

Synthesis and Characterization of BaCaO₂ Nanoscale Metal Oxide and Photocatalysis of Acridine orange Dye

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Abstract:

The photocatalytic characteristics of BaCaO₂ metal oxide nanoparticle (NPs) is well studied against Acridine orange dye. Solution combustion method is employed in the synthesis of BaCaO₂ NPs. The average particle size of BaCaO₂ NPs is analyzed with SEM and XRD methods. Various parameters like diverse catalyst dosage, pH, dye concentration and different irradiations implied in the photo degradation of Acridine orange dye. The BaCaO₂ NPs proved to be remarkable and 96.3% of colored solution of Acridine orange dye degraded at a pH 6 and catalyst dosage of 0.5g/100 ml. The BaCaO₂ nanoparticle is got to be very effective in photocatalysing Acridine orange and proved to be very cost effective.

Keyword: Nanoparticles, XRD, SEM, Photocatalytic Degradation.

1. INTRODUCTION

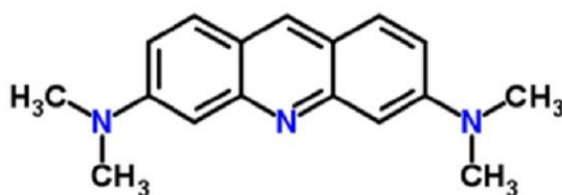
Among various transition metal oxides, NPs has gained more importance due to its wide range of applications, such as as catalysts,^{1,3} battery cathodes/anodes,^{4,6} sensor materials,^{7,9} solar cells.^{10, 11} electrochemical super capacitors,^{12,13} electrochromic films, and fuel cell electrodes.^{14,15} NPs can be prepared using a variety of techniques, such as thermal decomposition, micro emulsion, precipitation, electrochemical deposition, flame spray pyrolysis reactor, sol-gel technique, surfactant mediated method, solution combustion method, etc. Among these, solution combustion has an advantage over other approaches since it is regarded as simple, quick, one-stage, and vitality-saving. Additionally, this

method produces a uniform, incredibly fine crystalline product without the need for mild crushing or calcination.¹⁶ In fact, because of their size and large surface area, nano-sized BaCaO₂ materials are quite intriguing in comparison to bulk BaCaO₂. Here, we describe the union of BaCaO₂ NPs using the solution combustion method with urea as fuel and Barium and Calcium nitrates as oxidizers. Because urea is nontoxic, economical, and rich in carbon, nitrogen, hydrogen, and oxygen, all of which are released as comparable gasses during combustion, it is used as fuel. These gasses cause BaCaO₂ NPs to form that are very permeable, voluminous, and have a large surface area. The obtained product exhibits strong photocatalytic activity against acridine orange.

As of late, the control of contamination from organic pollutant are considered as serious issue.¹⁷ Hued effluents discharged by various ventures might be mutagenic, cancer-causing and harmful. Acridine orange (AO), a heterocyclic hue with nitrogen atoms, is widely used in lithography, printing and coloring, and printer ink.¹⁸ It has also been extensively used in organic stains. Aminoacridine may be mutagenic, according to toxicological analyzes.¹⁹ Being a sweet-smelling compound Acridine orange intercalates inside the sets of bases in the DNA preferring additions and erasures of nucleotide bases upon replication.^{20,23} A nearby consideration has been given to creating color treatment techniques from squander stream at its source. An option in contrast to regular strategies, "advanced oxidation process" (AOPs) have been created dependent on the age of profoundly responsive species, for example, hydroxyl radicals. The produced hydroxyl radicals can oxidize a wide scope of natural contaminations rapidly and non-specifically. Among the (AOPs), heterogeneous photocatalysis shows up as a developing answer for the natural contamination of oceanic framework. This procedure comprises of the nonselective devastation of natural mixes in nearness of regular light and photocatalysis frameworks, for example, TiO₂, ZnO, and CdS.^{24,25} In this examination we have combined BaCaO₂ NPs by straightforward solution combustion technique and we have applied these integrated NPs for the debasement of Acridine orange color in nearness of regular daylight by various boundaries catalyst dosage, diverse pH, and diverse light conditions.

2. MATERIALS AND METHOD

The commercially accessible water dissolvable color Acridine Orange (λ_{max} 492nm) was gotten from Sigma Aldrich, Mumbai, India (Figure 1). Hi Media Chemicals provided the synthetic materials (99% A.R.), barium nitrate (Ba(NO₃)₂), calcium nitrate (Ca(NO₃)₂), and urea (NH₂CO NH₂). The absorbance at λ_{max} has been recorded using the visible spectrophotometer (Elico, SL 177). Subsequently, the absorbance was measured using an Elico SL 177 visible spectrophotometer.



Molecular weight: 265

Figure 1. Chemical structure of Acridine orange

3. SYNTHESIS OF NANOPARTICLES



After the crucible solution was implanted in a muffle furnace that had been warmed to 500°C, the incorporated nanoparticles were crushed in a mortar to make them amorphous and used for further illustration. Using a Rigaku diffractometer with Cu-K α radiation (1.5406 Å) in a θ -2 θ configuration and a scanning electron microscope (SEM), nanoparticles were shown by powder X-ray diffraction (XRD). Using a Ultraviolet-Visible spectrophotometer, the photocatalysts' UV-visible spectra were completed in the λ range of 350 to 800 nm. An Energy Dispersive X-ray (EDX) spectrometer was used to confirm the components' proximity.

4. PORTRAYAL OF INCORPORATED NANOPARTICLE

4.1 X Ray diffraction (XRD)

The X-ray diffraction examples of BaCaO₂ nanoparticles uncover that, the presence of Rhombo Hedral structure and the 2 θ tops were identified with Barium calciate, (37.29°, 43.30°, 62.87°, 75.40°, 79.33°) (JCPDS card No.01 Calciate (23.13°, 29.48°, 39.48, 48.59°, 57.48°) (JCPDS card No.00-024-0027). As per the Debye Scherrer's formula: The example got from the XRD analysis of the readied BaCaO₂ nanoparticles is appeared in (Fig. 2)

$$D = K\lambda/\beta \cos\theta$$

Equation (2)

Where

K = Scherrer's Constant

λ = X-Ray Wavelength

β = Peak width at half-maxima

θ

= Bragg's Diffraction angle

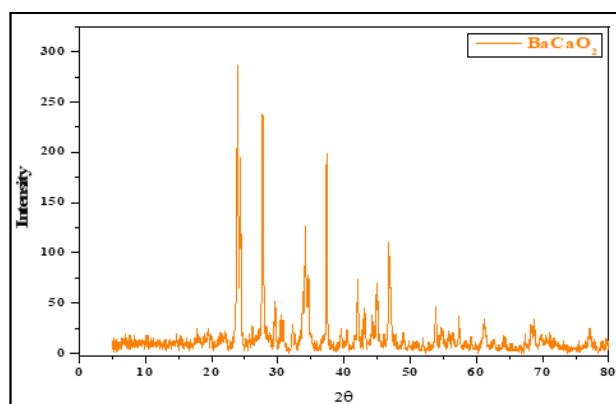


Figure 2. XRD of the synthesized BaCaO₂ Nanoparticles.

The XRD studies conducted on the powdered sample of Barium calciate in the present work revealed that its size varied from 26 nm to 59 nm, with an average size of 40 nm.

4.2 SEM

Scanning Electron Microscope images show BaCaO₂ nanoparticles. The photo shows crystals that are

scattered and have uneven, irregular shapes. The enlarged image reveals the sharp-edged, uneven texture of the various nanoparticles, as well as their strong bonding on top of one another (Fig. 3).

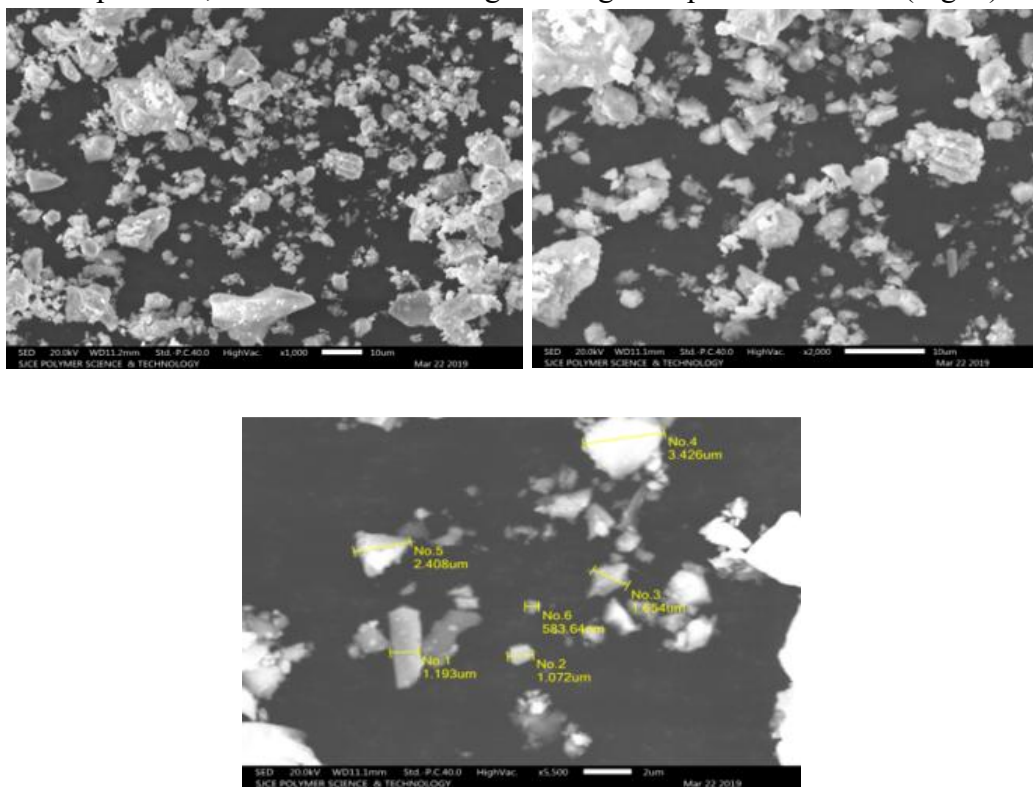


Figure 3. Scanning electron micrographs of produced $BaCaO_2$ nanoparticles.

4.3 UV Vis Spectroscopy

The optical absorption serves as an important method for determining the optical energy band gap of both crystalline and amorphous materials. The fundamental assimilation is akin to the electron hopping from the valence band to the conductivity band. The spectrum reveals that $BaCaO_2$ nanoparticles are incorporated into visible radiation with a frequency exceeding 350 nm. The optical band gap (OBG) estimation is derived from the TAUC's relationship:

$$ah\nu = \beta h\nu - E_n \quad (3)$$

Here, ' $h\nu$ ' represents the photon energy, ' β ' denotes the constant, and ' n ' is the power factor, which takes the values of 1/2, 2, 3/2, and 3 for allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions, respectively. The OBG of the barium calcite nanoparticle was determined to be 3.57 eV.

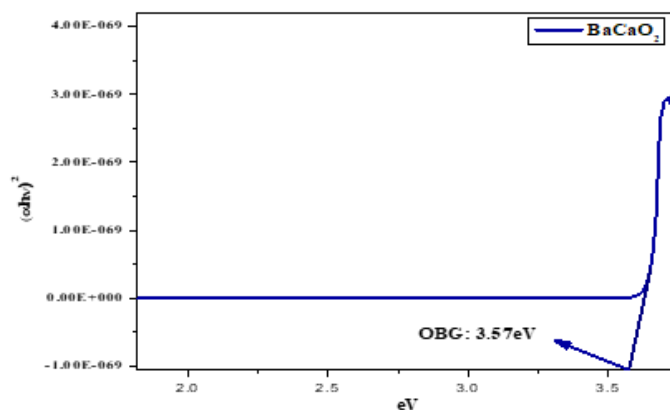


Figure 4. UV-absorption spectra of synthesized Barium calcite Nanoparticles.

4.4 Energy Dispersive X-Ray

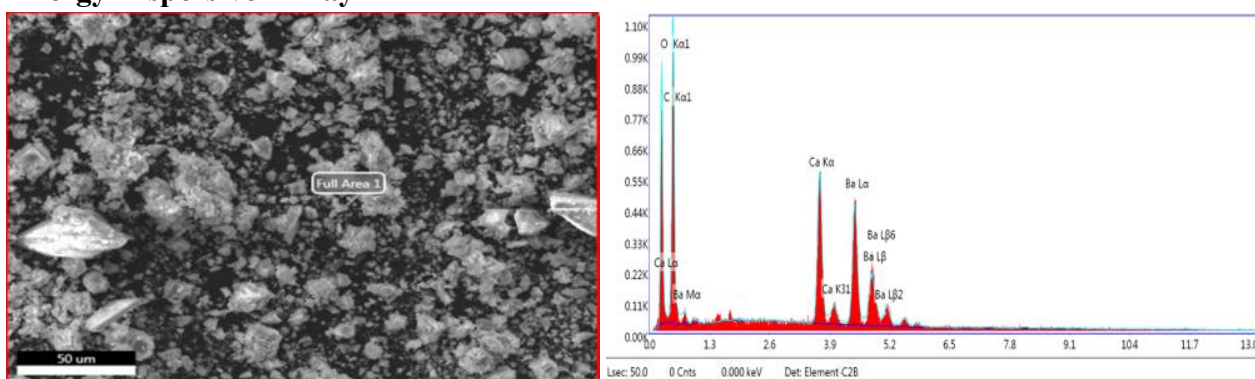


Figure 5. Energy Dispersive X-ray of synthesized BaCaO₂ nanoparticles

Table 1. Percentage Weight

Element	Weight %	Atomic %
C	17.87	36.89
O	31.23	48.41
Ca	12.59	7.79
Ba	38.31	6.92

The corroborative presence of components was completed utilizing EDAX spectrometer. The presence of Barium, Calcium, Carbon and Oxygen nanoparticles were confirmed. The vertical pivot shows the measure of x tallies in spite of the fact that, the level hub shows energy in KeV (Fig. 5). The weight and nuclear level of Carbon, Oxygen, Calcium, and Barium was seen as 17.87, 31.23, 12.59, 38.31 and 36.89, 48.41, 7.79, 6.92 these relates, the spectrum without contaminations peaks.

5. RESULT AND DISCUSSION EXPERIMENTAL PROCEDURE

The debasement of the dye molecules was evaluated using UV and visible absorption spectroscopy. The color solution's absorbance was measured using a UV-VIS Spectrophotometer 119 (Systronics) across a range of 350 to 800 nm. The λ max of Acridine orange was seen as 492 nm. The photocatalytic response

tests were completed within the sight of direct daylight. The norm (20mg/L) color solution was set up by dissolving 20 mg of Acridine orange color in 1 liter distilled water and explored for its decolourization by utilizing Barium calcite nanoparticles as catalyst at various measurements and pH levels. The pH of the color solution was balanced by utilizing weaken hydrochloric acid and sodium hydroxide. For each pH level (ranging from pH 2 to pH 10), the response volume of a 100 ml color solution (with a concentration of 20 mg/L) was measured, and catalyst doses ranging from 0.1 g to 1 g were added to assess the effectiveness of color degradation under direct sunlight. Once the impetus was scattered, the absorbance of the color solution was measured at intervals of minutes with a UV-VIS Spectrophotometer - 169 (Systronics). The accompanying equation was used to determine the percentage of decoloration.

$$\text{Decolorization} = \frac{V_0 - V_t}{V_0} \times 100 \quad (4)$$

$$V_0 - V_t + V_0 \times 100$$

Where, V_0 is the initial absorbance of dye solution and A_t is absorbance at time 't'

5.1 Effect of Catalyst Concentration on Barium calcite

The impact of catalyst concentration on the photocatalytic degradation was concentrated over a range of catalyst from 0.1 to 1g/100ml for Acridine orange. The incorporated nanoparticles have demonstrated obvious outcomes. The Acridine orange with the nano-molecule size 40 nm has indicated 88% degradation. Since, the photodegradation was best at 0.5g/100ml in a short time for Acridine orange nanoparticle measurements appeared in (Fig. 6) tests were proceeded with same measurements.

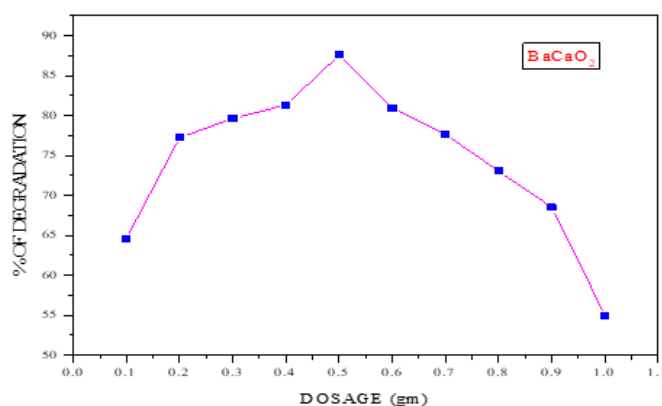


Figure 6. Effect of catalyst concentration on Acridine orange at 120 minutes. (Acridine orange =20 ppm, pH=4, BaCaO₂)

Mechanism of the Photocatalytic degradation



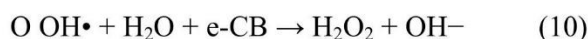
Nanoparticle molecules get excited and transfer electrons to the conduction band.



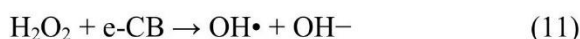
An electron in the conduction band of the nanoparticles can reduce molecular oxygen and produce the super oxide radical.



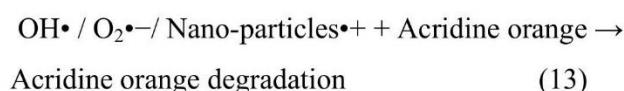
Adsorbed molecular oxygen on the surface of photocatalysts prevents the recombination of hole-electron pairs¹⁴ The rate of photocatalytic degradation diminishes due to the recombination of hole-electron pairs. In the presence of oxygen and an organic molecule, this radical may produce hydrogen peroxide or an organic peroxide.



Hydrogen peroxide can be generated in another path



Hydrogen peroxide can form hydroxyl radicals which are powerful oxidizing agents.



The radicals produced are capable of attacking dye molecules and degrade them.

5.2 Effect of pH on Acridine orange

So as to examine the impact of pH on the debasement effectiveness of Barium calciate as catalyst, the trials were done at pH running from 2 to 10. The outcomes indicated that pH fundamentally influenced the debasement effectiveness (Fig. 7). The degradation pace of Acridine orange for BaCaO₂ have ascended from 83.4% to % 88% from pH 2 to 4 and unexpected diminishing in degradation from 88% at pH 4 to 83.7%, 83% and 82.7% for the Ph 6, 8 and 10 watched after 120 minutes for 0.5g/100ml. The most extreme debasement rate for the nanoparticle was accomplished at pH 4.¹⁵

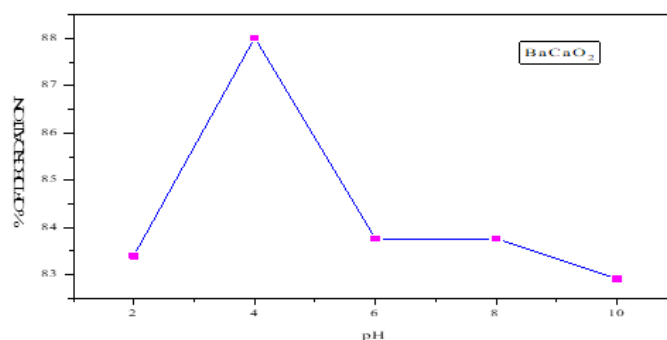


Figure 7. Impact of pH on Acridine orange at 120 minutes. (Acridine orange=20 ppm, BaCaO₂)

5.3 Effect of initial dye concentration

The analyses were directed to consider the impact of initial color concentration by changing the Acridine orange fixation from 20 ppm to 50 ppm. The outcomes acquired for BaCaO₂ is 88% for 20ppm, 71% for 30ppm, 69 % for 40ppm, 44% for 50ppm, individually (Fig. 8). These trials delineated that the degradation proficiency was legitimately influenced by the fixation. The reduction in debasement with increased color concentration was ascribed to the equilibrium adsorption of dye molecules on the catalyst surface, resulting in a decrease in active sites.¹⁶ According to the Beer Lambert law, as the initial concentration of dye increases, the path length for photons entering the solution decreases. “This results in the reduced photon assimilation of the impetus particles, leading to a decline in the photocatalytic response rate”

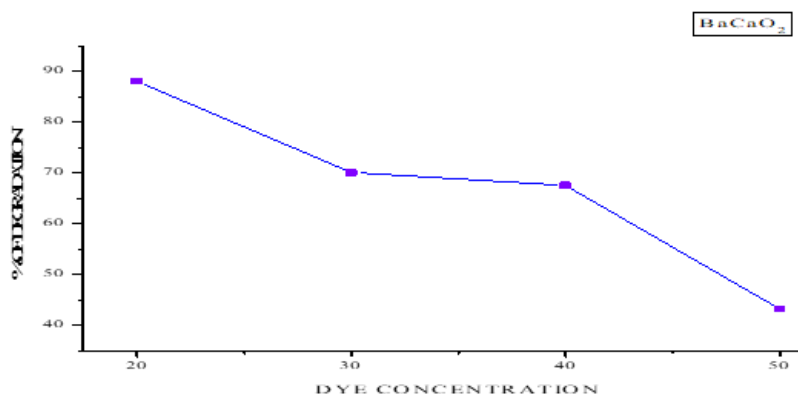


Figure 8. Effect of initial dye concentration on the photocatalytic degradation of Acridine orange. (BaCaO₂ g/pH=0.5/4 and Acridine orange = (20+30+40+50) ppm)

5.4 Effect of sunlight irradiation on Acridine orange

Acridine orange (20 mg/L) was subjected to photocatalytic degradation under three different experimental conditions: through sunlight alone, dye/dark/catalyst, dye/UV/catalyst, and dye/sunlight/catalyst. When the acridine orange dye solution was exposed to sunlight directly without a catalyst, its degradation was found to be zero throughout the experiments. It was observed that the degradation rate rises with longer irradiation times. Specifically, for dye/sunlight/BaCaO₂, it reached 88%, for dye/UV/catalyst it was 43%, and for dye/dark/BaCaO₂ it was recorded at 54.04% (Fig. 9). The results clearly demonstrate that photodegradation happens most effectively in sunlight.

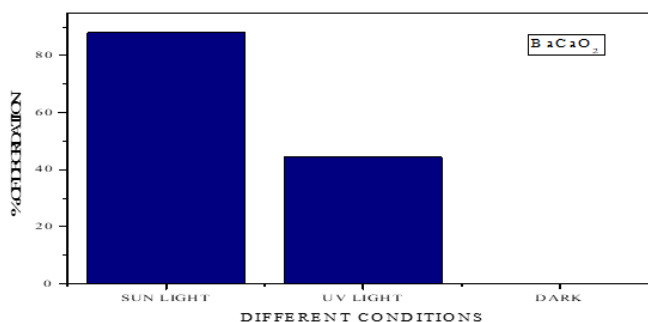


Figure 9. Effect of sunlight irradiation with respect to Dark condition and UV condition on photocatalytic degradation of Acridine orange in 120 minutes

6. CONCLUSION

The integrated Barium Nitrate is end up being photocatalytic and successful in degrading the Acridine orange dye in a shorter time frame. The photocatalytic degradation of Acridine orange utilizing daylight as a source of illumination was examined. The proposed photocatalytic strategies end up being extremely powerful for the degradation of color Acridine orange. For the dye Acridine orange we have accomplished 88% degradation in pH 4. With this outcome we can say that the utilization of nano estimated materials is progressively reasonable for degradation of color effluents in research center conditions. This will help in the treatment of material effluents which are causing water contamination.

REFERENCES:

1. Ray, Chaiti, and Tarasankar Pal. "Recent advances of metal-metal oxide nanocomposites and their tailored nanostructures in numerous catalytic applications." *Journal of Materials Chemistry*. 2017; 9465-9487.
2. Habibi MH, Fakhri, J. *Mater. Sci. Mater. Electron*. 2017. doi:10.1007/s10854-017-7261-3
3. Kianfar AH, Dehghani P, Momeni MM. *J. Mater. Sci. Mater. Electron*. 2026. Vol.27; 3368–3375.
4. Zheng F, Xu S, Zhang Y. *J. Mater. Sci. Mater. Electron*. 2016.Vol. 27; 3576–3582
5. Cao T, Fang D, Liu L, Luo Z, Wang Q, Dong L, Xiong C, J.*Mater. Sci. Mater. Electron*.2015. Vol. 26; 5279–5286
6. Wang Y, Su Q. *J. Mater. Sci. Mater. Electron*. 2016. Vol.27; 4752–4759
7. Li D, Li Y, Li F. Zhang J, Zhu X, Wen S, Ruan S. *Ceram. Int*. 2015 Vol. 41; 4348–4353
8. Hassan ES, Saeed AA, Elttayef AK. *J. Mater. Sci. Mater. Electron*. 2016. Vol. 27; 1270–1277
9. Gao Q, Zeng W, Miao R. *J. Mater. Sci. Mater. Electron*. 2016. Vol. 27;9410–9416
10. Xu X, Liu Z, Zuo X, Zhang M, Zhao Z, Shen Y. *Nano Lett*.2015. Vol.15; 2402–2408
11. Raissi M, Pellegrin Y, Jobic S, Boujtita M, Odobel F. *Sci. Rep*. 2016. Vol.6; 24908
12. Cheng J, Zhao B, Zhang W, Shi F, Zheng G, Zhang D, Yang J. *Adv. Funct. Mater*.2015. Vol. 25;7381–7391
13. Kim S, Lee J, Ahn H, Song H, Jang J. *ACS Appl. Mater. Inter*.2013. Vol. 5;1595–1603
14. Park B, Cairns EJ, *Electrochem. Commun*. 2011.Vol. 13; 75–77
15. De Souza S, Visco S, De Jonghe LC. *Solid State Ion*.1997.Vol. 98; 57–61.
16. Shivaraj B. Patil1, Ravishankar TN, Lingaraju K, Raghu GK, Nagaraju G. Multiple applications of combustion derived nickel oxide, *J Mater Sci: Mater Electron*.2018;29:277–287.

17. Tadjarodi A, Imani M, Kerdari H, Bijanzad K, Khaledi D, Rad M. Preparation of CdO Rhombuslike Nanostructure and Its Photocatalytic Degradation of Azo Dyes from Aqueous Solution. *Nanomaterials and Nanotechnology*. 2014 Vol. 4(16); 1-10.
18. Chung-Shin Lu, Chiing-Chang Chen, Ling-Kuen Huang, Peir-An Tsai, Hsiao-Fang Lai. Photocatalytic Degradation of Acridine Orange over NaBiO₃ Driven by Visible Light Irradiation, *Catalysts*. 2013. Vol.3; 501-516; doi:10.3390/catal3020501
19. Brinker CJ, Cornils B, Bonet M, Ullmann's Encyclopedia of Industrial Chemistry, Part A27. In Triarylmethane and Diarylmethane Dyes, 6th ed.; Wiley-VCH: New York, NY, USA, 2001.
20. Young GO, "Synthetic structure of industrial plastics (Book style with paper title and editor)," in *Plastics*, 2nd ed. vol.3, J. Peters, Ed. New York: McGraw-Hill, 1964, pp. 15–64.
21. Chen WK, *Linear Networks and Systems* (Book style). Belmont, CA: Wadsworth. 1993; 123–135.
22. Poor H, *An Introduction to Signal Detection and Estimation*. New York: Springer-Verlag. 1985; ch. 4.
23. Smith B, "An approach to graphs of linear forms (Unpublished work style),"
24. Yogendra K, Suneel Naik, Mahadevan KM, Madhusudhana N. A comparative study of photocatalytic activities of two different synthesized ZnO composites against Acridine orange dye in presence of natural solar light, *International Journal of Environmental Sciences and Research* 2011. Vol.1(1); 11-15.
25. Madhusudhana N, Yogendra K, Mahadevan KM. Photocatalytic decolourization of Textile Effluent by Using Metal Oxide Nanoparticles, *Journal of Science and Arts*. 2013. Vol. 3(24); 303-318.