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SOL-GEL SYNTHESIZED SnO_2 NANOPARTICLES SHOWING ADVANCED PHOTOCATALYTIC ATTRIBUTES FOR ENVIRONMENTAL POLLUTION CONTROL

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ABSTRACT

Tin oxide (SnO_2) is an interesting material having novel structural and optical properties. To investigate the above properties, the sol-gel route is selected to prepare SnO_2 nanoparticles. Detailed investigation of the structure such as; phase analysis and crystallinity was accomplished by the X-ray diffraction (XRD) method. It has been observed that the as-synthesized tin oxide has a tetragonal rutile structure. The synthesized SnO_2 samples have an average crystallite size from 20 nm to 26 nm as ascertained from the XRD study. Morphology study by field emission scanning electron microscopy (FESEM) shows the evolution of monodispersed nanocrystallites of SnO_2. The photocatalytic property of SnO_2 nanoparticles was studied in degrading a cationic dye such as; methylene blue with the application of UV-Vis light. The dye degradation rate before & after illumination of UV-Visible light at (λ = 664 nm) was calculated which follows pseudo-first-order kinetics. The parameters such as catalyst dosage and pH have influences on the degradation rate which has been studied systematically. A degradation of 84.23 % has been obtained by tin oxide nanoparticles after 120 min of UV irradiation. This will eventually help in treating the industrial wastes mixed with water bodies targeting water pollution.

Keywords: SnO_2 Nanoparticles, Methylene Blue, Photocatalysis, Water Pollution, Dye Degradation.
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INTRODUCTION

Nanomaterials of metal oxides show interesting properties which find many applications in diversified areas of science and technology like memory drives, LEDs, sensors, solar cells, LASERs, paint, sunscreens, antibacterial coatings, and wastewater treatment.[1-8] These nanomaterials with novel morphology and size below 100 nm have created renewed interest among scientists and engineers due to their stimulating characteristics and enchanting applications in the above fields.[9-15] As an efficient class of materials, semiconducting metal oxides like ZnO and SnO_2 with controlled size and morphology have presented themselves with superiority with footprints in different areas of science and technology.[16-24] With a selective synthesis method and precursor concentration, one can tune the structure of these materials leading to a large variation in their optical, electrical, and magnetic properties. These nanomaterials also show good photodegradation properties in the mineralization of harmful contaminants. So, they are always treated with great applause as these have a great role in environmental clean-up. Tin oxide (SnO_2) is involved hugely in this research area due to its exceptional physical and chemical properties with excellent optical, electronic, and chemical stability. SnO_2 nanoparticles demonstrate elevated surface-to-volume ratio, superior quantum size effect & a good fraction of similar surface sites which elevate their applicability.[25-28] SnO_2 being a semiconductor of n-type nature has a broad and room temperature energy band gap of 3.6 eV. Tin oxide possesses very good electro-optical attributes such as; minimum resistivity, high optical transparency, and improved specific capacity (theoretical).[29,30] Furthermore, the high electron mobility feature of tin oxide makes it a good transporter of photo-excited electrons.[31-33] Again, SnO_2 has been considered a capable material and it possesses interesting attributes such as; photoluminescence and photocatalysis which are related to the surface.[34-36] Tin oxide nanoparticles having a size less than 10 nm have a special quality of demonstrating increased photodegradation rate of the organic dyes which is possible due to the high surface area amplifying the reactions involved in the photocatalytic process and raising the competency of separation between the electron-hole pairs.[37-39] Several low-cost methods of synthesis are widely reported

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by which nano tin oxide of different size and shapes and sizes can be prepared for possible use in the making of catalysts, solar cells, flat panel displays, gas sensors, etc.[40,41] A variety of notable and efficient processes were used to synthesize SnO_2 nanoparticles with improved command over particle size/shape and physical properties comprises co-precipitation, sol-gel method, hydrothermal method, polymeric, organo-metallic precursor synthesis, sonication, microwave, and surfactant-mediated method.[42-50] Out of the above-described methods, nanoparticles with good crystallinity at a lower operating temperature can be prepared by sol-gel synthesis.[51] Among other reported procedures deployed for preparing SnO_2 nanoparticles, the sol-gel process provides numerous benefits such as; lower operating temperature, better homogeneity of product, and preparation of nanosized particles with accurate composition. In the current work, the method of sol-gel was used to prepare tin oxide nanopowder and we carried out the experiment to study its structure and optical properties. Photo-degradation of cationic dye (methylene blue) has also been studied by taking SnO_2 nanoparticles as the photocatalyst.

EXPERIMENTAL

Sol-gel method is an efficient and simple method of preparation of nanoparticles which was used in our experiment for SnO_2 nanoparticle synthesis. The chemical reagents were taken such as Tin (II) chloride dihydrate ($SnCl_2$), isopropyl alcohol, sodium hydroxide (NaOH), and methylene blue. These chemicals were of high purity (99.99 %) and purchased from M/s Merck. Precursor materials like $SnCl_4.5H_2O$ and isopropyl alcohol were considered with different concentrations. In $SnCl_4.5H_2O$ solution, isopropyl alcohol (50 mL) was mixed. The final solution was allowed to stir for 2 h in a stirrer. Through this process, we obtained a homogenous solution. To attain the pH of the solution around 9-11, it was mixed with 0.1 M NaOH solution drop by drop manner from a burette. We allowed the solution to settle down for 2 to 3 h before which it was stirred for 30 minutes more in the same stirrer. Acetone and distilled water were used to wash the precipitates and let for drying at 80° C. The dried sample was collected in powdered form. Different weights of $SnCl_4.5H_2O$ i.e. 1 gm, 1.5/2.0/2.5 gm were taken and the above process was followed to synthesize samples named as S1, S2, S3, and S4 respectively. XRD method was used for the identification of phase and crystal structure analysis of thin films and nanoparticles. X-ray diffraction measurement (M/s Panalytical) was used to study the structural properties of SnO_2 nanopowders with a radiation source comprised of Cu Kα (1.5406 Å). Debye-Scherer formula (as given below) was utilized to ascertain the average grain size (d).

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

SnO_2 morphology was investigated by FESEM (Zeiss Supra). The photocatalytic activity was studied by degrading harmful contaminants like methylene blue taking tin oxide nanoparticles as photocatalysts under UV-Vis light irradiation. In the first step, an amount of 5 milligrams of sample S1 was put in the container with 100 mL of dye (10 mgL^{-1}) and subjected to stirring conditions for 1 h. From this above solution, 2 mL of the reactant was pipetted out and we used a spectrometer to record the absorbance. Next to it, the same dye solution with catalysts was illuminated with the source of light, and for every 10 min interval, we collected some fixed quantity of the sample (3 mL) and used a centrifuge for the above purpose. We measured absorbance every 10 min and the alternation in the color of the contaminant was recorded by a spectrophotometer. Our earlier study reports the detailed experiment.[20]

RESULTS AND DISCUSSION

XRD measurement reveals some interesting results on the crystal structure of the synthesized tin oxide samples that have been analyzed and discussed. The diffraction patterns obtained for all the synthesized products with variable concentrations have been represented in Fig.-1. It has been observed that tin oxide has been formed with a tetragonal rutile structure as confirmed by the diffraction peaks observed in Fig.-1. This matches well with the standard diffraction database (JCPDS Card No 14-1445).[20,28] XRD peaks were observed at different 2θ values of 26.76° (110), 33.88° (101), 38.05° (200), 51.76° (211), and 54.85° (220) corresponding to the corresponding crystal planes respectively. The long-range of crystallinity of the SnO_2 nanoparticles is understood from the high intense and narrow diffraction peaks as depicted in Fig.-1. We have estimated the values of average grain size and other unit cell parameters of the tin oxide samples which have been given in Table-1. Calculation of average grain sizes of nano SnO_2 shows the value from 20 nm to 26 nm and also the lattice parameters remain slightly different for SnO_2 prepared with different

concentrations. It is not possible for our part to observe the existence of tin oxide in the monoclinic phase or high-temperature cubic phases in the XRD pattern.

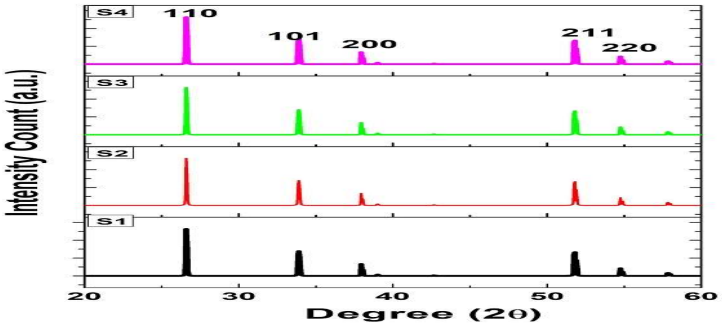

Fig.-1: XRD Spectra of Synthesized SnO_2 Nanoparticles with Various Concentrations

The estimated values of a = 4.737 Å and c = 3.186 Å indicate that these values are close to consistent with the values obtained for the standard.[28] The unit cell volume has also been calculated and summarized in Table-1. It shows that these values are close to the volume of the cubic system which is found to be 71.497 $Å^3$ after calculation using the formula ($V= a^2 x c$). From the obtained data, the density value was calculated and found to be higher than the standard value indicating the prepared powder to be dense. It also intends that the unit cells of the material are closely packed with each other. Lattice microstrain was also estimated and given in Table-1. The FESEM image showing the surface morphology of the sample (S4) has been displayed in Fig.-2. Spherical-shaped nanoparticles of tin oxide are formed as noticed from the FESEM image. These nanoparticles are uniformly distributed with an average size of 20-40 nm and are also found to be agglomerated.

Table-1: Crystallographic Parameters of Nanocrystalline SnO_2

Name of Sample	Average grain Size (nm)	Lattice Micro-stain	Lattice Parameter			Density (gm/cm^3)	Volume $(Å)^3$
			a (Å)	c (Å)	c/a		
S1	22	0.0012	4.321	3.187	1.355	6.472	71.047
S2	24	0.0011	4.322	3.178	1.359	6.500	71.123
S3	25	0.0017	4.331	3.174	1.156	6.492	71.214
S4	26	0.0012	4.301	3.175	1.354	6.502	71.221

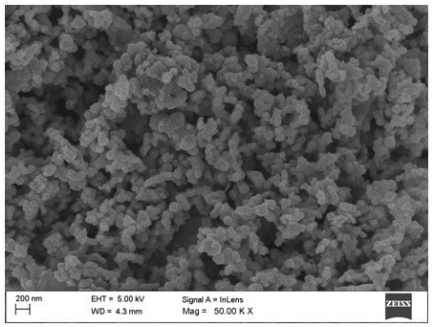

Fig.-2: FESEM Image of SnO_2 Nanoparticles (S4)

The photocatalytic property of a material defines its ability to degrade harmful contaminants. The decomposition is carried out with the application of UV-Vis light and the corresponding absorbance spectrum indicates the degradation (%). The degradation of the contaminant in the solution is evident from the lowering of the absorbance peak intensity as recorded by a UV–Vis spectrophotometer. So, the same process was followed to check the degradation ability of tin oxide nanoparticles. The pH of most natural and industrial wastewater appears from 6 to 8. So, we maintained the above value for the dye solution (MB) in that range with SnO_2 catalysts. A solution (10 mL) was prepared by taking 10^{-4} M of MB and we varied the concentration (1 to 5 mg/L) along with SnO_2 photocatalysts. A magnetic stirrer was deployed to stir the mixture continuously for 30 min before exposing it to light. Adsorption-desorption equilibrium is thus

achieved between the photocatalyst surface and MB dye.[12,20] The result shows that a dominant peak is seen at 664 nm in the absorbance spectrum of methylene blue dye solution whose intensity is observed to decrease with the increase in light irradiation time.[12] This gives a hit of successful degradation of the dye under the influence of the tin oxide photocatalyst.

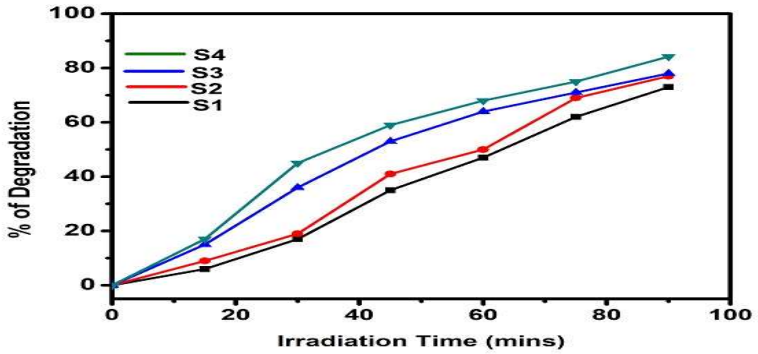

Fig.-3: Degradation (%) of MB with Varying SnO_2 Concentrations at Different Light Exposure Times

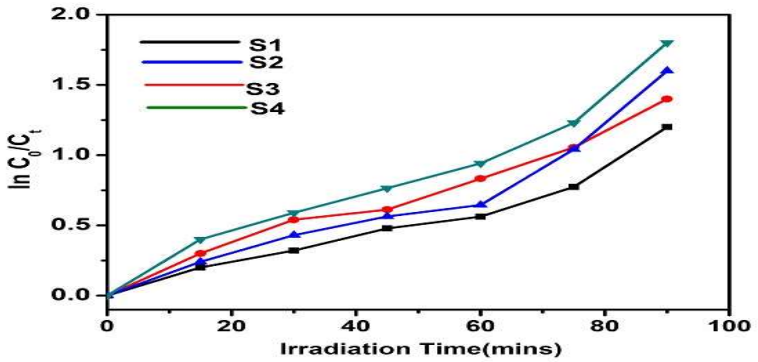

Fig.-4: Variation in $\ln(C_o/C_t)$ with Change in Light Exposure Time Showing First-Order Kinetics

Figure-3 illustrates the change in degradation (%) with variation in light exposure time which tells that the increase in light irradiation time leads to an enhancement in dye degradation. It was observed that no degradation occurred for the dye solution in the dark with and without photocatalyst. About 84.23 % of degradation was achieved for the S4 sample as compared to the other three samples (Fig.-3). With the increase in the amount of catalyst, we observed an increment in the degradation (%) for all the prepared samples. There may exist two reasons for this enhanced photocatalytic activity. The first reason is the small crystallite size of nanoparticles of SnO_2 having a high surface area. The second reason is the retardation in the recombination of electron-hole on the surface of SnO_2.[12,20,51,52] SnO_2 with smaller grain size and variable morphology has resulted in increased photocatalytic efficiency due to the modification in the separation of charge carriers.[50,51,53] In addition to that, the uniform morphology of SnO_2 photocatalysts is another parameter that favors the transfer of both electrons and holes inside the crystal lattice. These carriers facilitate the degradation of dye solutions. The degradation of methylene blue by photocatalysts of nano tin oxide obeys the first-order kinetics as depicted in Fig.-4.[12] The study further enumerates that photocatalysis is an effective method for the degradation of organic contaminants.[54,55,56,57]

CONCLUSION

We have carried out an investigation on the synthesis tin oxide nanoparticles and study on its structure and photocatalytic properties. A simple wet chemical method like the sol-gel route was adopted for the preparation of SnO_2 nanomaterials with variable concentrations of the reactants. The polycrystalline nature of the samples with tetragonal rutile structure has been observed from XRD analysis. The XRD data is further analyzed to find out the nanoparticle size which was found in the range of 22-26 nm. The uniform distribution of spherical-shaped nanoparticles is observed from FESEM measurement. Methylene blue as a model dye was taken for degradation by using SnO_2 nanocatalysts and the photodegradation efficiency

has been calculated. It has been observed that under UV-Vis light illumination, 84.23 % degradation is achieved in 120 min. This result will find the application of metal oxide nanoparticles like tin oxide in controlling environmental pollution.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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REFERENCES

1. D. Sahu, N.R. Panda, B.S. Acharya, A.K. Panda, *Optical Materials*, **36**, 1402(2014), http://dx.doi.org/10.1016/j.optmat.2014.03.041
2. D. Sahu, B.S. Acharya, A.K. Panda, *Ultrasonics Sonochemistry*, **18**, 601(2011), https://doi.org/10.1016/j.ultsonch.2010.08.012
3. D. Sahu, N.R. Panda, B.S. Acharya, A.K. Panda, *Ceramics International*, **40**, 11041(2014), http://dx.doi.org/10.1016/j.ceramint.2014.03.119
4. D. Sahu, B.S. Acharya, B.P. Bag, T.B. Singh, R.K. Gartia, *Journal of Luminescence*, **130**, 1371(2010), https://doi.org/10.1016/j.jlumin.2010.02.049
5. N.R. Panda, D. Sahu, B.S. Acharya, P. Nayak, *Current Applied Physics*, **15**, 389(2015), http://dx.doi.org/10.1016/j.cap.2015.01.014
6. D. Dash, N.R. Panda, D. Sahu, *Applied Surface Science*, **494**, 666(2019), https://doi.org/10.1016/j.apsusc.2019.07.089
7. D. Sahu, N.R. Panda, B.S. Acharya, *Materials Research Express*, **4**, 114001(2017), https://doi.org/10.1088/2053-1591/aa9597
8. N.R. Panda, D. Sahu, B.S. Acharya, *Journal of nanoscience and nanotechnology*, **12**, 6977(2012), https://doi.org/10.1166/jnn.2012.6567
9. N.R. Panda, D. Sahu, S. Mohanty, B.S. Acharya, *Journal of nanoscience and nanotechnology*, **13**, 427(2013), https://doi.org/10.1166/jnn.2013.7073
10. N.R. Panda, D. Sahu, B.S. Acharya, P. Nayak, S.P. Pati, D. Das, *Acta Metallurgica Sinica (English Letters)*, **27**, 563(2014), https://doi.org/10.1007/s40195-014-0093-8
11. D. Sahu, B.S. Acharya, N.R. Panda, *AIP Conference Proceedings*, **1728**, 020165(2016), https://doi.org/10.1063/1.4946216
12. D. Dash, N.R. Panda, D. Sahu, *Nano Express*, **2**, 010007(2021), https://doi.org/10.1088/2632-959X/abd90b
13. N.R. Panda, D. Sahu, *Heliyon*, **6**, e04717(2020), https://doi.org/10.1016/j.heliyon.2020.e04717
14. D. Sahu, *Russian Journal of Chemistry*, **93**, 905(2020), https://doi.org/10.1134/S107042722006018X
15. A. Palai, N.R. Panda, D. Sahu, *Journal of Molecular Structure*, **1244**, 131245(2021), https://doi.org/10.1016/j.molstruc.2021.131245
16. D. Sahu, N.R. Panda, B.S. Acharya, A.K. Panda, *AIP Conference Proceedings*, **1591**, 276(2014), https://doi.org/10.1063/1.4872571

17. N.R. Panda, S.P. Pati, D. Sahu, D. Das, *Materials Letters*, **300**, 130170(2021), https://doi.org/10.1016/j.matlet.2021.130170
18. D. Sahu, N.R. Panda, *Current Nanoscience*, **17**, 162(2021), https://doi.org/10.2174/1573413716999200728175722
19. D. Sahu, A. Palai, N.R. Panda, *Journal of Materials Science: Materials in Electronics*, **33**, 8504(2022), https://doi.org/10.1007/s10854-021-06401-8
20. P.K. Mishra, N.R. Panda, S.P. Pati, S.K. Biswal, D. Sahu, *ECS Journal of Solid State Science and Technology*, **10**, 071006 (2021), https://doi.org/10.1149/2162-8777/ac0cc6
21. S. Dhal, P. Das, A. Patro, M. Swain, S.R. Hota, D. Sahu, S. Chatterjee, *Radiation Physics and Chemistry*, **188**, 109649(2021), https://doi.org/10.1016/j.radphyschem.2021.109649
22. D. Sahu, N.R. Panda, D. Dash, *Asian Journal of Chemistry*, **32**, 1809(2020), https://doi.org/10.14233/ajchem.2020.22726
23. D. Sahu, N.R. Panda, B.S. Acharya, *AIP Conference Proceedings*, **1665**, 050013(2015), https://doi.org/10.1063/1.4917654
24. N.R. Panda, D. Sahu, B.S. Acharya, P. Nayak, *AIP Conference Proceedings*, **1665**, 050027(2015), https://doi.org/10.1063/1.4917668
25. H. Zhu, D. Yang, G. Yu, H. Zhang, and K. Yao, *Nanotechnology*, **17**, 2386(2006), https://doi.org/10.1088/0957-4484/17/9/052
26. E. Abdelkader, L. Nadjia and V. Rose-Noelle, *International Journal of Industrial Chemistry*, **7**, 53(2016), https://doi.org/10.1007/s40090-015-0061-9
27. N. Srivastava and M. Mukhopadhyay, *Industrial & Engineering Chemistry Research*, **53**, 13971(2014), https://doi.org/10.1021/ie5020052
28. P. K. Mishra, S.K. Biswal, D. Sahu, *Materials Today: Proceedings*, **68**, 80(2022), https://doi.org/10.1016/j.matpr.2022.06.104
29. S. Sheng Pan, S. Fung Yu, Y. Xia Zhang, *Journal of Applied Physics*, **113**, 143104(2013), https://doi.org/10.1063/1.4800896
30. L. Shi and H. Lin, *Langmuir*, **26**, 18718(2010), https://doi.org/10.1021/la103769d
31. C. Gao, X. Li, and B. Lu, *Nanoscale*, **4**, 3475(2012), https://doi.org/10.1039/C2NR30349C
32. D. Dash, D. Sahu, *IOP Conference Series: Materials Science and Engineering*, **1219**, 012037(2022), https://doi.org/10.1088/1757-899X/1219/1/012037
33. E. J. H. Lee, C. Ribeiro, T. R. Giraldi, E. Longo, E. R. Leite, and J. A. Varela, *Applied Physics Letters*, **84**, 1745(2004), https://doi.org/10.1063/1.1655693
34. H. J. Ahn, H. C. Choi, K. W. Park, S. B. Kim and Y. E. Sung, *Journal of Physical Chemistry B*, **108**, 9815(2004), https://doi.org/10.1021/jp035769n
35. S. Wu, H. Cao, S. Yin, X. Liu, and X. Zhang, *Journal of Physical Chemistry C*, **113**, 17893(2009), https://doi.org/10.1021/jp9068762
36. X. Xu, J. Zhuang and X. Wang, *Journal of the American Chemical Society*, **130**, 12527(2008), https://doi.org/10.1021/ja8040527
37. V. T. Agekyan, *Physica Status Solidi (A) Applied Research*, **43**, 11(1977), https://doi.org/10.1002/pssa.2210430102
38. Z. Ying, Q. Wan, Z. Song, S. Feng, *Nanotechnology*, **15**, 1682(2004), https://doi.org/10.1088/0957-4484/15/11/053
39. A. Singh, U. Nakate, Advances in Nanoparticles, **2**, 66(2013), http://dx.doi.org/10.4236/anp.2013.21012
40. H-C Chiu and C-S Yeh, *Journal of Physical Chemistry C*, **111**, 7256(2007), https://doi.org/10.1021/JP0688355
41. A. Firooz, A. Mahjoub, A. Khodadadib, *Materials Letter*, **62**, 1789(2008), https://doi.org/10.1016/j.matlet.2007.10.004
42. E. Leite, I. Weber, E. Longo, J. Varela, *Advanced Materials*, **12**, 965(2000), https://doi.org/10.1002/1521-4095(200006)12:13<965::AID-ADMA965>3.0.CO;2-7C

43. Nayral, E. Viala, P. Fau, F. Senocq, J. Jumas, A. Maisonnat, B. Chaudret, *Chemistry A European Journal*, **6**, 4082(2000), https://doi.org/10.1002/1521-3765(20001117)6:22<4082::AID-CHEM4082>3.0.CO;2-S
44. J. Zhu, Z. Lu, S. Aruna, D. Aurbach, A. Gedanken, *Chemistry of Materials*, **12**, 2557(2000), https://doi.org/10.1021/cm9906831
45. G. Pang, S. Chen, Y. Koltypin, A. Zaban, S. Feng, A. Gedanken, *Nano Letter*, **1**, 723(2001), https://doi.org/10.1021/nl0156181
46. V. Subramanian, W. Burke, H. Zhu, B. Wei, *Journal of Physical Chemistry C*, **112**, 4550(2008), https://doi.org/10.1021/jp711551p
47. J. Jouhannaud, J. Rossignol, D. Stuerga, *Journal of Solid State Chemistry*, **181**, 1439(2008), https://doi.org/10.1016/j.jssc.2008.02.040
48. Y. Wang, C. Ma, X. Sun, H. Li, *Nanotechnology*, **13**, 565(2002), https://doi.org/10.1088/0957-4484/13/5/304
49. P. Baker, R. Sanderson, A. Crouch, *Thin Solid Films*, **515**, 6691(2007), https://doi.org/10.1016/j.tsf.2007.01.042
50. W. Chen, D. Ghosh, S. Chen, *Journal of Material Science*, **43**, 5291(2008), https://doi.org/10.1007/s10853-008-2792-x
51. S. P. Kim, M. Y. Choi, H. C. Choi, *Materials Research Bulletin*, **74**, 85(2016), https://doi.org/10.1016/j.materresbull.2015.10.024
52. A. Palai, N. R. Panda, M. R. Sahoo, and D. Sahu, *Journal of Materials Science: Materials in Electronics***, 33**, 9599(2022), http://dx.doi.org/10.1007/s10854-021-07583-x
53. D. Dash, A. Palai, D. Sahu, *Ceramics International*, **48**, 28835(2022), https://doi.org/10.1016/j.ceramint.2022.03.139
54. M. Singh, P. Kumar, N. S. Singh and A. Jain, *Rasayan Journal of Chemistry*, **16(1)**, 268(2023), http://doi.org/10.31788/RJC.2023.1618076
55. H. Sutanto, I. Alkian, U. Hasanah, E. Hidayanto, I. Marhaendrajaya and Priyono, *Rasayan Journal of Chemistry*, **16(1)**, 140(2023), http://doi.org/10.31788/RJC.2023.1617061
56. P. P. Mandrekar and A. D'Souza, *Rasayan Journal of Chemistry*, **16(1)**, 276(2023), http://doi.org/10.31788/RJC.2023.1616889
57. N. Usha Rani, P. Pavani, C. N. S. S. P. Kumar, S. S. Marok and S. L. Tulasi, *Rasayan Journal of Chemistry*, **16(1)**, 398(2023), http://doi.org/10.31788/RJC.2021.1618165

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