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Review Paper

A review of synthesis of Nickel Oxide by different routes and its Photocatalytic and Microbial study

Deepa M. Audi
Dept of Chemistry, Dhempe College of Arts and Science, Miramar, Goa, India
audim@rediffmail.com

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Abstract

NiO nanoparticles are synthesised by co-precipitation, nanocomposite and precursor routes. The co-precipitation method have resulted in maximum yield. The synthesised nanoparticles were charecterised by x-ray diffraction, SEM methods. The crystallite size obtained from XRD using Debye Scherrer formula is found to be in nano range from all 3 methods. The precursor method has resulted in smallest nanoparticles of 12nm.The SEM image shows formation of tetragonal grains by co-precipitation method, nanocomposites have formed spherical clusters and agglomerates by precursor method. The synthesised NiO nanoparticles have found to be an efficient photocatalyst for degradation of methylene blue and have found to have antimicrobial properties.

Keywords: Co-precipitation, Nanocomposites, Co-precipitation, Precursor, Crystallite, Clusters, Photocatalyst.

Introduction

Nickel Oxide NiO, a well characterised oxide of Nickel compared to its other oxides. It exists in two forms rhombohedral, black in colour and is antiferromagnetic in nature. The other Cubic form, green in colour and is paramagnetic in nature. It is used as catalyst in hydrogenation, antiferromagnetic material, and a metal deficient p-type semiconductor with 3.6 ev band gap[1].

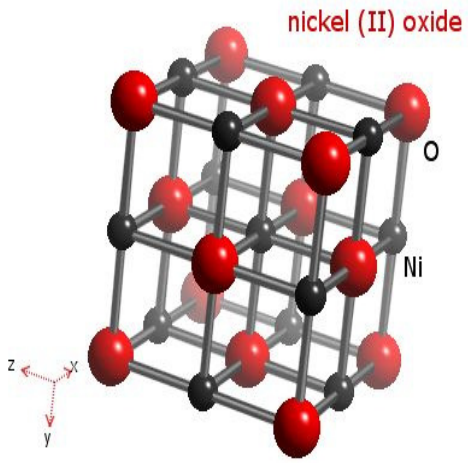

Figure-1: Cubic form of NiO[2].

Nickel is one of the transition metal that has magnetic property in relation with bulk state and has interesting applications such as hydrogen storage and catalytic property. Among magnetic nanoparticles it is difficult to synthesize NiO nanoparticles as they easily get oxidise[3].

Green NiO has a cubic rock salt structure and is stoichiometric unlike the black form which is non- stoichiometric in nature[3]. Temperature plays a very significant role in determining the magnetic behaviour of NiO .Bulk NiO is rhombohedral and is antiferromagnetic below 329 K and above this temperature it is found to exhibit Cubic structure and is paramagnetic. Nickel is one of the transitional metals that has a magnetic property in relation with its bulk state and thus has interesting applications and properties such as hydrogen storage and catalytic properties[4].

NiO nanoparticles differ from the bulk in terms of crystal structure and physical properties due to energy state and symmetry changes taking place at the surface. The crystal structure of the surface is affected by the development of lattice strain[5].

Synthesis

I have prepared NiO by chemical precipitation method, Nano composite method, and by precursor method of $[Ni(NH_3)_6]$ NO_3 followed by decomposition of the products and the final oxide product.

Method-1: By Chemical Precipitation method: 100ml of 0.1M $Ni(NO_3)_2.6H_2O$ solution was prepared by dissolving 0.4g of $Ni(NO_3)_2.6H_2O$ in distilled water and dilute the solution in a 100ml standard measuring flask. Pour this solution of Nickel nitrate in a 250 ml beaker.

100ml of 0.1M NaOH Solution was prepared by dissolving 2.908g of NaOH in distilled water and dilute the solution in a

100ml standard measuring flask. Pour this solution in a 250ml separating funnel.

NaOH solution from separating funnel was slowly added drop wise to $Ni(NO_3)_2.6H_2O$ by vigorously stirring, followed by filtration and washing with water. Precipitate obtained was oven dried for 70°C overnight.

The product obtained was decomposed at 300°C in the furnace, later cooled and weighed.

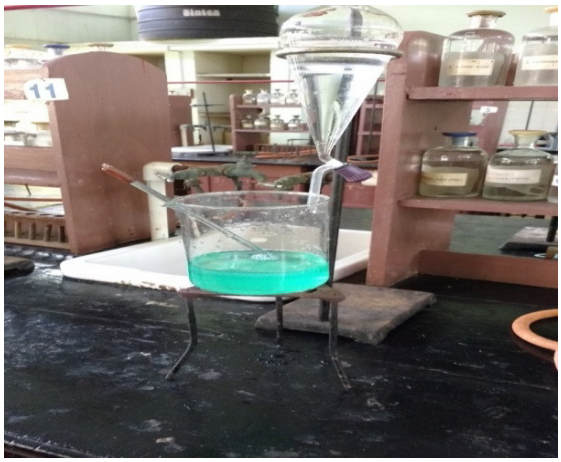

Figure-2: Precipitation of Nickel Nano particles.

Figure-3: Nickel oxide by co-precipitation.

Experimental yield = 0.544g, % Yield = 72.8%.

Method-2: Preparation of nickel oxide by nancomposite: 500ml of 0.1M $NiCl_2$ was prepared by dissolving 11.885g of $NiCl_2$ powder in distilled water. Similarly 500ml 0.1M $KMnO_4$ was prepared by dissolving 7.901g in distilled water. Also 500ml 0.05M Urea was prepared by dissolving 1.5015g in distilled water. $KMnO_4$ was added to $NiCl_2$, to this urea was added very slowly which acts as the fuel and the mixture was stirred at room temperature. The solution was kept for boiling for about 4-5 hour. The product obtained is centrifuged and placed in an electric oven for 12hours. The Color of NiO composite obtained is black in color. The product obtained was decomposed at 800°C in the furnace.

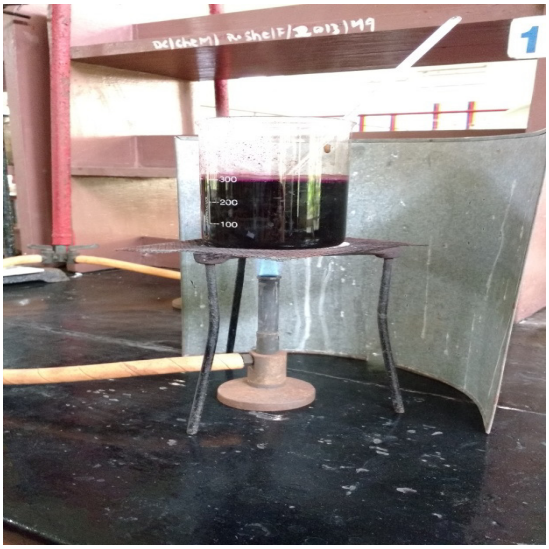

Figure-4: Nickel oxide prepared by Nano composite method.

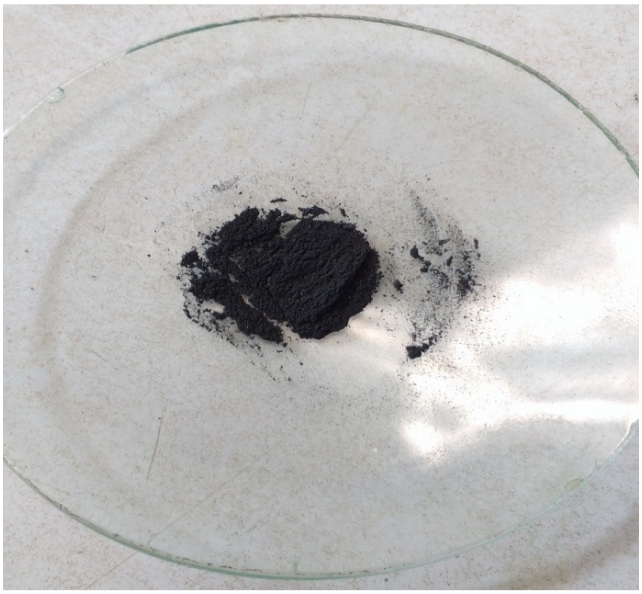

Figure-5: Nanocomposite NiOMnO.

Experimental yield = 1.763g, % Yield = 50.54%.

Method-3: By Precurssor method: 100 ml of 2 M NH_4OH solution was added drop wise into 50 ml of 0.5 M $Ni(NO_3)_2.6H_2O$ solution which was continuously stirred at 70°C temperature.

The resultant light-green suspension was filtered, and then washed with deionized water and ethanol in molar ratio of 1:1 for 5 to 10 times.

It was then dried at 70°C for 24 h, and finally calcined at 400°C for 2-3 hrs.

The product was weighed to obtain the yield.

Figure-6: Nickel oxide prepared by using $[Ni(NH_3)_6]NO_3$ as a precursor.

Experimental yield = 0.436g
Percentage yield= 58.37%.

X-ray Diffraction for structure determination: The Nickel Oxide samples prepared were charecterised for structure determination by X-ray diffraction. The graphs were obtained by plotting Intensity v/s 2θ values.

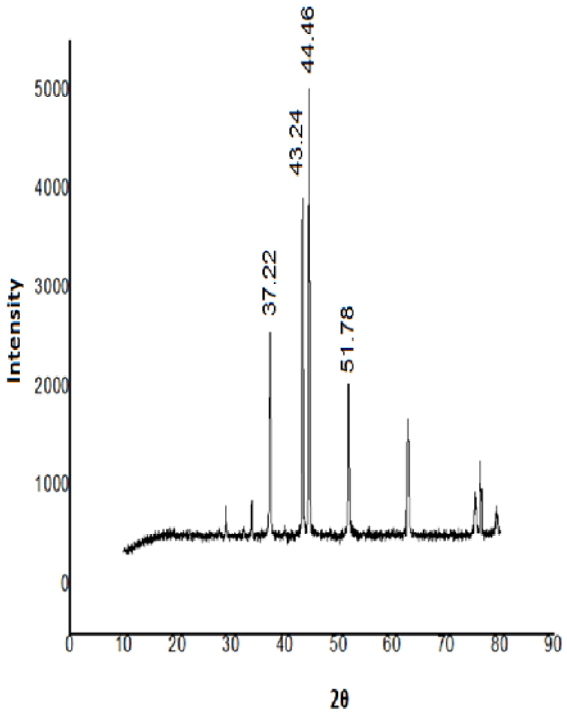

Figure-7: XRD pattern of Sample 1.

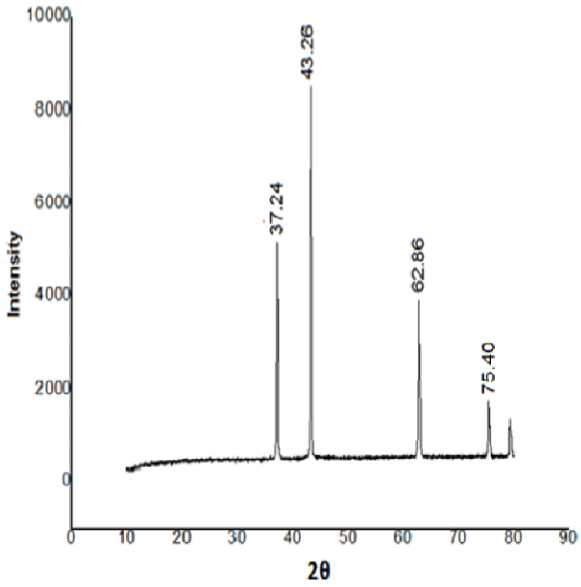

Figure-8: XRD pattern of Sample 2.

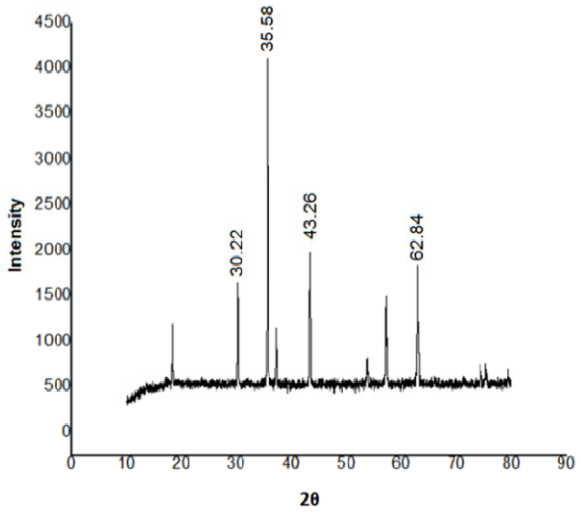

Figure-9: XRD pattern of Sample 3.

Table-1: d values of sample 1.

Sample 1: NiO by chemical/complexation-precipitation method.		
2θ	Experimental d values	Standard d values
37.22	2.47	2.410
43.24	2.09	2.088
44.46	2.03	2.088
51.78	1.765	1.476

Table-2: d values of sample 2.

Sample 2: NiO by nano-composite method.		
2θ	Experimental d values	Standard d values
30.22	2.957	2.410
35.58	2.523	2.410
43.26	2.091	2.088
62.84	1.478	1.476

Table-3: d values of sample 3

Sample 3: NiO by using $[Ni(NH_3)_6]NO_3$ as a precursor.		
2θ	Experimental d values	Standard d values
37.24	2.414	2.410
43.26	2.09	2.088
62.86	1.478	1.476
75.4	1.260	1.259

The interplanar spacing values so calculated using Braggs law $n\lambda = 2d\sin\theta$, agrees well with standard card data (JCPDS card no- 47-1049). The peaks are sharp and intense which proves that samples are crystalline in nature. There is broadening of peaks in all three samples which indictes that the crystallites are of nano size[6]. The XRD graph of NiO prepared by Nano-composite method differs from others as it has different peaks wherein we can conclude that it is not present as a single entity of nickel oxide but we can assign a probable formula for this composite as [NiO.MnO]. The particle size was calculated using Debye Scherrer formula has given the following results $D= 0.9 \lambda / \beta \cos\theta$[1].

Co-precipitation method— 23nm
Nanocomposite— 14nm
Precurssor method--- 12 nm

All the three methods have resulted in nanoparticles. The crystal structure is size dependent which is clearly revealed from their XRD which shows some additional peaks in XRD graphs[7].

Scanning Electron Microscopy

The surface morphology was determined by Scanning Electron Microscopy. The SEM analysis was carried out at Instrumentation centre Goa University.

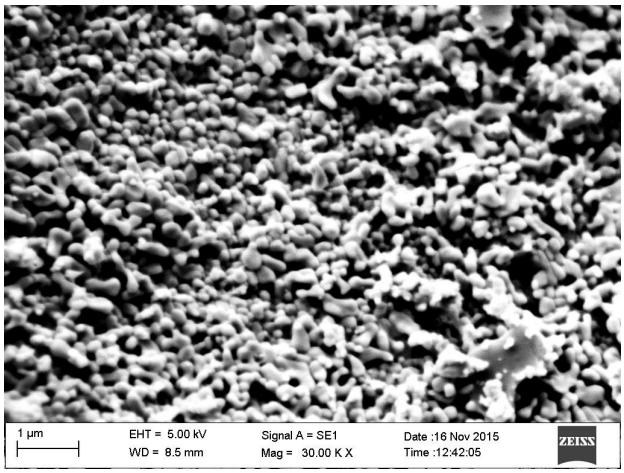

Figure-10: SEM image of Sample 1.

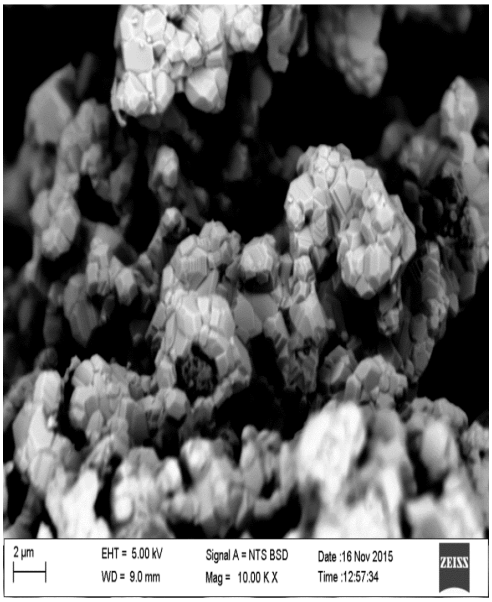

Figure-11: SEM image of Sample 2.

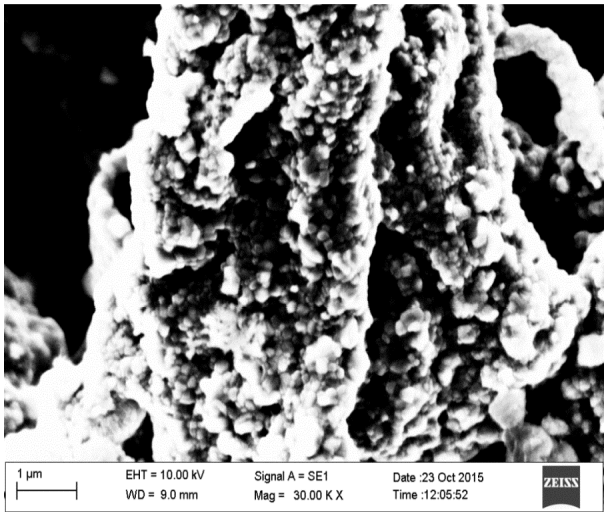

Figure-12: SEM image Sample 3 shows agglomeration.

Since SEM images do not focus on grain boundaries it cannot be used to determine the exact particle size.

Microbial studies: Method 1 Using agar gel.

Preparation of nutrient plates: 1.2grams of nutrient agar powder was weighed and heated in a heat proof dish with the mixing of 60ml hot water.The solution was boiled till all the powder dissolves and clear liquid is obtained. When the solution is warm it is poured into petri dish and the top half of the petri dishis closed immediately to avoid contamination with air-borne bacteria. The petri dishis kept in refrigerator for 24 hours till agar hardens.The Nickel oxide sample is stored in the sterile tubes ,a pinch of sample to another sterile tube and to this about 1-2ml of NaCl saline is added . The solution is mixed by shaking for about 5 minutes.The petri dish containing agar is removed and the solution of NiO sample is poured with the help of micropipette on the surface of agar drop wise and spread well with the help of a glass rod.The petri dish is labelled and kept in the incubator for 24 hours at a room temperature.

The petri dish was observed for the presence/absence of bacteria.

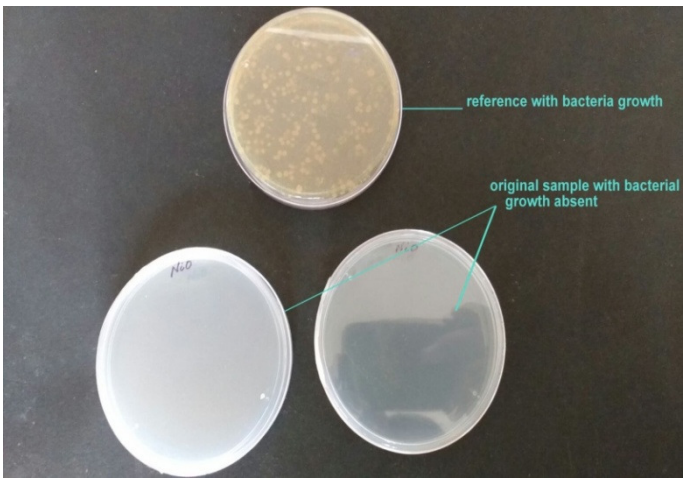

Figure-13: Petridish with NiO and agar gel.

Method 2 Using Saline: A pinch of NiO sample was transfered to a sterile tube and add to it 1-2ml of saline of NaCl was added. The solution was shaken well for about 5 minutes and keep it in the incubator at a room temperature for 24 hours.The tubes for the presence/absence of bacteria.

Both the methods did not show growth of bacteria which proved that NiO has antimicrobial properties.

Photocatalytic study: Dye degradation is a process in which large dye molecule is broken down chemically into smaller molecules by certain chemical compounds[8]. In Photodegradation this is carried out in presence of light. The rate of this photocatalytic degradation depends on the basic structure of catalyst and the nature of auxiliary group attached to aromatic dye. The catalytic action of NiO on dye degradation was experimented and to understand this Methylene blue was selected as dye as it has well resolved spectrum in visible region[9]. i. To prepare 16ppm of methylene blue, 0.016g of the same was weighed and diluted to 1000ml using a standard measuring flask. ii. 50ml of this solution was taken using a graduated pipette and to this 100ml of distilled water was added. iii. 0.5g of the prepared NiO sample was then added to this diluted solution and kept under sunlight. iv. Absorbance of this solution was found out using a UV-Visible spectrophotometer after intervals of 30, 60, 90, 120minutes.

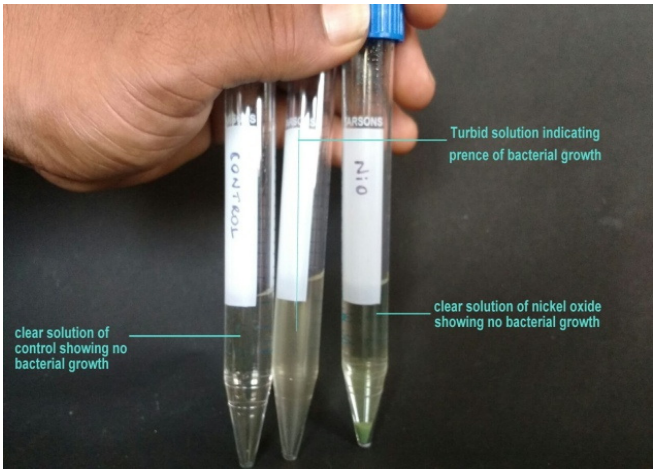

Figure-14: Tubes containing NiO in saline medium.

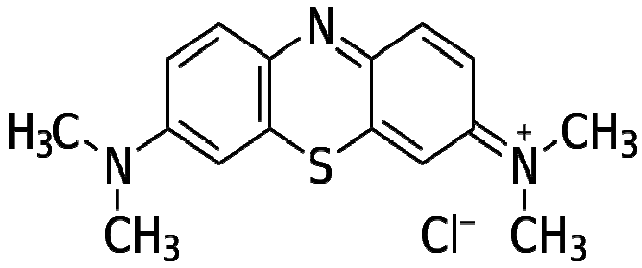

Figure-15: Structure of Methylene Blue[10].

Table-4: Absorbance values of NiO nanoparticles in degaradation of Methylene Blue.

Time	Blank	Sample-1	Sample-2
0	0.85	-	-
30	0.85	0.83	0.82
60	0.85	0.74	0.81
90	0.85	0.68	0.78
120	0.85	0.66	0.75

The NiO nanoparticles show a decrease in the absorbance with an interval of 30min, we can say that NiO helps in the photodegradation of methylene blue.

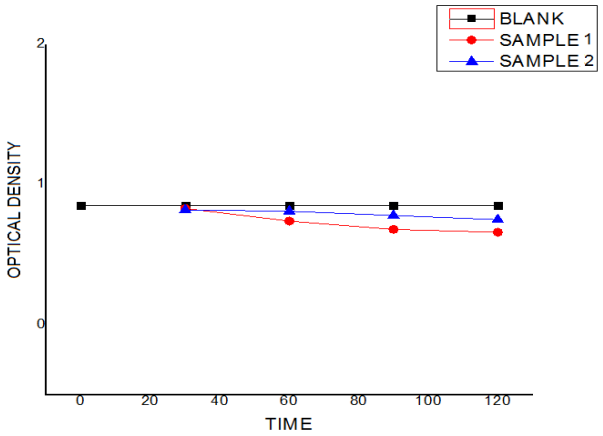

Figure-16: Graph showing photodegradation of Methylene blue with NiO.

Therefore NiO can be used for treatment of waste waters likely to be contaminated with organic based pollutants.

Results and Discussion

In the present work, NiO has been synthesized by co-precipitation, Nanocomposite and precursor methods. The co-precipitation method has given maximum yield. All methods have resulted in non-stoichiometric oxide.

The XRD spectra shows resemblance of peaks and d values with standard values which confirms the formation of NiO. The XRD of Nanocomposite is slightly different than others, which reveals that product exists as composite NiOMnO The particle size of the three samples were calculated using Debye Schherer formula have confirmed the formation of nano particles. The precursor method has resulted in smallest nanoparticles of NiO with dimensions of 12 nm. The SEM images have shown formation of tetragonal grains and spherical clusters for the first two methods and agglomerates by last one. The NiO nanoparticles were shown to exhibit antimicrobial properties.

The synthesized NiO nanoparticles were found to be an excellent photocatalyst for treatement of waste waters likely to be contaminated with organic based pollutants. These could be preferred over TiO_2 which has low photonic efficiency and requires u.v light for band gap excitation[10]. In contrast to this NiO is a p-type semiconductor with a band gap of Eg= 3.5 ev[11].

Conclusion

NiO prepared by all 3 methods have yielded black colour nanoparticles, with rhombohedral structure. Size dependence of crystal structure is verified from XRD graphs. SEM images show formation of tetragonal grains and spherical clusters for first two samples and agglomerates in case of Precurssor. NiO nanoparicles have also shown to exhibit anti microbial properties. NiO is found to be an excellent photocatalyst and can be used in treatment of waste waters.

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