCs	Solution method	Photocatalytic activity and catalyst	7
Pd and Au NCs	High temperature method	Sensing	55
Pd–ZnO NCs	Solution method	Adsorbed oxygen and photocatalytic activity	56
NiO-CdO-ZnO NCs	Solution method	Photocatalytic activity	57
Ag–ZnO NCs	High temperature method	Photocatalytic activity	58
Pd–ZnO NCs	High temperature method	Sensing	59
Pt–ZnO nanorods	Electrical method	Photoelectrochemical water splitting	62
Ag–ZnO NCs	High temperature method	Enhanced photo-induced electron-transfer reactions	65
Pt–ZnO NCs	High temperature method	Sensing	66
Pt–ZnO NPs	High temperature method	Phenol degradation	67
ZnO-Fe_2O_3	Solution method	Photocatalytic activity	68
ZnO/maghemite	High temperature method	Photocatalytic activity	69
Fe_2O_3@ZnO	Hydrothermal method	Photocatalytic activity	70
NiO–Fe_2O_3–ZnO	Solution method	Photocatalytic activity	71
Y doped ZnO	Solution method	Antibacterial and photocatalytic activity	72
Pt–ZnO NCs	Electrical method	Sensing	73
Au–ZnO nanosheets	High temperature method	Sensing	73

Structure of material	Method of synthesis	Uses	Ref.
Au–ZnO nanoflowers	High temperature method	Sensing	74
Mg^{2+} doped Pd–ZnO	High temperature method	Oxidative reaction	75
Graphene-Pt/Pd–ZnO	High temperature method	Oxidative reaction	76
Pd/ZnO NCs	Solution-Precipitation	Catalysis	79
Ag-ZnO nanosheets	Liquid-liquid two phase	Photocatalysis	80
Pd-ZnO NPs	Calcination	Photocatalysis	81
Ag-ZnO NPs	LASER induction	Photocatalysis	82
Pd-ZnO NPs	Calcination	Gas sensing	83
Au-ZNO coreshell NPs	Low temperature solution route	Gas sensing	84
Pd-ZnO NPs	Flame spray pyrolysis	Gas sensing	85
Pt-ZO nanorods	Electrochemical	Photoelectrochemistry	87
Pd-ZnO nanowires	Self-assembly	Gas sensing	116
Pd-ZnO nanoarchitectures	Solvothermal	Acetone sensing	117
Au-ZnO nanowires	Solution-reduction	Gas sensing	118
Polythiophene-ZO NC	chemical oxidative polymerization	Gas sensing	119
$ZnFe_2O_4$/ZnO NCs	Ultrasound Solution	Photocatalysis	136
Au/Ag-ZO NCs	Chemical precipitation	Antimicrobial	143
Seaweed-ZO NCs	Chemical precipitation	Antibacterial	145
$H_yZnxNa_{2-x}Si_{14}O_{29}n$ H_2O	Ion exchange reaction	Ion exchange method	147
ZnO –Au NCs	Solution method	DNA binding	148
ZnO-TiO_2 NCs	Solution combustion	Antibacterial and anticancer	149
TiO_2@ZnO–GO	Sono-chemical	Drug delivery	150
ZnO/CoO NCs	Sol-gel	Magnetic interaction	151
Ag-ZnO/GO	Solvothermal	Photocatalysis	152
Co3O4@ZnO NCs	Electrodeposition	Photoelectrodes	153
Carbon nanotubes/reduced GO/ZO NCs	Solution method	Gas sensing	154
Ag/ZO NC	Precipitation	batteries	155
ZnO/NiO NCs	Solid-state reaction	Solid oxide fuel cell	156
GO-ZO NCs	Solvothermal, Spin-spray coating	UV detection	157
Graphene-Pd/Ag/Pt/Au–ZnO	High temperature method	Reduction of H_2O_2	158

5. Future Challenges and Perspectives

Since noble M -ZO NPs have previously been fundamentally investigated in their synthesis processes, structures and application, few alterations in physical properties can be additionally made by adapting the operational conditions or modifying the nano forms. Therefore, according to the aforementioned works, numerous other nanostructures can be produced for improved or unique applications with modifications in the materials. One methodology for further enhancement of the catalytic activity of nanostructures from noble M-ZO was the metal ion doping. As a future research, applications that employ synthetic materials should also be investigated. Moreover, the lifetime of photoluminescence is typically a significant factor. The future works of science and engineering experts in this domain will therefore be the design, syntheses and optimisation of noble metal ZO NCs.

6. Conclusion

Noble M-ZO NCs were considered to be one of the most functional photocatalysts, and their superior catalytic properties and super stability have attracted growing interest towards research and development. This present study addresses the noble M-ZO nano composites by different composites or catalytic arrangements. In this review, the synthesis process (Solution-based methods, High temperature-based methods and Electrical methods) were documented and the characterisation technique such as XRD, SEM and TEM on various noble NCs of metal M-ZO were also addressed. So as to report the ongoing research issues, multiple applications like photocatalytic, catalyst, sensor and biological activity were investigated. It was obvious that, the catalytic activity of noble M-ZO nanostructures depends not only on the noble metal species, but on the catalytic material structural design as well. The noble metal-ZO nanostructures have proved their catalytic activity depending not only on species of noble metals, but also on the architectural features of the catalyst. In addition, standard modification works have been implemented on noble ZO nanostructures. The opportunities for future research and development, and future prospects were clearly illustrated.

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