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REVIEW ARTICLE

Bimetallic Oxide Nanocomposites for Better Photocatalytic Activity: A Review

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ABSTRACT: Bi-metallic oxide photo-nanocatalysts are being explored extensively for removal of organic and inorganic pollutants like dyes and pesticides in an environmental benign and sustainable manner. The problems associated with the existing catalyst, are their high band gap values and large particle sizes. In this review, the photocatalytic degradation of pollutants from industrial waste water by using negligible amount of bi-metallic oxide photo-nanocatalysts has been covered as a solution of such types of problems. The photocatalytic activity of the nanocomposites was reported to be affected by main components that include the particle size, nature of crystallinity, band gap, morphology and surface area of the photocatalysts. Despite various required optimizations, the bi-metallic oxide nanocomposites like Cu/ZnO, Zn/CuO, Cu/NiO and Zn/NiO synthesized by using different methods have been shown to act as better photocatalysts as compared to others. This review article may open a new avenue to control the industrial waste water pollution in efficient and cost-effective way.

Keywords: Bi-metallic nanocomposite; Dye; Industrial waste water; Pesticide; Photocatalyst

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1. INTRODUCTION

The technology involves the treatment of atoms/molecules at nanoscale known as nanotechnology [1]. It is the manipulation of things with at least one dimension sized from 1 to 100 nm. Recently, in nanotechnology, scientists are focusing on the synthesis of nanomaterials by using green technology for various unique and effective properties required for applications in different fields [2-5]. Further, nanocomposite is a mixture of different materials with heterogeneous phases and applications in different fields (figure 1), as sensors, photocatalysts, drug carriers, cosmetics, filling materials in medical industries and antimicrobial agents [6].

A number of physical and chemical methods including microwave-irradiation, sol-gel, co-precipitation, chemical vapour deposition and mechanical alloying have been investigated for the synthesis of potential metal oxide nanocomposites [7-9]. Medicinal plant mediated microwave methods have many advantages to other physical and chemical methods, as over conventional heating, this method includes profound inside heating and decreases the reaction time. Moreover, green synthesis eliminates the use of costly chemicals and provides financial as well as green benefits. The use of various concentrations of plant extract led to the formation of shape- and size-based metal oxide nanocomposites for improved antimicrobial, antifungal, anti-inflammatory, antioxidant, catalytic and photocatalytic applications [10-12].

With the day-by-day developments in the industrial sector, a large number of effluents containing carcinogenic and toxic chemicals that harmfully affect the living organisms and the environment are being released into the water bodies. This is main reason for water crisis in our daily life, despite the truth that three fourth of earth's part is submerged in water. Even the presence of traces of heavy metals and toxic chemicals can persuade toxicity of water. Consequently, it is necessary to degrade and remove the water contaminants truthfully before its uses in various fields to eliminate the severe threats to public as well as aquatic lives. In this context, the catalytic methods under UV or sun light are proved very significant for the purification of

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contaminated water (figure 2).

The heavy metals contact results into the developmental retardation, cancers, kidney failures, and even death in instances of very high exposure. Moreover, we cannot think of life without water or clean water, indeed, as it accomplishes various biological actions in the living organisms and used for various purposes such as household and industrialized activities, power generation, crop irrigation, and so on [13]. Consequently, water contamination remediation at large scale needs efficient and cost-effective approach like nano-photocatalysts. The various metal oxides nanocomposites, in contrast to micro and macro-materials, are playing crucial role as adsorbents and catalysts for degradation or removal of heavy metals, SO_2, CO, NO_X, organic and inorganic dyes, hydrocarbons, bacteria, viruses, parasites and antibiotics [14, 15]. In addition, they have high chemical and thermal stability and easily recyclable.

2. METAL OXIDES

2.1. Copper Oxide

The copper is a 3d-transition metal with atomic number 29 and pure copper occurs rarely in nature. Mainly copper founds in minerals such as azurite $[Cu_{39}(CO_3)_2)(OH)_2]$ and malachite $[Cu_2(CO_3)(OH)_2]$. Copper oxide nanoparticles (CuO NPs) are monoclinic in nature (figure 3) and are being used as catalysts, anti-oxidants, and anti-cancer agents as well as drug delivery mediators in the pharmaceutical field [16]. CuO NPs also playing a significant role in the field of sensor, catalyst, solar cell, and high temperature semiconductor devices [17]. In addition, these nanostructures are extremely helpful in antibacterial activities with very large surface area and show genotoxic effects in neuro cell cultures [18]. CuO with a low energy band gap of 1.2 eV is frequently used as p-type semiconductor. It has a monoclinic structure, great chemical constancy, and possesses anti-inflammatory, antibacterial, and ecologically friendly properties [10-12]. It is one of the most dazzling semiconductors available and mostly used in photo-electrochemical water reduction, gas sensing, catalytic activity, solar hydrogen production, photo-degradation processes, and photo-voltaic applications [19, 20]. Due to their distinct and promising features, CuO has recently received a lot of attention in scientific community for a wide range of applications in modern life.

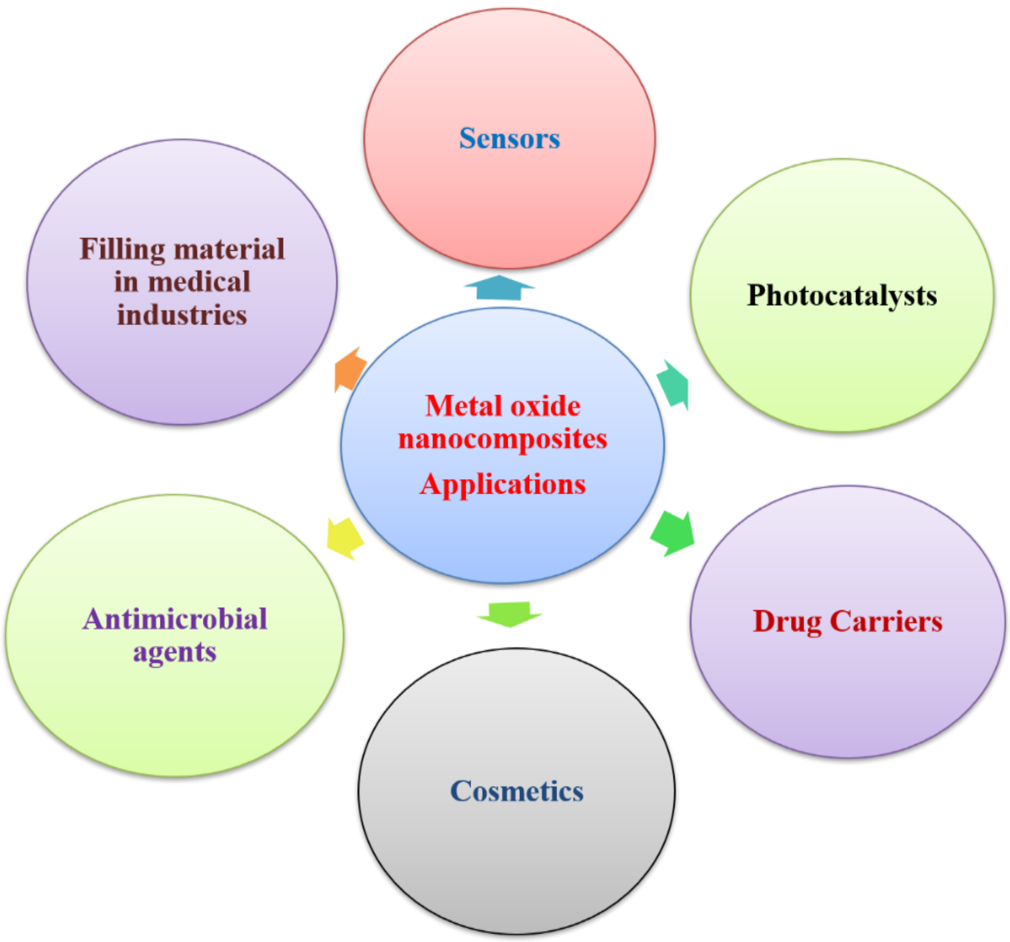


Fig. 1. Role of metal oxide nanocomposites in different fields.

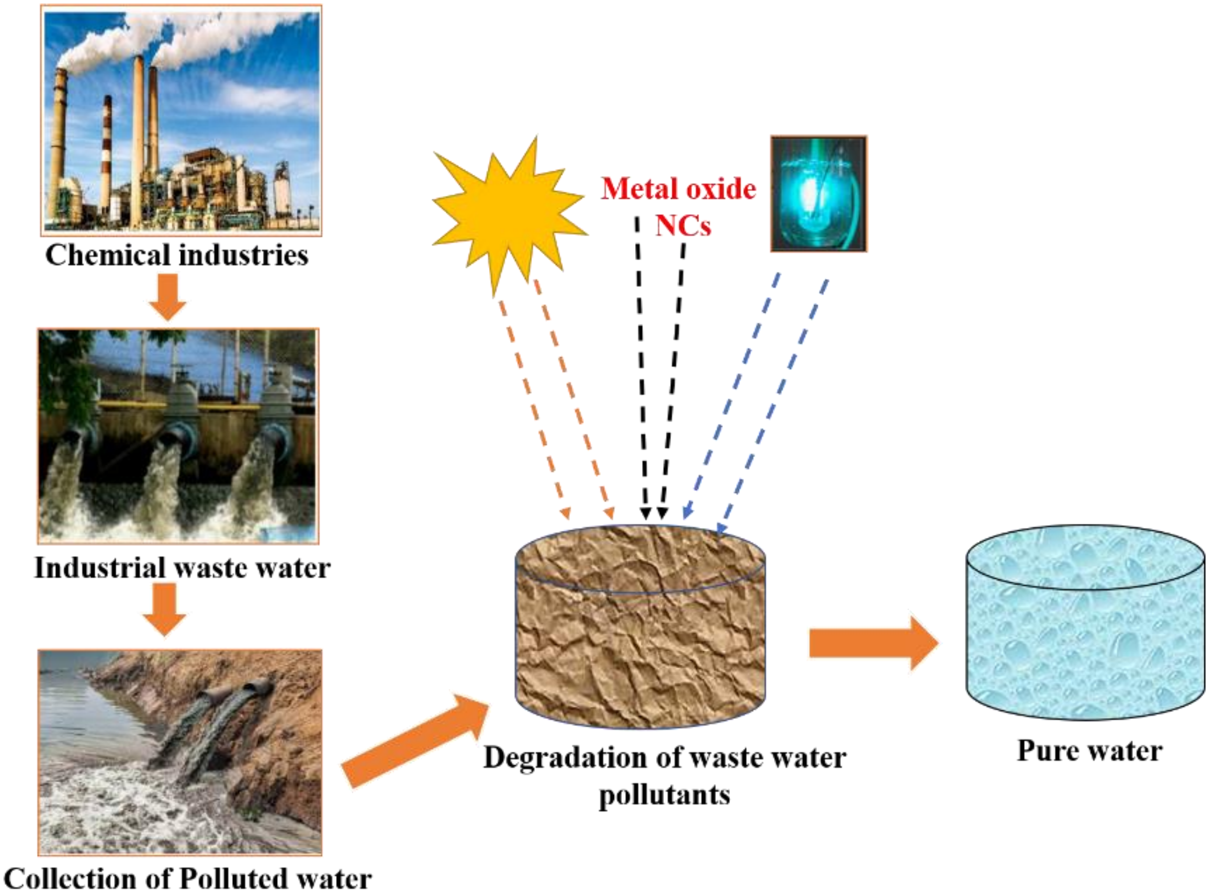


Fig. 2. Photocatalytic degradation of pollutants from industrial waste water by using metal oxide nanocomposites as photocatalysts.

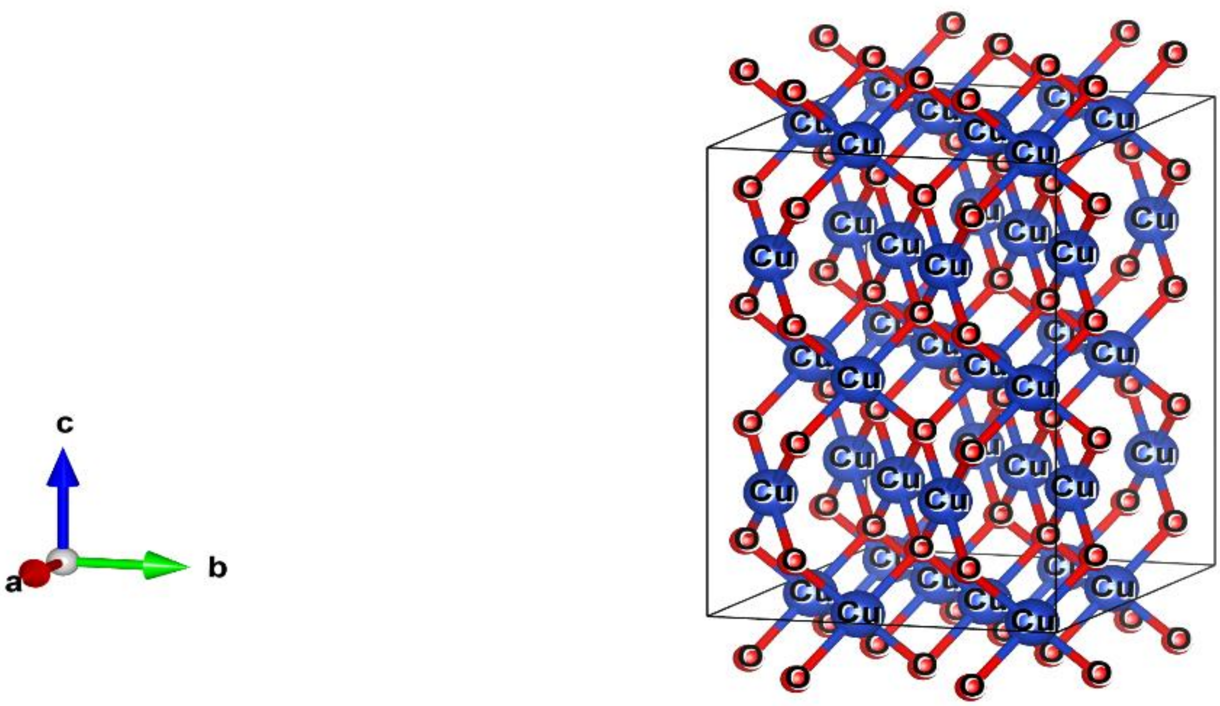


Fig. 3. Monoclinic crystal lattice of CuO**.**

Vaidehi et al. [21] studied an environmentally friendly synthesis of CuO NPs by using *S. lycopersicum* leaf extract and reported spherical NPs with size between 20 to 40 nm from scanning electron microscopy (SEM) and tunneling electron microscopy (TEM) images. The antibacterial action of so-obtained NPs shows concentration-dependence against pathogens, *B. spizizenii, S. aureus,* and *E. coli*. Furthermore, when exposed to regular visible light, CuO NPs demonstrated potential as photocatalyst against crystal violet (CV) cationic dye. Behera and Giri [22] synthesized Cu_2O NPs by a green chemical process for photodegradation of MB dye in the visible range. The SEM and TEM images depict the nanoclusters of diverse architectural types CuO_2 NPS with average size between 5 and 15 nm. The degradation of MB dye, according to absorption spectra, decreases non-linearly with Cu_2O concentrations and reaches a value of 90% after 120 minutes of exposure to light. Kayalvizhi et al. [23] reported the use of *A. muricata* leaf extract in the synthesis of CuO NPs with a roughly spherical shape and typical particle size 30 to 40 nm, as illustrated in figure 4. The so-synthesized CuO NPs have demonstrated effective dye removal up to 90 and 95% when tested on RR 120 and MO, respectively. Aminuzzaman, Kei, and Liang [24] have used banana peels, affordable, nontoxic, eco-friendly, and widely accessible green waste to synthesize well-crystalline spherical CuO NPs with an average particle size of 60 nm. The outcomes demonstrated that the biologically produced CuO NPs displayed exceptional photocatalytic performance against Congo red (CR) dye and may have potential uses in the remediation of industrial waste water.

2.2. Zinc oxides

The zinc, most abundant element in the earth crust, is also one of the 3d-transition metals with atomic number 30. Zinc exists in two types of crystalline structures namely, wurtzite and zinc blende, however, wurtzite structure is most common as shown in figure 5 [25]. Zinc oxide nanoparticles (ZnO NPs) exhibit the properties such as antimicrobial, photocatalytic and anti-oxidant activities. ZnO NPs are reported in unlike forms, for examples, rod-like, star like, isomeric, etc. and form clusters with a wide range of size from 30-150 nm. The ZnO, a n-type semiconductor with wide band gap (~3.3 eV) and high exciton binding energy of ~60 meV, form wurtzite crystal structure (figure 5), and shows piezoelectric properties.

Anbuvannan et al. [26] have used a facile green method to fabricates ZnO NPs from different amounts of *A. carnosus* leaf extract. The diffraction patterns reveal that the particle size could be controlled by increasing the amount of leaf extract addition. The SEM and TEM analysis displayed quasi-spherical shapes with a rough surface and size between 30 to 40 nm (figure 6). The photocatalytic performance of the synthesized ZnO NPs proved its enhanced activity against the organic dye methylene blue (MB) under UV irradiation, which shows that *A. carnosus* leaf extract assisted ZnO NPs can open up a new route for controlling the organic pollutants. Zheng et al. [27] described a straightforward and environmentally friendly approach for developing ZnO NPs that makes use of a stabilizing agent, *C. citriodora* leaf extract. According to XRD patterns, the ZnO NPs were found to exists in hexagonal wurtzite. This method is also mentioned as the one which can be used to synthesize ZnO NPs on an industrial scale. The small size (64 nm) biosynthesized ZnO NPs are more efficient photocatalysts than that of those synthesized conventionally through hydrothermal preparation. Aminuzzaman et al. [28] were reported the green synthesis of well-crystalline ZnO NPs with hexagonal wurtzite phase and an average size of 21 nm by using *G. mangostana* fruit pericarp extract. The so-obtained spherical or hexagonal shaped ZnO NPs as shown in figure 6, displayed exceptional photocatalytic efficiency by degrading malachite green (MG) dye up to 100 % when exposed to natural sunshine.

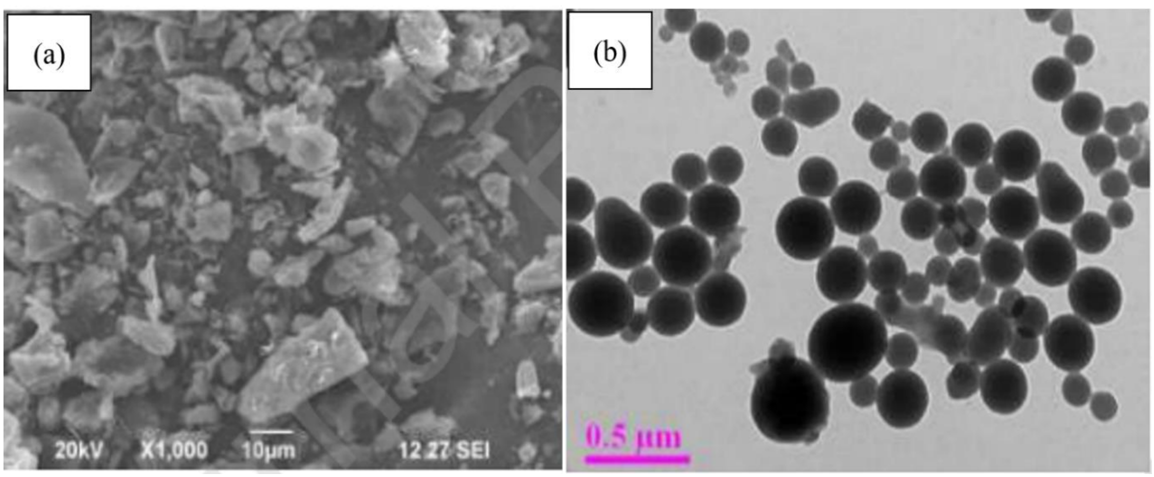


Fig. 4. (a) SEM and (b) TEM images of CuO nanoparticles. Reprinted with permission from ref. [29], Kayalvizhi, S., Sengottaiyan, A., Selvankumar, T., Senthilkumar, B., Sudhakar, C., Selvam, K., **2020**. Eco-friendly cost-effective approach for synthesis of copper oxide nanoparticles for enhanced photocatalytic performance. *Optik*, 202, p. 163507. Copyright © ScienceDirect.

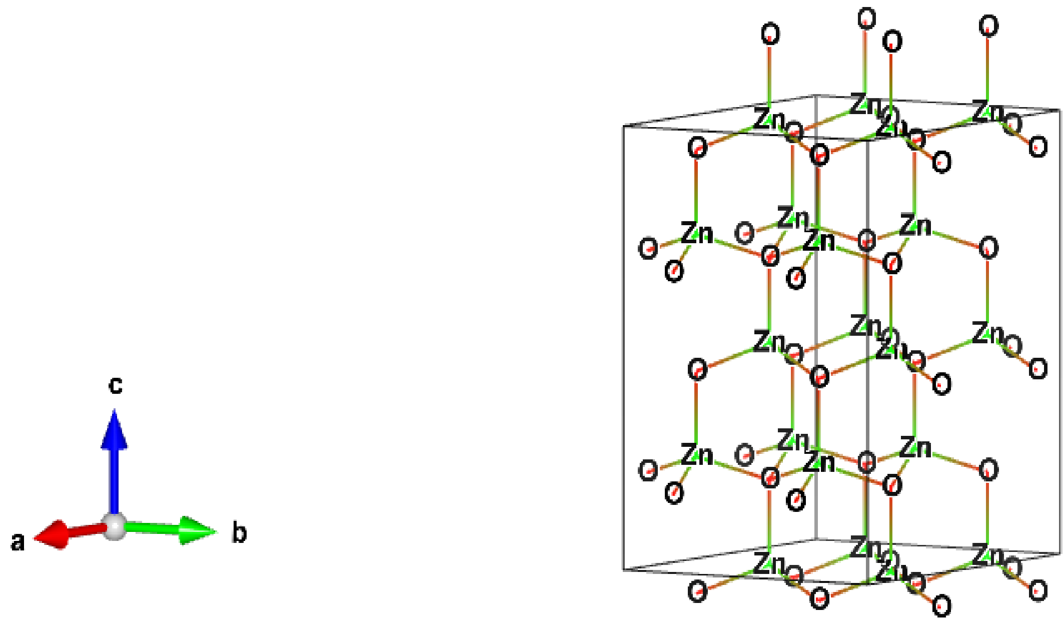


Fig. 5. Wurtzite hexagonal crystalline structure of ZnO.

Balcha et al. [30] compared the photocatalytic activity of ZnO nanoparticles synthesized by precipitation and sol-gel techniques against the degradation of MB dye and reported that 81 and 92.5%, respectively, degradation of 20 mg/L MB in 3 hours. Therefore, the sol-gel method is preferred over the precipitation method in order to produce ZnO nanostructures with better photocatalytic activity. However, the selection of the capping ligand is also essential in this procedure. By correctly altering the synthesis pathways, ZnO nanostructures with creation of required defects can result in even higher photocatalytic activity results.

2.3. Nickel oxide

The nickel is a transition metal with atomic number 28 and mostly found in limonite [$(Ni,Mg)_3Si_2O_5(OH)$] and pentlandite [$(Ni,Fe)_9S_8$] ores. It also found in magmatic sulfide deposits, where the principal ore mineral is pentlandite [$(Fe,Ni)_9S_8$] and sometimes found free in nature. Nickel oxide nanoparticles (NiO NPs) are electrically conductive and hence used for various applications specially as a potential antioxidant. NiO NPs are existing as nanofluids, ultra-high pure, coated, and dispersed forms.

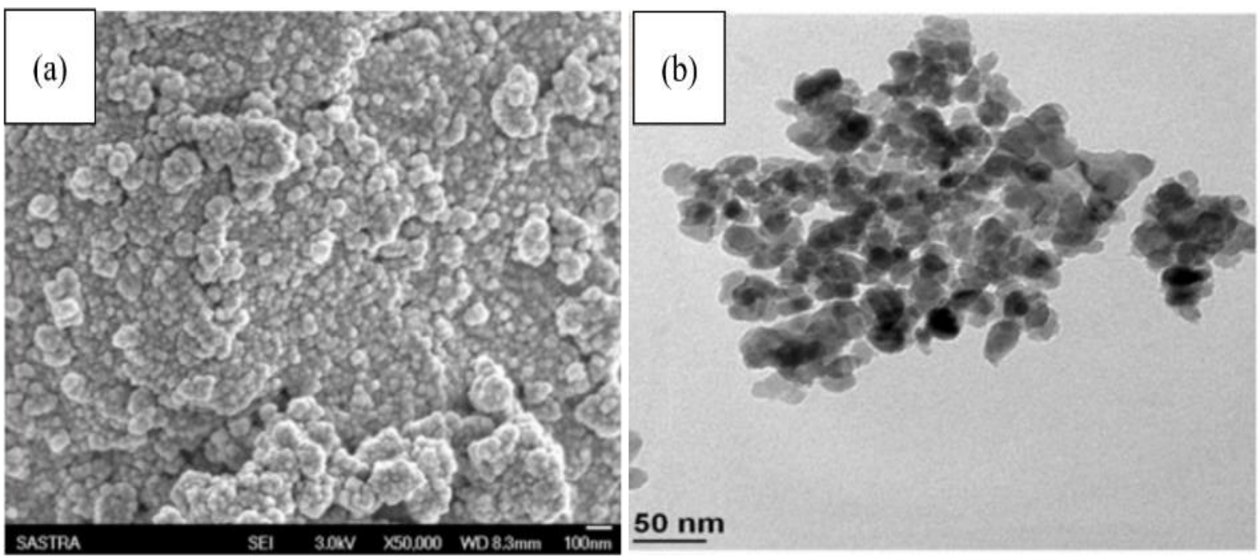


Fig. 6. SEM (a) and TEM (b) images of ZnO NPs. Reprinted with permission from ref. [26], Anbuvannan, M., Ramesh, M., Viruthagiri, G., Shanmugam, N., and Kannadasan, N., **2015**. *Anisochilus carnosus* leaf extract mediated synthesis of zinc oxide nanoparticles for antibacterial and photocatalytic activities. *Materials Science in Semiconductor Processing*, 39, pp. 621-628. Copyright © ScienceDirect.

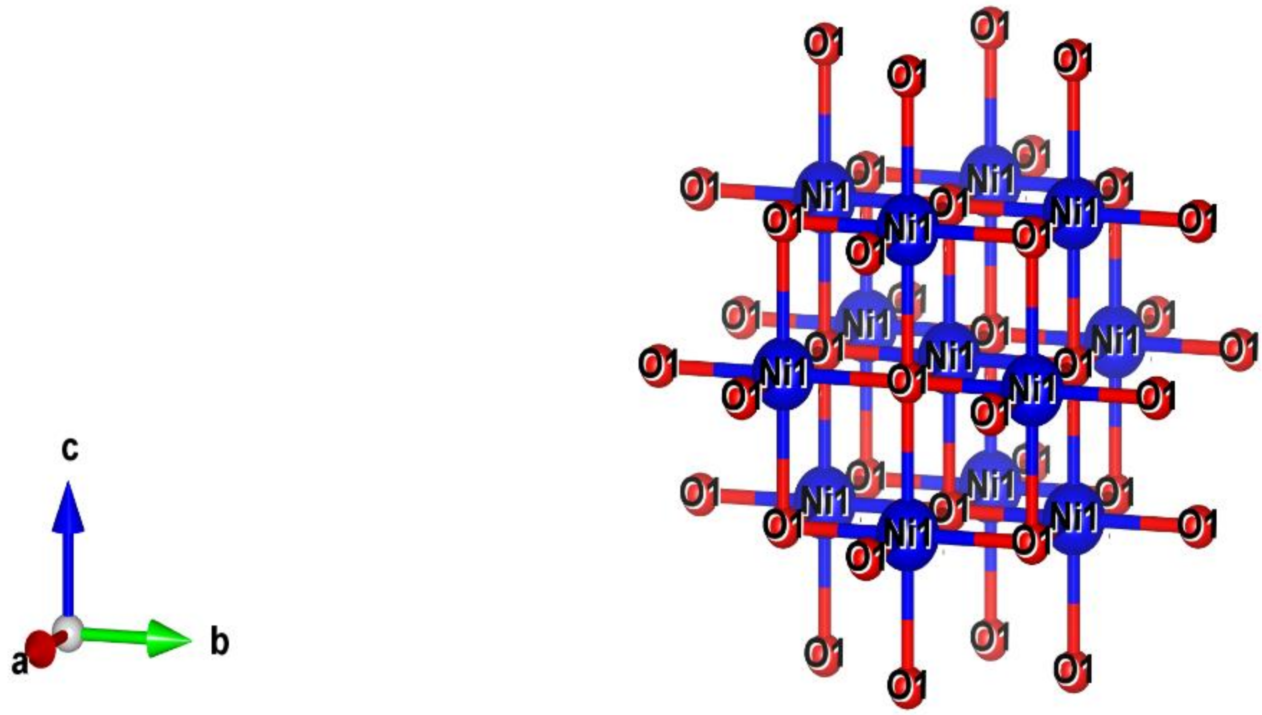


Fig. 7. Cubic crystalline structure of NiO.

In recent past, NiO has attracted the attention of scientists worldwide for various technological applications including the uses as anti-ferromagnetic material [31], electrode materials for lithium-ion batteries [32], and electro chemical super capacitors [33]. Being a wide band gap (3.6-4.0 eV), as a p-type semiconductor it is extensively used in many fields as adsorbents, solar and fuel cells, photocatalytic agents, gas sensors, magnetic and antibacterial materials. The cubic crystalline structure of NiO is shown in figure 7.
Kannan et al. [34] have successfully synthesized bio-mediated NiO NPs by using citrus fruits as the fuel. The formation of a cubic structure was revealed by the typical reflections with a most intense (200) peak in the XRD patterns. The SEM images reveal the uniform distribution of NiO nanospheres. The ZnO NPs degraded up to 91% of Evans blue (EB) dye through a photocatalytic process. Accordingly, the NiO NPs were found suitable for photocatalytic, optoelectronic, and medicinal applications. Ezhilarasi et al. [35] were proposed an *Aegle marmelos* leaf extract as a reducing and capping agent to form aggregated spherical NiO NPs. The so-obtained small sized 8-10 nm NPs (figures 8a-b) have been reported as strong cytotoxic agents for the A549 cell lines in addition to antibacterial and photocatalytic activities. Karthik et al. [36] were reported the microwave assisted green method for the synthesis of cubic NiO NPs. SEM and TEM images (figures 8c-d) illustrate the uniform morphology of nanosized spherical NiO NPs. In this study, NiO NPs were used as photocatalyst to degrade EB dye and superior anticancer agents against the human breast cancer MCF-7 cell line. Ezhilarasi et al. [37] were proposed the *Solanum trilobatum* leaf extract for the production of NiO NPs with cylindrical and rod-like morphology (figures 8e-f). They are reported to show effective optoelectronic characteristics with significant surface defects, photocatalytic degradation of 4-CP up to 92% in 210 min, antibacterial activity against Gram positive bacteria, and cytotoxic activity against A549 cell lines.

2.4. Bimetallic oxides

Transition metal nanocomposites are significant and promising materials that have drawn attention due to their unique properties that are not present in traditional composites. Additionally, metal oxide nanocomposites have been recognized as substitutes to get rid of drawback of cluster formation in NPs [38]. Due to their unique remarkable features, transition metal oxide nanoparticles, particularly CuO and ZnO, have attracted considerable interest in scientific research for a wide range of applications in recent years [39]. The main disadvantage which limited the use of NPs in various fields is the increase in their size because of agglomeration, which reduces the surface area and, as a result, their activity and effectiveness in different aspects [40]. Consequently, a lot of scientific work is now being focused on the synthesis of metal oxide nanocomposites to increase surface area to enhance the photocatalytic, antibacterial, antifungal, and antioxidant capabilities of the nanomaterials. The Cu/ZnO, Zn/CuO, Cu/TiO_2, Zn/TiO_2, and Cu/NiO nanocomposites are some of the recent materials that have been used to enhance the photocatalytic activities of CuO and ZnO nanoparticles. The microwave mediated co-precipitation method was used to create the Cu/Graphene oxide nanocomposites [41].

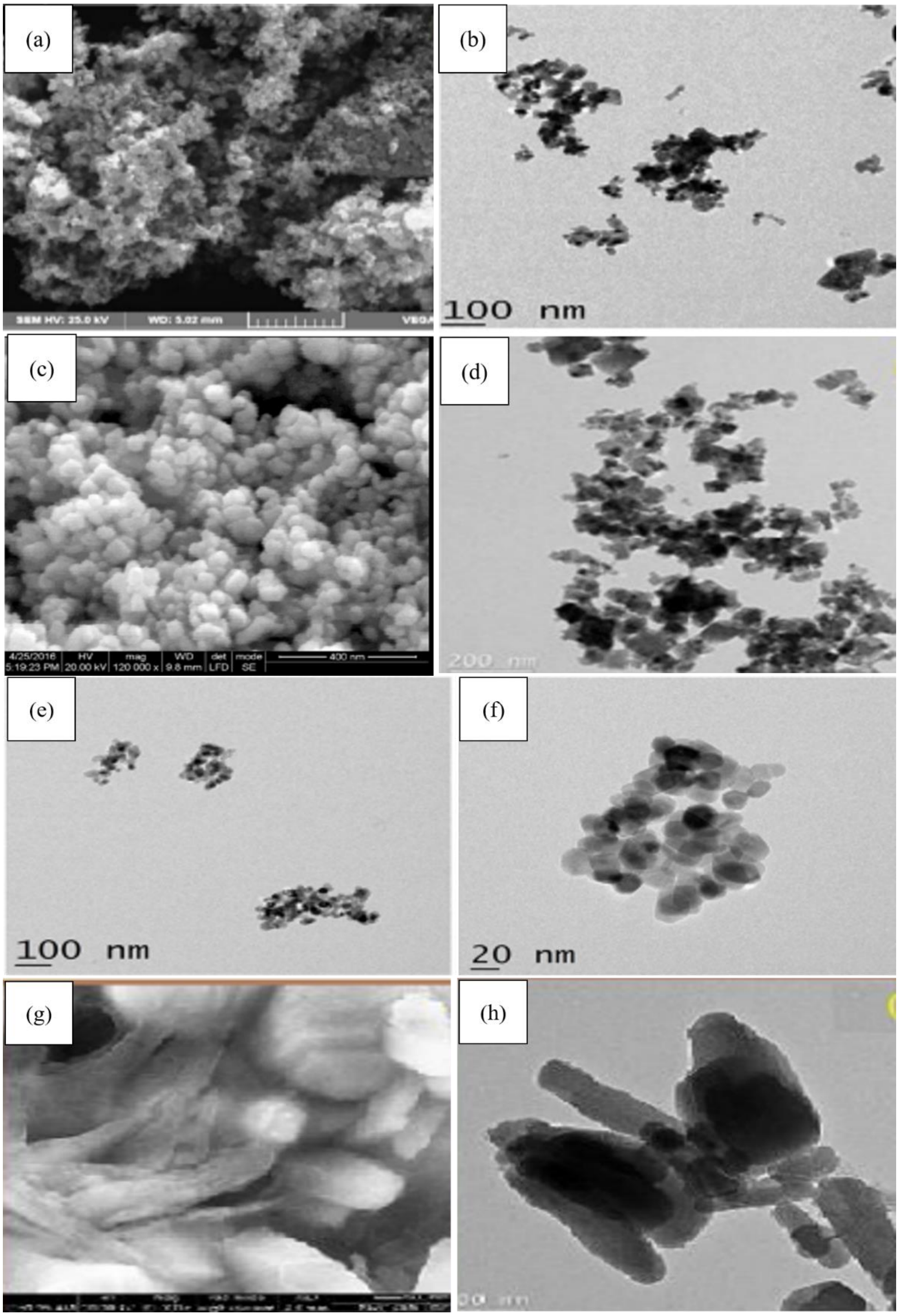


Fig. 8. SEM (a, c & e) and TEM images (b, d & f) of NiO nanoparticles reported in literature. Reprinted with permission from ref. [31], Krishnakumar, S.R., Liberati, M., Grazioli, C., Veronese, M., Turchini, S., Luches, P., Valeri, S., Carbone, C., **2007**. Magnetic linear dichroism studies of in situ grown NiO thin films. *Journal of magnetism and magnetic materials.* 310(1), pp. 8-12. Copyright © ScienceDirect; ref. [32] Ni, S., Li, T., and Yang, X., **2012**. Fabrication of NiO nanoflakes and its application in lithium ion battery. *Materials Chemistry and* Physics. 1(1) pp. 1108-1111. Copyright © ScienceDirect; and ref. [46] Gerawork, M., **2020**. Photodegradation of methyl orange dye by using Zinc Oxide-Copper Oxide nanocomposite. *Optik*, 216, p. 164864. Copyright © ScienceDirect.

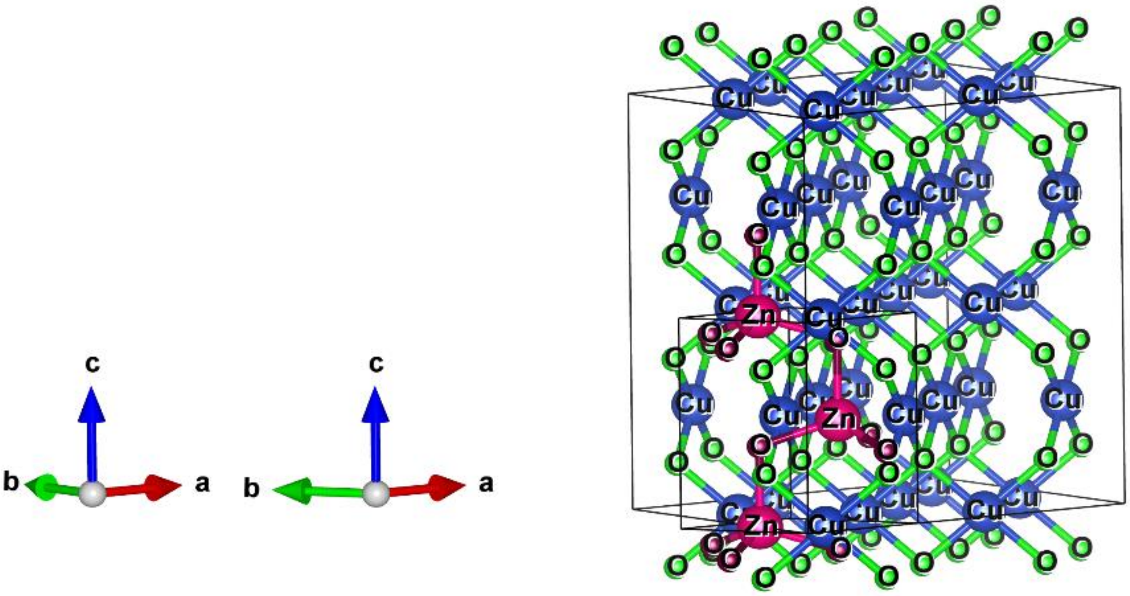


Fig. 9. The monoclinic-hexagonal wurtzite structure of bimetallic copper/zinc oxide. Reprinted with permission from the International Union of Crystallography, ref. [42]. Momma, K., and Izumi, F., 2011. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography*, *44*(6), pp. 1272-1276. Copyright © International Union of Crystallography.

Although, limited research has been reported on the synthesis of bimetallic nanocomposites, such as Cu/ZnO at varying concentrations of the precursors, for employing in photocatalytic, antioxidant, and antibacterial applications. Numerous drug resistant pathogens have been reported to contaminate the soil and water and, therefore, causing serious health issues. Consequently, the copper and zinc oxides like nanocomposites, which are non-toxic and friendly to human cells at low concentrations are becoming a required material to use as antimicrobial agents. In addition, all Gram-positive and Gram-negative bacteria are vulnerable to the antibacterial action of CuO and ZnO nanoparticles as well as nanocomposites. The crystal lattice structure of bimetallic nanocomposites is shown in figure 9.

Mohammadi-Aloucheh et al. [43] have proposed a microwave-assisted, environmentally friendly, and a quick method for synthesizing ZnO/CuO nanocomposites in the presence of *M. longifolia* leaf extract. The spherical shape of nanocomposites has been seen in SEM images. The antibacterial action of ZnO/CuO nanocomposites was examined from the SEM pictures of the bacterium, which shows that the Gram-negative bacterial strains were more sensitive to the tested nanocomposites than Gram-positive strains. Elemike, Onwudiwe & Singh [44] were proposed a *Alchornea cordifolia* leaf extract for the synthesis of the Cu_2O/CuO-ZnO nanocomposites via hydrothermal method. It is noteworthy that the nanocomposites have estimated average size of 3.54 nm and a moderate degree of mono-dispersity, whereas the normal metal oxides form agglomerated particles. These micrographs show the aggregation of the monometallic oxides, and a uniform and well-distributed quantum dots for the nanocomposites. These nanocomposites are proved effective against cervical cancer using the MTT assay method. Nanomaterial's effectiveness against cervical Hela cell lines during *in vitro* cytotoxicity studies was demonstrated in the following order: Cu_2O/ CuO-ZnO>ZnO NPs>Cu_2O/CuO NPs [44]. Da'na, Taha & Hessien [45] were reported the synthesis of several ZnO:NiO nanocomposites employing a green and affordable technology by using *Neem plant* leaf extract. Figures 10 (a, c, e, g) and (b, d, f & h) show the SEM and TEM images, respectively, for 3Z:1 N, 1Z:1 N, 1Z:3 N, and 1Z:1 N nanocomposites. The rod-shaped arrangements appeared in figure 10 are due to the capping effect of the *Neem* leaf extract. In this study, the main role of the *Neem* leaf extract was to increase the length of the rod-shaped nanoparticles. The comparison of 1Z:1 N prepared samples prepared with and without the extract (figures 10 c and g) shows the benefits of using the plant extract to minimize agglomeration of particles. It is very clear in figure 10 (g) that the sample without extract has a high degree of agglomeration as compared to the samples prepared by using the *Neem* plant extract (figure 10 c). It is concluded that composition of the nanocomposites influences the morphological structures of both types of samples (figure 10 (a, c, e & g) and (b, d, f & h)). The removal of MO dye with a maximum equilibrium adsorption capacity is reported in this work with dosage of 34 mg/g in a time of less than an hour. After five times use, the nanocomposites continue to retain 100 % removal capacity, demonstrating a good recycling capability. All of these outcomes enable the environmentally friendly route of synthesis to compete with existing methods for treating water in terms of safety, simplicity, affordability, and removal efficiency, which make this method ready to use commercially.

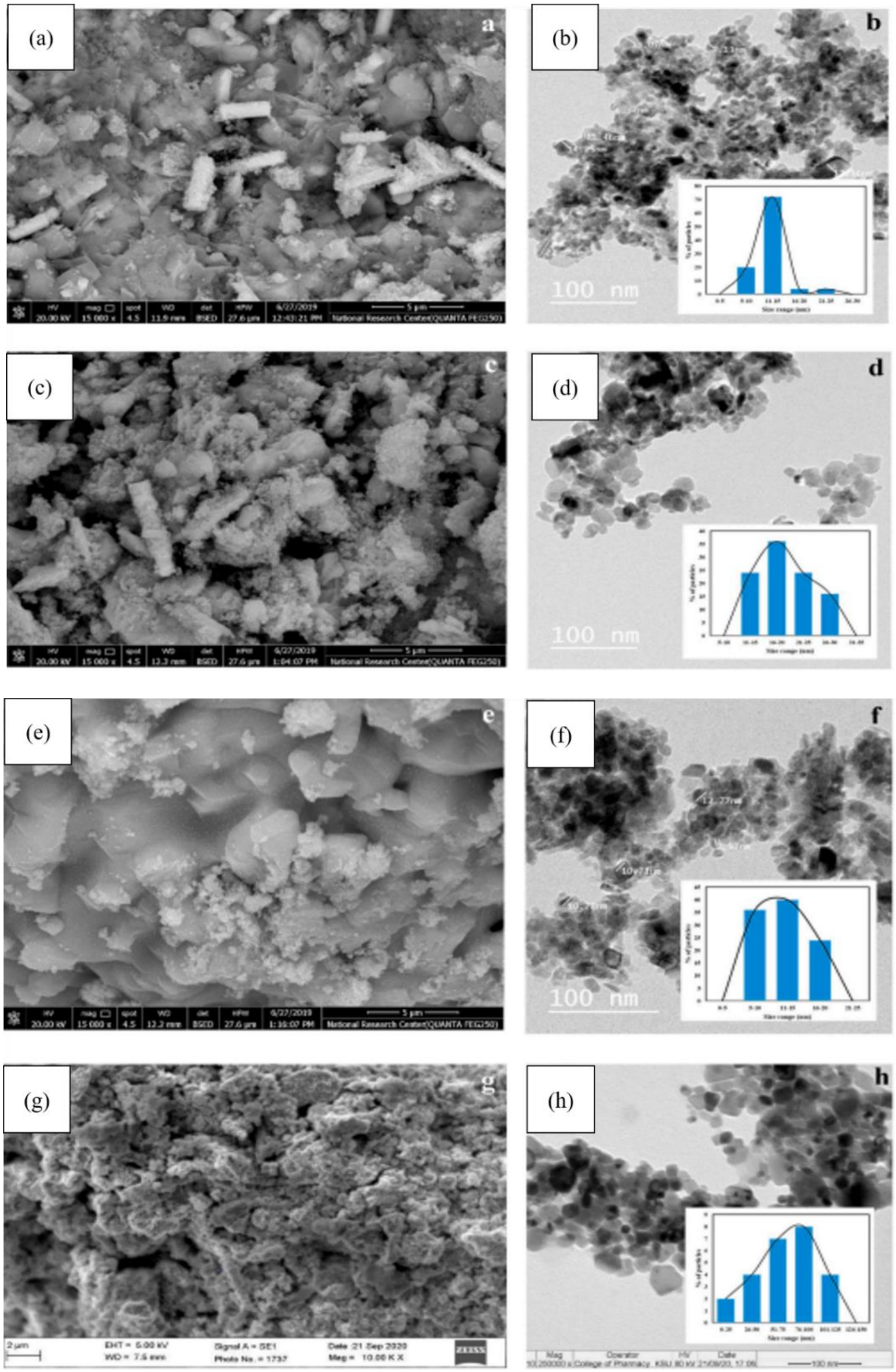


Fig. 10. SEM (a, c, e & g) and TEM images (b, d, f & h) of ZnO/NiO nanocomposites. Reprinted with permission from ref. [45], Da'na, E., Taha, A., Hessien, M., **2021**. Application of ZnO-NiO greenly synthesized nanocomposite adsorbent on the elimination of organic dye from aqueous solutions: Kinetics and equilibrium. *Ceramics International*, *47*(4), pp. 4531-4542. Copyright © ScienceDirect.

3. Photocatalytic activity

The nanocomposites of different transition metal oxides have a great scope for removal of pollutants from waste water. The photocatalytic degradation of dyes (organic and inorganic) from industrial polluted water requires a small amount of nanocomposite photocatalysts. The photocatalytic activity of different transition metal nanocomposites was enhanced through their method of synthesis, size, surface area, nature of crystallinity, band gap, and morphology as well. In following paragraphs, the scope of CuO, ZnO and NiO nanocomposites as photocatalysts has been discussed.

Gerawork [46] investigated the Zn/CuO nanocomposites for the degradation of MO dye under ultraviolet irradiation. The study indicated that the Zn/CuO nanocomposites has decomposed up to 92.18% MO dye within time of two hrs. Kanimozhi et al. [47] prepared Zn/CuO nanocomposites by using co-precipitation method at different concentrations of precursors, which show MB dye degradation up to 99.73 % at a time of approximately 120 min. In another study, Hitkari et al. [48] synthesized Cu/ZnO nanocomposite via co-precipitation method and reported approximately 95 % photo degradation of Congo red dye. Biju et al. [49] have also synthesized Cu/ZnO nanocomposites but through co-precipitation and *in-situ* polymerization method and used the samples for the degradation of Metanil yellow (MY) dye. The study revealed that about 90 % of the MY dye is degraded, which was better than the chemically synthesized Cu/ZnO nanocomposites. Das and Srivastava [50] observed that as compared to pure copper and zinc oxide NPs, the Zn/CuO nanocomposites act as better photocatalysts for the degradation of MB dye with enhancement rate ~20-30 %. Mansournia & Ghaderi [51] synthesized Cu/ZnO core-shell nanocomposites by using hydrothermal method to enhance the photocatalytic degradation of MB dye under UV irradiation. The 100 ml of 5 ppm MB solution has been degraded with 20 mg of synthesized catalyst with continuously stirring in 90 minutes.

A thermal decomposition method was used by Saravanan et al. [52] to fabricate Zn/CuO nanocomposites for the decolorization of MO and MB dyes under visible light at different Zn/CuO ratios, 99:1, 97:3, 95:5, 90:10 and 50:50. But the ratio 95:5 act as better photocatalyst for the maximum percentage of dye degradation in 120 minutes. Chang et al. [53] synthesized Zn/CuO nanocomposite by hydrothermal method and it is revealed that the nanocomposites are six times superior rate-wise than pure ZnO NPs for the complete degradation of MB and MO dyes within 25 and 15 minutes, respectively. In other study, Zn/CuO nanocomposite are synthesized by using sono-co-precipitation method and are used for the photodegradation of methyl parathion (MP) within 60 minutes under the visible light. This study revealed that the 90:10 ratio of Zn/CuO nanocomposites acts as better photocatalyst for the 100 % removal of parathion.

Kumaresan et al. [54] synthesized a Zn/CuO/rGO nanocomposites by using solid-state method under the visible light for 99 and 93 % degradation against RhB dye and 4-chlorophenol for about 20 minutes. Mansoori, Yamgar & Rathod [55] prepared Zn-Cu-Fe (II, III) oxide nanocomposites to increase the efficiency towards photocatalysis for crystal violet dye degradation. The 1:3:4 ratio possessed higher photocatalytic activity than 1:1:4 and 3:1:4 ratios. This study concludes that the maximum concentration of copper acts as good photocatalyst for the degradation of crystal violet. The nanocomposites of different transition metal oxide, their method of synthesis and enhanced photocatalytic efficiency have been summarized in the table 1.

From the literature survey the Zn/CuO, Cu/ZnO, Zn/NiO, and Cu/NiO nanocomposites act as excellent photocatalyst but Zn/CuO as synthesized by hydrothermal method have shown excellent photocatalytic degradation i.e. 99% within less than 25/15 minutes. However, among all these metal oxide nanocomposites, Cu-ZnO/Zn-CuO is the most commonly used photocatalyst for water purification.

Table 1. The photocatalytic activity of different transition metal oxide nanocomposites against different pollutants.

S. No.	Nanocomposite	Method of synthesis	Photocatalytic activity			Ref.
			Dye	Percentage degradation (%)	Time (min)	
1.	Zn/CuO	Co-precipitation	Methyl orange	92.18	120	[46]
2.	Zn/CuO	Co-precipitation	Methylene blue	97.39, 99.73, 86.99 & 81.96	100-120	[47]
3.	Cu/ZnO	Co-precipitation	Congo red	~ 95	-	[48]
4.	Zn/CuO	Co-precipitation	MB	96	30	[50]
5.	Cu/ZnO	Co-precipitation	Metanil yellow	90	-	[49]
6.	Cu/ZnO	Hydrothermal	MB	-	90	[56]
7.	Zn/CuO	Thermal decomposition	MB & MO	96 & 69	120	[52]

8.	Zn/CuO	Hydrothermal	MB & MO	99	25 & 15	[53]
9.	Zn/CuO	Sono Co-precipitation	Methyl parathion	100	60	[57]
10.	Zn/CuO/rGO	Solid- state	RhB dye & 4-chlorophenol	99 & 93	20	[54]
11.	Zn-Cu-Fe (II, III)	Co-precipitation	Crystal violet degradation	-	-	[55]
12.	Cu/NiO	Hydrothermal	Volatile organic compounds	-	-	[58]
13.	Graphene/NiO	Chemical reduction	MB & MO	100	90 & 120	[59]
14.	NiO/Cobalt oxide	Wet- chemical method	MB	89.88	360	[60]
15.	Cerium/NiO	Co-precipitation	MB	87	180	[61]
16.	Carboxymethyl cellulose/Cu-NiO	Co-precipitation	Congo red & Eosin yellow	93 & 96.4	300	[62]
17.	NiO/Nanoclay	Chemical reduction	Orange II	93 & 96	20	[63]
18.	Heuandite/polyaniline @NiO	Physical method	Safranin-T dye	~ 100	1	[64]
19.	NiO/TiO_2	Sol-gel method	MB	90	120	[65]
20.	NiO-ZnO/NiO-CuO	Precipitation method	MB	94.5 & 90.7	175	[66]
21.	NiO/ZnO	Co-precipitation & Ultra-sonication	MB, Rhodamine-B & Benzoic acid	97.1, 88.1 & 93.2	-	[67]
22.	NiO-CuO/CuO-ZnO/ZnO-NiO	Co-precipitation method	Aniline blue, brilliant green & direct red 80	91, 82 & 67	60	[68]
23.	$CuO/TiO_2/ZnO$	Sol-gel method	MB	100 & 98	120	[69]
24.	Zn/NiO	Solvo-thermal method	Rhodamine B	Excellent	180	[33]
25.	ZnO-NiO	Sono-chemical route	MB	91	40 mins	[70]
26.	ZnO/NiO	Facile ultrasonic-assisted method	RhB	Excellent	30	[71]
27.	NiO-ZnO	Microwave method	Rhodamine B & MB	70 & 65	120	[72]
28.	ZnO	Chemical method	MO	-	-	[73]
29.	ZnO/NiO	Modified-chemical bath deposition	MB	90 & 95	150	[74]
30.	ZnO@NiO	Electrochemical deposition method	MB & RhB	~ 95	180	[75]
31.	NiO/ZnO	Sol-gel method	MB	~ 75	195	[76]
32.	ZnO/NiO	Co-precipitation method	Rose Bengal (RB) & Methylene Blue (MB)	83.3, 72 80 & 81 for RB and 83, 64.2, 67.4 & 70.9 for MB	60	[77]
33.	$ZnO/NiFe_2O_4$	Green route	MB	Maximum degradation	70	[78]

34.	NiO/ZnO	Sol-gel method	MB	76	200	[79]
35.	ZnO-NiO	Green method	MB	~ 100	<60	[80]
36.	ZnO/NiO	Hydrothermal method	MB	~ 70	180	[81]
37.	ZnO-NiO/rGo	Precipitation method	MB	79.76 & 89.72	120	[82]

3.1. Mechanism of photo-catalysis

Photocatalysis is a process of accelerating light action in the presence of a photocatalyst. Photocatalysis is the best and cost-effective route to use solar light as a renewable source of energy or UV radiations for the purification of contaminated water (figure 11). In this context, a photo-nanocatalyst with very large surface area is being used effectively to remove dyes from the aqueous medium where water molecules oxidized to $OH^{\bullet}$ free radicals on the nano-catalyst surface. Since the process is usually performed in dark conditions, a species which reduced is oxygen which in turn generate $O_2^{\bullet-}$ (superoxide) radical. For bimetallic nanocomposite photocatalysts, the redox potential of valence and conduction bands must be adequately positive and negative, respectively. Through the reduction process, the electron can generate the superoxide anion ($O_2^{\bullet-}$) by reacting with oxygen molecule. However, by oxidation process, the hole can abstract electron from water or hydroxide ion to generate $OH^{\bullet}$ free radical [73]. Both $OH^{\bullet}$ and $O_2^{\bullet-}$ are strong oxidants that can destroy all sort of organic, inorganic and bio-molecules such as dyes, carbohydrates, proteins, lipids, nucleic acids, etc. and, therefore, can be used to disinfect the polluted water. In other words, the oxygen molecule scavenges electron from the conduction band, thereby, prevent recombination and increase the life time of holes in the aerated aqueous medium. And again, the reaction of $OH^{\bullet}$ and $O_2^{\bullet-}$ eventually proceeds toward the photo-degradation of the organic compounds. Both, organic and inorganic molecules, and microbes in water are destroyed by oxidizing agents ($OH^{\bullet}$, $O_2^{\bullet-}$ and H_2O_2) produced by photo nanocatalysts in the presence of solar or UV light. The mechanistic view of bimetallic based photocatalysis has been illustrated in Figure 11.

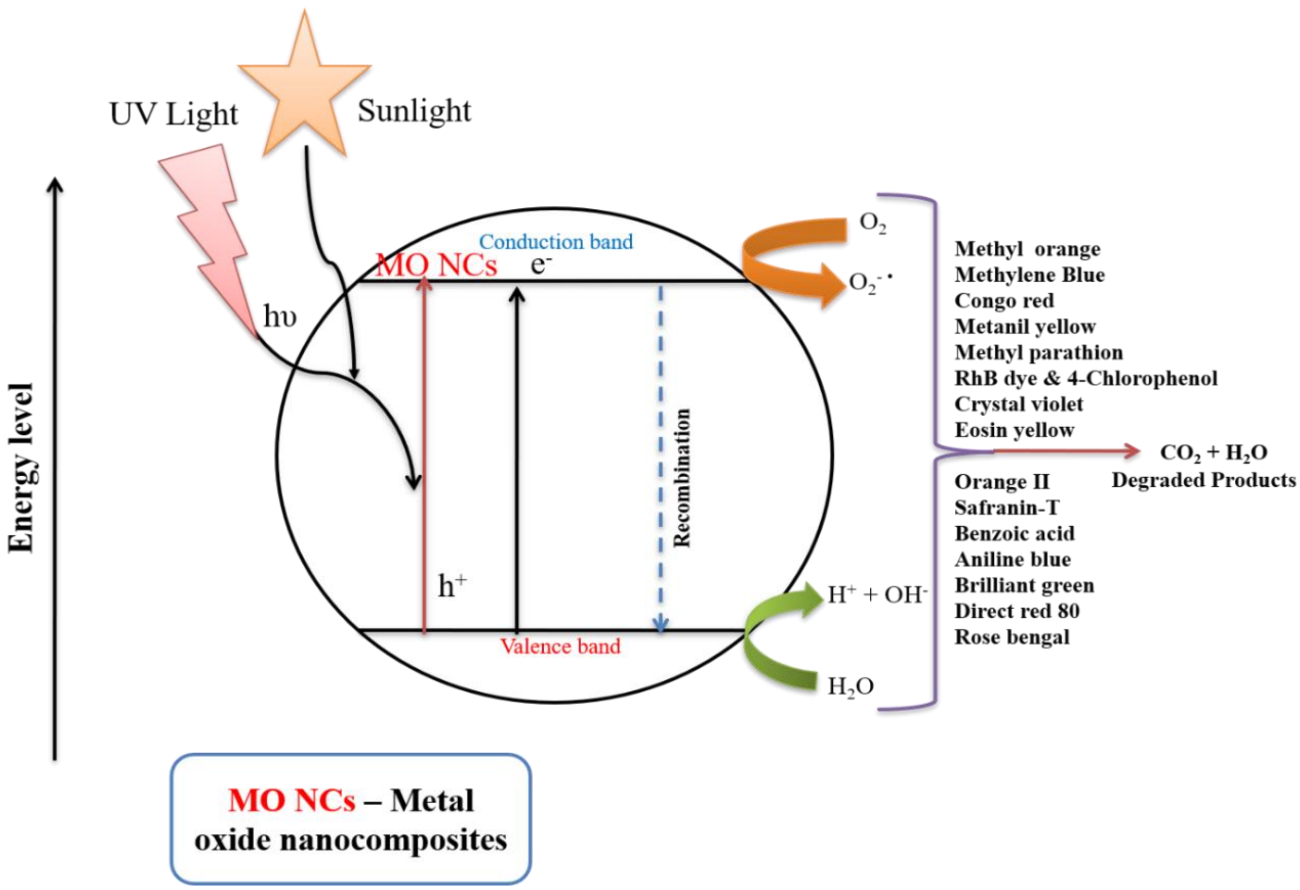


Fig. 11. Mechanism of photocatalytic degradation of dye in the presence of nanocomposites.

$$NCs\left(\frac{MO}{XO}\right) + h\upsilon \rightarrow e^{-} + h^{+} \quad (1)$$

$$O_2 + e^{-} \rightarrow O_2^{-\bullet} \quad (2)$$

Superoxide

$$h^{+} + OH^{-} \rightarrow OH^{\bullet} \quad (3)$$

$$O_2^{-\bullet} + H_2O \rightarrow HO_2^{\bullet} + OH^{\bullet} \quad (4)$$

$$HO_2^{\bullet} + H_2O \rightarrow H_2O_2 + OH^{\bullet} \quad (5)$$

$$H_2O_2 \rightarrow 2\ OH^{\bullet} \quad (6)$$

$$OH^{\bullet} + Dye \rightarrow Dye\bullet + H_2O \quad (7)$$

Degradation

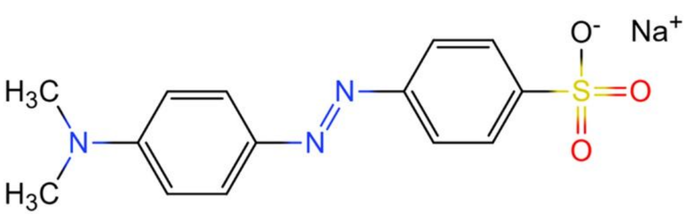
$$H_2O \rightarrow H^{+} + OH^{-} \quad (8)$$

$$OH^{-} + h^{+} \rightarrow OH^{\bullet} \quad (9)$$

$$Dye + h^{+} \rightarrow Dye\bullet \rightarrow Final\ degraded\ products \quad (10)$$

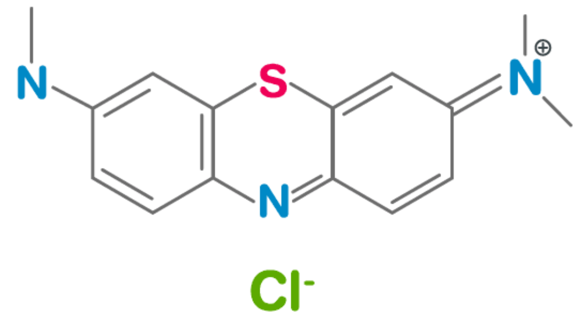
3.2. Structures of different organic dyes

The release of dyes from the textile and chemical industries into the water bodies has become a critical health problem to humans and aquatic lives. To cope up with this problem, the bimetallic oxide nanocomposites have now been employed for the photocatalytic degradation of water contaminants like dyes.

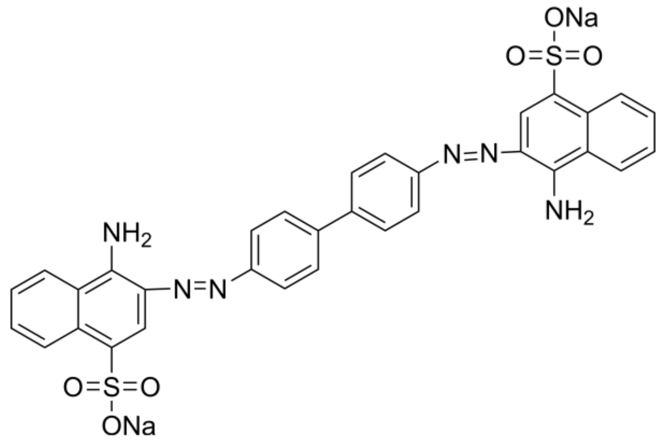


Sodium 4- {[4-(diethylamino) phenyl] diazenyl} benzene-1-sulfonate **(Methyl orange)**

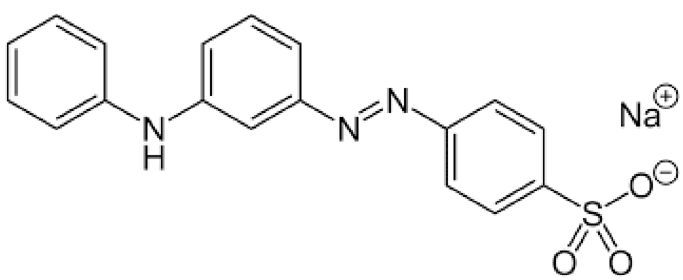
The photocatalysis is a photo-activated chemical reaction which takes place in the presence of free radicals formed by nanoparticles/nanocomposites in the presence of photons of light (figure 11). From this photo-activated chemical reaction, the complex structures of the different organic dyes degraded into simple compounds. The structures of various organic dyes discussed in the review are given below:



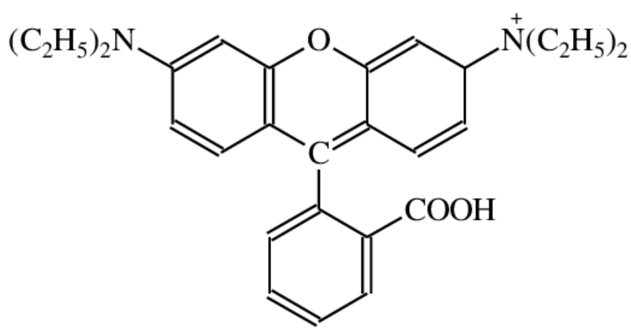
3, 7- bis (Dimethylamino)-phenothiazin-5-ium chloride **(Methylene blue)**



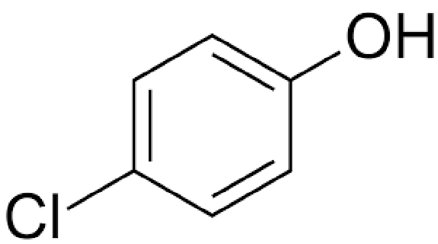
Disodium 4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen -2-yl) diazenylphenyl] phenyl] diazenyl-naphthalene-1-sulfonate **(Congo red)**



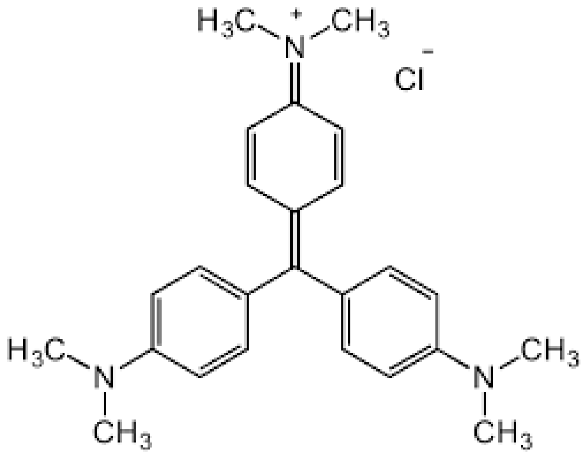
Sodium 3-[(4-anilinophenyl) diazenyl] benzene sulfonate **(Metanil yellow)**



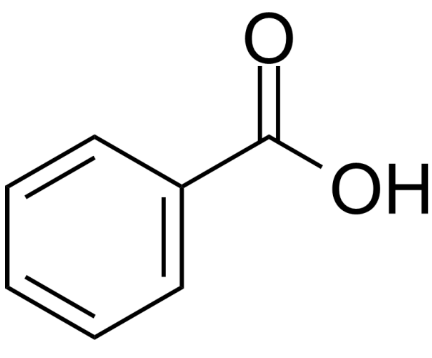
9-(2-carboxyphenyl)-6-(diethylamino)-N, N-diethyl-3H-xanthen-3-iminium chloride **(Rhodamine B)**



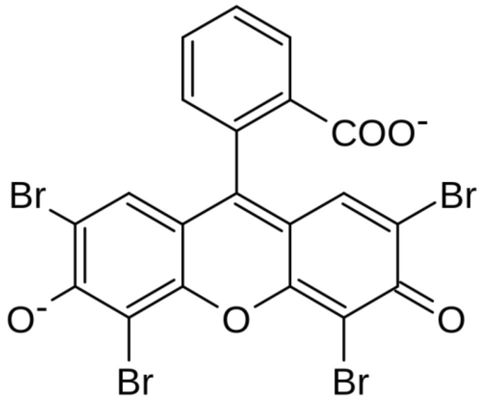
4-Chlorophenol



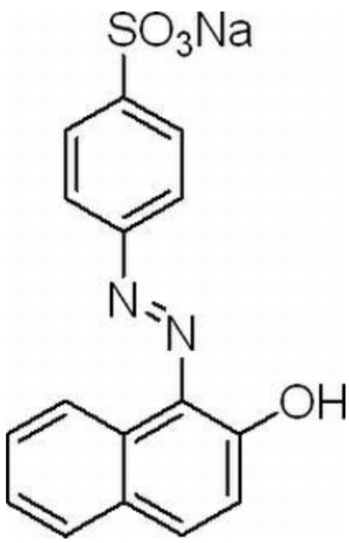
4-{Bis[4-(dimethylamino) phenyl] methylidene}-N, N-dimethylcyclohexa-2,5-dien-1-iminium chloride **(Crystal violet)**



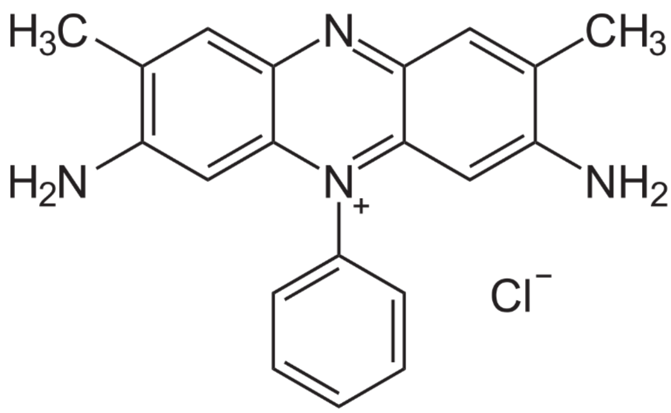
Benzoic acid



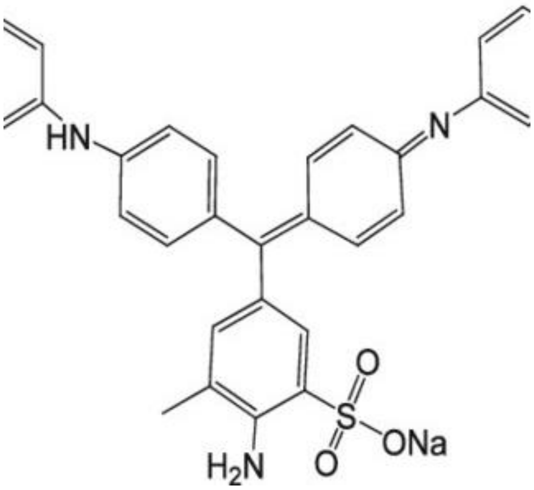
2-(2, 4, 5, 7-tetrabromo-6-oxido-3-oxo-3H-xanthen-9-yl) benzoate **(Eosin yellow)**



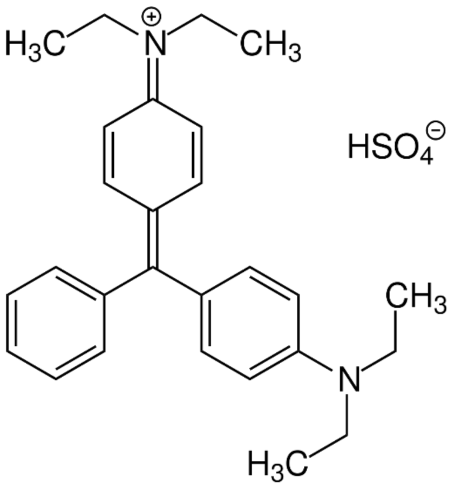
4-(2-Hydroxy-1-naphthylazo) benzene sulfonic acid sodium salt **(Orange II)**



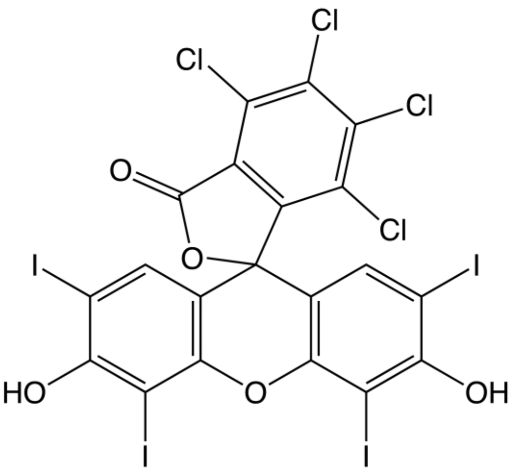
3, 7-Diamino-2, 8-dimethyl-5-phenylphenazinium chloride **(Safranin dye)**



Disodium; 2-amino-3-methyl-5-[[4-(4-sulfonatoanilino) phenyl]-[4-(4-sulfophenyl) iminocyclohexa-2,5-dien-1-ylidene] methyl] benzenesulfonate **(Aniline blue)**



[4-[[4-(diethylamino) phenyl]-phenyl methylidene] cyclohexa-2, 5-dien-1-ylidene]-diethylazanium; hydrogen sulfate **(Brilliant green)**



4,5,6,7-Tetrachloro-3′,6′-dihydroxy-2′,4′,5′,7′-tetraiodo-3H-spiro [[2] benzofuran-1,9′-xanthen]-3-one **(Rose Bengal)**

4. CONCLUSION

The photocatalytic processes are playing a crucial role to control the water contamination by eliminating the pollutants truthfully. In this review, the bimetallic nanocomposites, Cu/ZnO, Zn/CuO, Cu/NiO and Zn/NiO are considered as cost-effective, environmentally benign and recyclable photo-nanocatalysts. Moreover, these agents are used in very small amount for the purification of industrially contaminated water. From the above review studies, it can be concluded that, in general, the particles size of the monometallic oxide nanoparticles is greater than that of the bimetallic oxide nanocomposites synthesized from various chemical or biological methods. The SEM and TEM analyses also revealed agglomeration of the particles in case of monometallic oxide nanoparticles, but well dispersed uniform quantum sizes for the nanocomposites, especially when synthesized from green methods. From this review, we can also conclude that the nanocomposites synthesized from green approach need more attention to improve their structure-based catalytic or various other potential activities.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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