Synergistic Mechanism of $\text{ZnFe}_2\text{O}_4/\text{ZnO}$ Nanopowder in Photocatalytic Degradation of Acid Orange 7

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$\text{ZnFe}_2\text{O}_4/\text{ZnO}$ nanopowder was prepared by solution combustion method. The characterization of the nanopowder was done by powder X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy. Powder X-ray diffraction pattern of the nanopowder exhibited the spinel phase of zinc ferrite and wurtzite phase of zinc oxide. The nanopowder was used for the photocatalytic removal of acid orange dye 7 from its aqueous solution. The effect of various factors such as initial dye concentration, dosage of the photocatalyst and irradiation time was studied. An analysis of the results indicated that the dye degradation was more in case of 10 and 20 ppm dye solutions. The dye degradation decreased with increasing initial concentration. $\text{ZnFe}_2\text{O}_4/\text{ZnO}$ can be used as a better photocatalyst for the removal of dyes from their aqueous solutions.

Keywords: Solution combustion synthesis, $\text{ZnFe}_2\text{O}_4/\text{ZnO}$ nanopowder, Acid orange 7, Photocatalytic activity, Synergistic mechanism.

INTRODUCTION

The dye effluents released from textile and paper mills are an important source of environmental pollution. The use of synthetic dyes has increased considerably during the last few years. More than 10,000 dyes are being used by the dyeing industries. They are widely used in different industries including textile, paper, printing, food colouring, pharmaceutical units, cosmetics, leather industries, agricultural research, light harvesting arrays, *etc.* [1-6]. As a result, dye-containing industrial effluents are released into the soil as well as the aquatic ecosystems [7]. The presence of dyes in water bodies decreases the penetration of light into the water surface, thus decreasing the photosynthetic activity of the aqueous flora and fauna; besides being objectionable for drinking as well as other purposes. Some of the organic dyes and their derivatives exhibit mutagenic or carcinogenic effects on human beings [8-12].

Azo dyes are of much concern to the surrounding ecosystem. They are generally not amenable for removal by conventional biological wastewater treatment methods. The azo and nitro-compounds are reduced in sediments and intestinal environment, which results in the regeneration of the parent toxic amines [13,14]. Also, these azo dyes are largely non-biodegradable

under aerobic conditions and hence are reduced to more hazardous intermediates. Hence, there is a need to develop alternative methods for the removal of such dyes from wastewater [15-18].

The methods used for the removal of these dyes include adsorption, reverse osmosis, membrane filtration, electrocoagulation, ion exchange, electroflocculation, *etc.* [19]. These methods have various drawbacks such as long retention time, requirement of high dissolved oxygen concentration, high electricity consumption, short half-life, specificity only to certain dyes, *etc.* Some of the methods are expensive too. Additionally, they produce large quantities of sludge which poses disposal problems. Also, they only result in the separation of dyes without degrading them [20-23]. Heterogeneous photocatalysis using nano-materials is a cost effective method for water remediation. It is an important method for the treatment of waste water owing to its several advantages such as quick oxidation, no formation of polycyclic products, oxidation of pollutants in the ppb range, *etc.* [24,25]. In a photocatalytic system, the photoinduced reactions or molecular transformations occur at the surface of the photocatalyst. The process is highly efficient for the mineralization of hazardous inorganic materials, toxic organic compounds and microbial disinfection

in water. This high efficiency is due to the formation of highly reactive hydroxyl free radical ($\text{OH}^\bullet$), which is a strong oxidizing agent [26]. One of the major drawbacks of this technique is the recombination of electrons and holes resulting in a decrease in efficiency [27].

Several techniques are available for controlling this electron-hole recombination. Among these, semiconductor combination appears to be promising technique. The main feature of this technique is the formation of a composite semiconductor material. The formation of a coupled structure between a wide band gap and a narrow band gap semiconductor with matching band potentials is an important requirement of this technique. The irradiation of such a composite material with UV or visible light generates electron-hole pairs in the narrow band gap semiconductor thus initiating the photocatalytic reaction [28-30]. This results in an improvement in photocatalytic efficiency. Recently, a number of coupled photocatalysts have been prepared some which include $\text{NiFe}_2\text{O}_4/\text{TiO}_2$, $\text{MnFe}_2\text{O}_4/\text{TiO}_2$, $\text{CuFe}_2\text{O}_4/\text{TiO}_2$, $\text{MgFe}_2\text{O}_4/\text{TiO}_2$ and $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ [31-35]. Heterojunction photocatalyst $\text{TiO}_2/\text{AgGaS}_2$ was synthesized by solid state reaction and sol-gel synthesis [36]. The photocatalyst showed an enhancement in the photocatalytic activity compared to the individual constituents, which was attributed to an efficient charge separation at the interface followed by fast diffusion of the photoelectrons of AgGaS_2 towards surrounding TiO_2 . The synthesis of core-shell $\text{CoFe}_2\text{O}_4/\text{BaTiO}_3$ nanocomposites and a mixture of both by a combination of hydrothermal and sol-gel techniques has also been reported [37]. The magneto-electric coupling effect of the materials was determined by measuring the magneto-electric coefficient. It was found that the magneto-electric coefficient of the nanocomposite was 35 times larger than the mixture of NiO and Bi_2O_3 prepared by dissolving equimolar quantities of both $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in concentrated HNO_3 [38]. The nanocomposite exhibited better photocatalytic activity in the removal of methyl orange and methylene blue dyes than a physical mixture of NiO and Bi_2O_3 . It was concluded that the photocatalytic activity of relatively less active catalysts can be enhanced by intimate coupling which refers to the formation of composites having extended response in the wide region of the UV-visible spectrum. Nanostructured and mesoporous iron-cerium mixed oxides were prepared by co-precipitation method using Na_2CO_3 as the precipitating agent [39]. The mixed oxides were used as photocatalysts in the removal of phenol, methylene blue and congo red from water. It was observed that the mixed oxide with $\text{Fe}/\text{Ce} = 1$ resulted in 13 % removal of phenol, 93 % removal of methylene blue and almost complete removal of congo red. The higher photocatalytic activity of the mixed oxide was attributed to its higher surface area and surface acidity, which determine the active sites of the photocatalyst thus accelerating the photocatalytic reaction [40-45].

Solution combustion synthesis is an important method for the synthesis of a number of nanocrystalline materials. In the present study, we report the synthesis of $\text{ZnFe}_2\text{O}_4/\text{ZnO}$ nanopowder by solution combustion synthesis. The nanopowder was used as photocatalyst for the removal of the azo dye acid orange 7 (AO 7) from its aqueous solution. The photocatalytic

studies focussed on the study of the effect of various factors such as dosage of the photocatalyst, irradiation time and initial dye concentration.

EXPERIMENTAL

Preparation of the $\text{ZnFe}_2\text{O}_4/\text{ZnO}$ nanopowder: All the chemicals used in the study were of analytical grade and were used without purification. The chemicals were procured from SD Fine Chemicals Limited. The fuel oxalyldihydrazide (ODH) was prepared by the following method [46].

The preparation of oxalyldihydrazide involves the reaction between diethyl oxalate (1 mol) and hydrazine hydrate (2 mol) as indicated by eqn 1. 100.12 g of hydrazine hydrate was taken in a 1000 mL beaker. 146.14 g of diethyl oxalate was added to it and the mixture was dissolved in 225 mL of double distilled water. The entire addition was carried out in an ice bath with vigorous stirring. The resulting white precipitate was allowed to stand overnight. It was then washed with ethanol, filtered and dried.

In solution combustion synthesis, the combustion of a fuel by an oxidizer occurs. The oxidizer is usually a metal nitrate. Zinc nitrate and ferric nitrate ($\text{Zn}/\text{Fe} \sim 1.6$) were taken in a crystallizing dish of approximately 300 mL capacity and dissolved in minimum quantity of double distilled water. Calculated amount of the oxalyldihydrazide fuel was added to it and the mixture was stirred magnetically for about 10 min. The crystallizing dish was then placed on a hot plate to evaporate the excess water until a pasty mass was left. It was then introduced into a muffle furnace maintained at a temperature of around 350°C . It was observed that the reaction mixture first dehydrated and then ignited at one spot thus initiating the combustion. The combustion process reached completion in few minutes resulting in the formation of the nanopowder. The nanopowder was cooled to room temperature and then ground into a fine powder.

The formation of the nanopowder can be represented by eqn. 2.

Characterization of the $\text{ZnFe}_2\text{O}_4/\text{ZnO}$ nanopowder: In order to determine the phase purity and crystal structure of the nanopowder powder X-ray diffraction (PXRD) pattern was recorded. The PXRD data was recorded using CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV with the help of Philips X'Pert pro X-ray diffractometer. The mean crystallite size of the nanopowder was calculated from Scherer's formula given by eqn. 3 [47].

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (3)$$

where D is the mean crystallite size, k is a constant, λ is the wavelength of the X-rays used, β is the full width at half maximum (FWHM) and θ is the Bragg's angle.

The identification of various chemical groups present in the nanopowder was done by Fourier transform infrared spectroscopy (FTIR). The FTIR spectrum of the nanopowder

was recorded using Perkin-Elmer spectrometer (spectrum 1000) with KBr as reference.

Scanning electron microscopy (SEM) was used to determine the surface morphology of the nanopowder. The SEM micrograph of the nanopowder was recorded with the help of JEOL-2100F (Japan) scanning electron microscope.

Photocatalytic degradation of the acid orange 7: Acid orange 7 is an anionic azo dye with m.f. $\text{C}_{16}\text{H}_{11}\text{N}_2\text{NaSO}_4$ and molecular mass equal to 350.3 g mol^{-1} (Fig. 1). The IUPAC name of acid orange 7 is sodium 4-[(2-hydroxy-1-naphthyl)-azo]benzenesulfonate. It is available in the form of orange coloured powder and is soluble in water. Acid orange 7 is used in paper and textile industries, particularly in dyeing of various materials of silk, wool and nylon. In the past it was also used in tanneries. Acid orange 7 is highly toxic in nature. It causes nausea, dermatitis, methemoglobinemia, irritation of the skin, eyes, mucous membrane and the upper respiratory tract. It is also carcinogenic in nature [48-50].

The structure and absorption spectrum of acid orange 7 are shown in Fig. 1. The maximum absorbance was observed at 487 nm.

Fig. 1. (a) Structure of acid orange 7 (b) absorption spectrum of acid orange 7

A 1000 ppm solution of acid orange 7 was used as the stock solution. It was prepared by transferring 1 g of the dyestuff in a 100 mL volumetric flask, dissolving and diluting upto the mark with double distilled water. Appropriate dilution of the stock solution with double distilled water was done to obtain solutions of concentrations 10, 20, 40 and 60 ppm. Double distilled water was used throughout the experiments.

The photocatalytic removal of acid orange 7 was carried out in an approximately 500 mL capacity reaction vessel with a circumference of around 25.2 cm and an exposure area of about 50.3 cm^2 . A 25 Watt mercury vapour lamp was used as the source of ultraviolet radiation. A distance of around 20 cm was maintained between the source and the surface of the solution.

In order to know the extent of adsorption of the dye by the nanopowder in the dark prior to photocatalytic degradation experiments, the following procedure was adopted. 50 mL of the dye solution was transferred to the reaction vessel followed by the addition of 50 mg of the nanopowder (photocatalyst). The suspension was then stirred magnetically in the dark for about 30 min and centrifuged at 3000 rpm for about 10 min using KEMI C8C centrifuge. The UV-visible spectrum of the supernatant was recorded from 300 to 700 nm using ELICO SL-159 UV-visible spectrophotometer. It was observed that there was negligible degradation of the dye under dark conditions.

The effect of dosage of the photocatalyst was determined as follows. Appropriate amount of the photocatalyst was added to the reaction vessel containing 50 mL of the dye solution. The suspension was stirred magnetically under UV radiation for 30 min. It was then centrifuged at 3000 rpm for about 10 min and the UV-visible spectrum of the supernatant was recorded as described earlier. The percentage dye removal of acid orange 7 was calculated using eqn. 4 [51].

$$\text{Degradation efficiency (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (4)$$

where C_o and C_e are the initial and equilibrium concentrations of the dye.

The experiments were carried out by varying the dosage of the photocatalyst from 0.2 to 1.8 g L^{-1} . The optimum dosage of the photocatalyst was determined by plotting a graph of C_e/C_o versus the dosage of the photocatalyst.

After determining the optimum dosage, the effect of irradiation time on the rate of photocatalytic degradation was studied. 100 mL of the dye solution was taken in the reaction vessel and optimum amount of the photocatalyst was added to it. The suspension was exposed to UV radiation with constant stirring. A small aliquot of the suspension was taken out after every 5 min, centrifuged and the UV-visible spectrum of the supernatant was recorded. The experiment was performed for an irradiation time of upto 120 min. The optimum irradiation time was determined from the plot of C_e/C_o versus the irradiation time. The photocatalytic degradation experiments were performed for dye solutions of concentration 10, 20, 40 and 60 ppm.

RESULTS AND DISCUSSION

Nanopowder characterization results: The powder XRD pattern of the nanopowder (Fig. 2) exhibited peaks of both ZnFe_2O_4 and ZnO phases. The peaks at (111), (220), (311), (222), (400), (422) and (511) correspond to the cubic spinel phase of ZnFe_2O_4 ($a = 8.4411 \text{ \AA}$, JCPDS file number: 22-1012) while those at (100), (002) and (102) correspond to the hexagonal wurtzite phase of ZnO ($a = 3.249 \text{ \AA}$, $c = 5.206 \text{ \AA}$, JCPDS file

Fig. 2. Powder X-ray diffraction pattern of the nanopowder

number: 36-1451). Hence it was concluded that the compound is the nanocomposite $\text{ZnFe}_2\text{O}_4/\text{ZnO}$ having both zinc ferrite and zinc oxide phases [52,53]. The nanopowder exhibited high degree of crystallinity with no impurity peaks.

The peak around 352 cm^{-1} in the FTIR spectrum of the nanopowder (Fig. 3) corresponds to the stretching vibrations of the Zn-O. The stretching vibrations of the Fe-O bond appear at around 416 and 542 cm^{-1} . The peak at around 3500 cm^{-1} can be assigned to the -OH group of water adsorbed on the surface of the nanopowder [54,55].

Fig. 3. FTIR spectrum of the nanopowder

Fig. 4 shows the SEM micrograph of the nanopowder. The particles exhibit flake like morphology with high degree of agglomeration. The SEM micrograph exhibited high degree of porosity with large voids. The formation of large voids can be attributed to the liberation of large amounts of gases during the combustion process. This also facilitates the formation of tiny particles. The heat liberated is an important factor for crystal growth. The agglomeration of the nanoparticles is considered as a common way to minimize their surface free energy [56,57].

Photocatalytic degradation results: Fig. 5 shows the effect of dosage of photocatalyst and irradiation time on the rate of photocatalytic degradation of acid orange 7. With an

Fig. 4. SEM micrograph of the nanopowder

Fig. 5. Effect of (a) dosage of photocatalyst and (b) irradiation time on the photocatalytic degradation of acid orange 7 by nanopowder

increase in the amount of the photocatalyst, the dye removal also increases. This is because of the fact that an increase in the amount of the photocatalyst increases the number of active sites on the surface, which results in the adsorption of more number of dye molecules. The optimum dosage of the photocatalyst was 1.0 g L^{-1} for dye solutions of concentrations 10

and 20 ppm whereas it was 1.2 g L⁻¹ for 40 and 60 ppm solutions. An increase in dosage of the photocatalyst beyond the optimum value resulted in negligible increase in the dye removal. This is because of the fact that higher concentration of the photocatalyst increases the scattering of UV radiation. Additionally, it also decreases the penetration of UV radiation into the dye solution.

In case of 10 and 20 ppm dye solutions, the optimum irradiation time was found to be 40 min while the optimum irradiation time in case of 40 and 60 ppm dye solutions was found to be 45 min. Beyond the optimum irradiation time, there was negligible increase in dye removal.

The results for photocatalytic degradation of acid orange 7 by the nanopowder are listed in Table-1.

TABLE-1
RESULTS FOR THE PHOTOCATALYTIC REMOVAL OF
ACID ORANGE 7 BY ZnFe₂O₄/ZnO NANOPOWDER

Concentration of the dye solution	Optimum dosage (g L ⁻¹)	Optimum irradiation time (min)	Percentage dye removal
10	1.0	40	91.72
20	1.0	40	83.28
40	1.2	45	72.53
60	1.2	45	56.70

Mechanism of photocatalytic degradation by ZnFe₂O₄/ZnO nanopowder: The mechanism of photocatalytic degradation of acid orange 7 by the ZnFe₂O₄/ZnO nanopowder can be explained as follows. The exposure of ZnFe₂O₄/ZnO nanopowder with UV radiation excites both semiconductors ZnO and ZnFe₂O₄. There is promotion of electrons from the valence bands of both the semiconductors to their respective conduction bands. The holes are left behind in their valence bands. The electrons in the conduction band of ZnFe₂O₄ are then injected into the conduction band of ZnO. This results in an increase in the concentration of electrons in the conduction band of ZnO. There is migration of holes from the valence band of ZnO to that of ZnFe₂O₄ resulting in a high concentration of holes in it. The net effect is an increase in charge separation. The electrons and holes migrate to the surfaces of the respective particles and are involved in the redox reactions occurring around the surfaces as shown in Fig. 6. This increases the photocatalytic activity of the nanopowder. It was therefore concluded that the higher photocatalytic activity of ZnFe₂O₄/ZnO nanopowder is due to an increase in the electron hole separation. This type of interparticle charge transfer (synergistic mechanism) has also been reported in case of other nanocomposites such as SnO₂/Zn₂SnO₄ and TiO₂/SnO₂ [58,59].

Conclusion

ZnFe₂O₄/ZnO nanopowder was successfully prepared by solution combustion method. The nanopowder was used as photocatalyst for the removal of the azo dye acid orange 7 from its aqueous solution. It exhibited better photocatalytic efficiency for the removal of 10 and 20 ppm dye solutions. The photocatalytic process was found to be dependent on the dosage of the photocatalyst, irradiation time and initial dye concentration. This nanopowder can be used for effective removal of dyes from textile and paper effluents. The increased

Fig. 6. Mechanism of photocatalysis by ZnFe₂O₄/ZnO nanopowder

photocatalytic activity of ZnFe₂O₄/ZnO nanocomposite was attributed to the interparticle charge transfer between ZnO and ZnFe₂O₄, which increased the electron-hole separation.

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REFERENCES

1. C. Scarpi, F. Ninci, M. Centini and C. Anselmi, *J. Chromatogr. A*, **796**, 319 (1998); [https://doi.org/10.1016/S0021-9673\(97\)01015-7](https://doi.org/10.1016/S0021-9673(97)01015-7).
2. K. Diouri, A. Chaqroune, A. Kherbeche, J. Bentama and A. Lahrichi, *J. Mater. Environ. Sci.*, **6**, 79 (2015).
3. S. Buthelezi, A. Olaniran and B. Pillay, *Molecules*, **17**, 14260 (2012); <https://doi.org/10.3390/molecules171214260>.
4. A. Jaafar and A. Boussaoud, *J. Mater. Environ. Sci.*, **5**, 2426 (2014).
5. N. Mohan, N. Balasubramanian and C. Basha, *J. Hazard. Mater.*, **147**, 644 (2007); <https://doi.org/10.1016/j.jhazmat.2007.01.063>.
6. M. El Haddad, R. Mamouni, R. Slimani, N. Saffaj, M. Ridaoui, S. ElAntri and S. Lazar, *J. Mater. Environ. Sci.*, **3**, 1019 (2012).
7. Z. Aksu, *Process Biochem.*, **40**, 997 (2005); <https://doi.org/10.1016/j.procbio.2004.04.008>.
8. S. Sheshmani, A. Ashori and S. Hasanazadeh, *Int. J. Biol. Macromol.*, **68**, 218 (2014); <https://doi.org/10.1016/j.ijbiomac.2014.04.057>.
9. M.P. Elizalde-González and V. Hernández-Montoya, *J. Hazard. Mater.*, **168**, 515 (2009); <https://doi.org/10.1016/j.jhazmat.2009.02.064>.
10. M. Kornaros and G. Lyberatos, *J. Hazard. Mater.*, **136**, 95 (2006); <https://doi.org/10.1016/j.jhazmat.2005.11.018>.
11. L. Fan, C. Luo, X. Li, F. Lu, H. Qiu and M. Sun, *J. Hazard. Mater.*, **215-216**, 272 (2012); <https://doi.org/10.1016/j.jhazmat.2012.02.068>.
12. L.L. Lian, L.P. Guo and C.J. Guo, *J. Hazard. Mater.*, **161**, 126 (2009); <https://doi.org/10.1016/j.jhazmat.2008.03.063>.
13. E.J. Weber and N. Lee Wolfe, *Environ. Toxicol. Chem.*, **6**, 911 (1987); <https://doi.org/10.1002/etc.5620061202>.
14. S. Sirianuntapiboon and P. Srisornsak, *Bioresour. Technol.*, **98**, 1057 (2007); <https://doi.org/10.1016/j.biortech.2006.04.026>.

15. K. Golka, S. Kopps and Z.W. Myslak, *Toxicol. Lett.*, **151**, 203 (2004); <https://doi.org/10.1016/j.toxlet.2003.11.016>.
16. M. Wang, X. Liu, B. Pan and S. Zhang, *Chemosphere*, **93**, 2877 (2013); <https://doi.org/10.1016/j.chemosphere.2013.08.082>.
17. M.L.J. Richardson, *J. Soc. Dyers Colorists*, **99**, 198 (1983); <https://doi.org/10.1111/j.1478-4408.1983.tb03687.x>.
18. I. Oller, S. Malato and J.A. Sanchez Perez, *Sci. Total Environ.*, **409**, 4141 (2011); <https://doi.org/10.1016/j.scitotenv.2010.08.061>.
19. R.S. Raveendra, P.A. Prashanth, R. Hari Krishna, N.P. Bhagya, B.M. Nagabhushana, H. Raja Naika, K. Lingaraju, H. Nagabhushana and B. Daruka Prasad, *J. Asian Ceram. Soc.*, **2**, 357 (2014); <https://doi.org/10.1016/j.jascer.2014.07.008>.
20. C. Tang and V. Chen, *Water Res.*, **38**, 2775 (2004); <https://doi.org/10.1016/j.watres.2004.03.020>.
21. H. El Boujaady, M. Mourabet, M. Bennani-Ziatni and A. Taitai, *J. Assoc. Arab Univ. Basic Appl. Sci.*, **16**, 64 (2014); <https://doi.org/10.1016/j.jaubas.2013.09.001>.
22. A.R. Khataee and G. Dehghan, *J. Taiwan Inst. Chem. Eng.*, **42**, 26 (2011); <https://doi.org/10.1016/j.jtice.2010.03.007>.
23. B.B. Himanshu, Ph.D. Thesis, Bacterial Degradation of Azo Dyes and Its derivatives, Saurashtra University, Rajkot, India (2011).
24. H.R. Pouretedal, H. Eskandari, M.H. Keshavarz and A. Semnani, *Acta Chim. Slov.*, **56**, 353 (2009).
25. Z. Zainal, C.Y. Lee, M.Z. Hussein, A. Kassim and N.A. Yusof, *J. Hazard. Mater.*, **118**, 197 (2005); <https://doi.org/10.1016/j.jhazmat.2004.11.009>.
26. S. Baruah, S.S. Sinha, B. Ghosh, S.K. Pal, A.K. Raychaudhuri and J. Dutta, *J. Appl. Phys.*, **105**, 074308 (2009); <https://doi.org/10.1063/1.3100221>.
27. Z.-C. Wu, Y. Zhang, T.-X. Tao, L. Zhang and H. Fong, *Appl. Surf. Sci.*, **257**, 1092 (2010); <https://doi.org/10.1016/j.apsusc.2010.08.022>.
28. M.N. Rashed and A.A. El-Amin, *Int. J. Phys. Sci.*, **2**, 73 (2007).
29. R.Y. Hong, J.H. Li, L.L. Chen, D.Q. Liu, H.Z. Li, Y. Zheng and J. Ding, *Powder Technol.*, **189**, 426 (2009); <https://doi.org/10.1016/j.powtec.2008.07.004>.
30. R.V. Solomon, I.S. Lydia, J.P. Merlin and P. Venuvalingam, *J. Iran. Chem. Soc.*, **9**, 101 (2012); <https://doi.org/10.1007/s13738-011-0033-8>.
31. M.H. Habibi, A. Hassanzadeh and A. Zeini-Isfahani, *Dyes Pigments*, **69**, 93 (2006); <https://doi.org/10.1016/j.dyepig.2005.02.011>.
32. L. Cao, A. Huang, F.J. Spiess and S.L.J. Suib, *J. Catal.*, **188**, 48 (1999); <https://doi.org/10.1006/jcat.1999.2596>.
33. C.B. Almquist and P. Biswas, *J. Catal.*, **212**, 145 (2002); <https://doi.org/10.1006/jcat.2002.3783>.
34. O. Khaselev, *J. Sci.*, **280**, 425 (1998); <https://doi.org/10.1126/science.280.5362.425>.
35. J.S. Jang, D.W. Hwang and J.S. Lee, *Catal. Today*, **120**, 174 (2007); <https://doi.org/10.1016/j.cattod.2006.07.052>.
36. N.R. de Tacconi, C.R. Chenthamarakshan, K. Rajeshwar and E.J. Tacconi, *J. Phys. Chem. B*, **109**, 11953 (2005); <https://doi.org/10.1021/jp044156n>.
37. S.H. Xu, D.L. Feng, D.X. Li and W.F. Shangguan, *Chin. J. Chem.*, **26**, 842 (2008); <https://doi.org/10.1002/cjoc.200890156>.
38. H.M. Xiao, X.-M. Liu and S.-Y. Fu, *Compos. Sci. Technol.*, **66**, 2003 (2006); <https://doi.org/10.1016/j.compscitech.2006.01.001>.
39. A. Kezzim, N. Nasrallah, A. Abdi and M. Trari, *Energy Conserv. Manage.*, **52**, 2800 (2011); <https://doi.org/10.1016/j.enconman.2011.02.014>.
40. P. Cheng, W. Li, T.L. Zhou, Y.P. Jin and M.Y. Gu, *J. Photochem. Photobiol. Chem.*, **168**, 97 (2004); <https://doi.org/10.1016/j.jphotochem.2004.05.018>.
41. L. Zhang, Y. He, Y. Wu and T. Wu, *Mater. Sci. Eng. B*, **176**, 1497 (2011); <https://doi.org/10.1016/j.mseb.2011.09.022>.
42. J.S. Jang, S.J. Hong, J.Y. Kim and J.S. Lee, *Chem. Phys. Lett.*, **475**, 78 (2009); <https://doi.org/10.1016/j.cplett.2009.05.012>.
43. Chaudhuri and K. Mandal, *J. Magn. Magn. Mater.*, **377**, 441 (2015); <https://doi.org/10.1016/j.jmmm.2014.10.142>.
44. A. Hameed, V. Gombac, T. Montini, M. Graziani and P. Fornasiero, *Chem. Phys. Lett.*, **472**, 212 (2009); <https://doi.org/10.1016/j.cplett.2009.03.017>.
45. G.K. Pradhan and K.M. Parida, *Int. J. Eng. Sci. Technol.*, **2**, 53 (2010).
46. K.C. Patil, M.S. Hegde, T. Rattan and S.T. Aruna, *Chemistry of Nanocrystalline Oxide Materials: Combustion Synthesis, Properties and Applications*, World Scientific Publishing, Singapore, p. 332 (2008).
47. P. Muthirulan, C.N. Devi and M.M. Sundaram, *Mater. Sci. Semicond. Process.*, **25**, 219 (2014); <https://doi.org/10.1016/j.msssp.2013.11.036>.
48. V.K. Gupta, A. Mittal, V. Gajbe and J. Mittal, *Ind. Eng. Chem. Res.*, **45**, 1446 (2006); <https://doi.org/10.1021/ie051111f>.
49. J.P. Silva, S. Sousa, J. Rodrigues, H. Antunes, J.J. Porter, I. Goncalves and S. Ferreira-Dias, *Sep. Purif. Technol.*, **40**, 309 (2004); <https://doi.org/10.1016/j.seppur.2004.03.010>.
50. L. Zhang, Z. Cheng, X. Guo, X. Jiang and R. Liu, *J. Mol. Liq.*, **197**, 353 (2014); <https://doi.org/10.1016/j.molliq.2014.06.007>.
51. A.O. Ibhadon, G.M. Greenway, Y. Yue, P. Falaras and D. Tsoukleris, *Appl. Catal. B*, **84**, 351 (2008); <https://doi.org/10.1016/j.apcatb.2008.04.019>.
52. R.R. Shahraki and M. Ebrahimi, *J. Nanostruct.*, **2**, 413 (2013); <https://doi.org/10.7508/JNS.2012.04.002>.
53. T.M. Hammad and J.K. Salem, *J. Nanopart. Res.*, **13**, 2205 (2011); <https://doi.org/10.1007/s11051-010-9978-2>.
54. B.P. Ladgaonkar, C.B. Kolekar and A.S. Vaingankar, *Bull. Mater. Sci.*, **25**, 351 (2002); <https://doi.org/10.1007/BF02704131>.
55. M. Thomas and K.C. George, *Indian J. Pure Appl. Phys.*, **47**, 81 (2009).
56. N.M. Deraz and A. Alarifi, *Int. J. Electrochem. Sci.*, **7**, 6501 (2012).
57. M.N. Zulfiqar Ahmed, K.B. Chandrasekhar, A.A. Jahagirdar, H. Nagabhushana and B.M. Nagabhushana, *Appl. Nanosci.*, **5**, 961 (2015); <https://doi.org/10.1007/s13204-014-0395-1>.
58. T. Jia, J. Zhao, F. Fu, Z. Deng, W. Wang, Z. Fu and F. Meng, *Int. J. Photoenergy*, **Article ID 197824** (2014); <https://doi.org/10.1155/2014/197824>.
59. A.S. Ganeshraja, A.S. Clara, K. Rajkumar, Y. Wang, Y. Wang, J. Wang and K. Anbalagan, *Appl. Surf. Sci.*, **353**, 553 (2015); <https://doi.org/10.1016/j.apsusc.2015.06.118>.