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Green Synthesis of Ni-Doped Magnesium Oxide Nanoparticles and its Effect on Photo Catalysis

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ABSTRACT

Pure and Ni-doped magnesium oxide (MgO) (1-5 mol %) nanoparticles (NPs) were synthesized by facile green synthesis using Synadenium grantii plant extract. The formed NPs were characterized by powder X-ray diffraction (PXRD), scanning electron microscopy, Fourier transform infrared, photocatalysis, and photoluminescence techniques. PXRD results exhibit the presence of cubic structure for all the synthesized samples. The photocatalytic activities of pure MgO and Ni-doped MgO photocatalysts were evaluated for the degradation of methylene blue (MB) under ultraviolet light. The photocatalytic results clearly demonstrate that Ni-doped MgO (5 mol %) has shown a good photocatalytic activity for degradation of MB for 60 min with a degradation rate of 94%. Therefore, this work directs new possibilities to provide some new insights into the design of new green synthesized photocatalysts with high photocatalytic activity for degradation of dyes.

Key words: *Green synthesis, Synadenium grantii, Methylene blue, Magnesium oxide.*

1. INTRODUCTION

Environmental problems related with hazardous wastes and toxic water-pollutants have attracted much attention. Organic dyes are one of the major groups of pollutants in wastewaters released from textile and other industrial processes. Those physical and biological techniques for the treatment of pollutants are non-destructive and merely transfer the non-biodegradable matter into sludge, giving rise to new type of pollution, which needs further treatment [1]. Among that heterogeneous photocatalysis is one which is cost-effective to treat the industrial waste water effluents which contain various types of organic and inorganic pollutants and have the capacity to convert them into safer products such as CO_2, H_2O and mineral acids [2,3]. Semiconductor nanoparticles (NPs), as heterogeneous photocatalysts, have attracted much interest due to their size-tunable physical and chemical properties. Magnesium oxide (MgO) exhibits a face-centered cubic (NaCl-type) crystal structure, high thermal stability, predominantly ionic nature, and insulating behavior [4].

MgO has been extensively used in catalysis, toxic waste remediation, antibacterial materials, refractories, paints, and superconductors due to its unique optical, electronic, magnetic, thermal, mechanical, and chemical properties [5]. Recently, it has found promising application in plasma display panels [6]. Of particular interest is MgO nanopowder because of inherent size effects, for example, large surface area-to-volume ratio. Various investigations have been undertaken earlier on its optical and electrical properties [7,8]. Surface anions with low coordination, considered to be chemically active sites, form excitons and give rise to specific optical transitions in the ultraviolet (UV) range. An attempt has been made here to study the effect of nickel doping on the crystal structure, morphology, particle size, optical absorption with the objective of its possible application in waste water treatment. Out of various methods of synthesis of NPs, solution combustion method has been chosen for synthesis because of its distinct advantage of being simple, cost effective, and as it is less energy and time consuming [9]. For the first time, an attempt has been made to green synthesize the Ni-doped MgO NPs using *Synadenium grantii* plant extract as a fuel. *S. grantii* is a succulent shrub with milky latex, leaves alternate, simple and fleshy flowers small and inconspicuous,

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and in a small cup with a red rim of glands belongs to the family Euphorbiaceous.

2. MATERIALS AND METHODS

2.1. Materials and Preparation of Plant Extract

All the chemicals used in the present investigation were of analytical grade purchased from Merck, India, and were used as received without further purification. Methylene blue (MB) was purchased from S. D. Fine Chemicals, Bombay, India, and used without further purification. The stock liquid dye solutions from MB dye were prepared by dissolving a known amount of the dye (0.1 g) in 100 mL of distilled water (1000 ppm).

Fresh leaves were collected from *S. grantii* plants in the Tumkur University campus. 50 g of washed dried fine cut leaves were taken in 250 ml glass beaker along with 100 ml of sterile distilled water. The mixture was then boiled for 60 min until the color of the aqueous solution changes from watery to dark brown. The extract was cooled to room temperature and filtered using filter paper. The extract was stored in a refrigerator to be used for further experiments.

2.2. Synthesis of Ni-doped MgO NPs

Ni-doped MgO NPs were prepared by the method of solution combustion using *S. grantii* plant extract as fuel. Stoichiometric amounts of $Mg(NO_3)_2$. $6H_2O$ and $Ni(NO_3)_2.6H_2O$ were dissolved in 10 ml of plant extract and kept in a preheated muffle furnace at 500°C about 10-15 min until milky white powder was obtained. The same procedure was repeated for the preparation of all the other samples by varying the dopant concentration (1-5 mol %) and finally the sample was calcined at 500°C and allowed to cool at room temperature. Finally, the samples are collected and used for further investigations.

2.3. Characterization Techniques

The crystallinity, structure, and crystallite size of Ni-doped MgO NPs were determined by powder X-ray diffraction (PXRD) employing the Shimadzu-7000 X-ray diffractometer with Cu K_α radiation source (1.540 Å). The XRD patterns were recorded in the range $2\theta = 20°$-$80°$ at voltage of 40 kV and current of 30 mA with scanning speed of 4°/min. The optical properties were characterized by employing the T80+ UV-visible spectrophotometer and photoluminescence studies were carried out using Horiba spectrofluorometer. The photocatalytic experiments were carried out at room temperature using a circular glass reactor whose surface area was 176.6 cm^2, an UV light wavelength 254 nm was chosen as the light source with a power of 30 W. The UV spectrophotometer was used at λ_{max} of 664 nm for the determination of the absorbance of MB.

3. RESULTS AND DISCUSSION

3.1. PXRD Analysis

Phase structures of the prepared samples were analyzed using PXRD. The XRD patterns of MgO and Ni-doped MgO (1-11 mol %) were shown in Figure 1. XRD clearly indicates the emergence of cubic structure and the peaks were absorbed at 37°, 42°, 62°, 74° and 78° with phases (111), (200), (220), (311) and (222) matched well JCPDS card number 75-1525. All the samples exhibit similar structure. The average grain size has been determined from both the Scherer's formula and W-H plot method, and the values are tabulated in Table 1.

3.2. Morphological Studies

Scanning electron microscopy (SEM) images of pure MgO and Ni-doped MgO (1-5%) are shown in Figure 2. It can be clearly observed from low-resolution SEM images that the MgO powders show many agglomerates with an irregular morphology. In the case of pure MgO, particles are connected to each other to make large network systems with irregular pore sizes and shapes. As the Ni concentration increases of the porous network with lot of voids is a typical of combustion synthesized powders due to escaping of gases.

3.3. Photocatalytic Performance on MB

The photocatalytic degradation of MB dye under UV light irradiation and spectral absorbance was depicted in Figure 3. The MB dye having a maximum absorbance of 664 nm was chosen for photocatalytic degradation of all the samples. No measurable dye degradation was observed without catalyst under UV light and in dark, which indicating that the catalyst and light were necessary for effective degradation of the

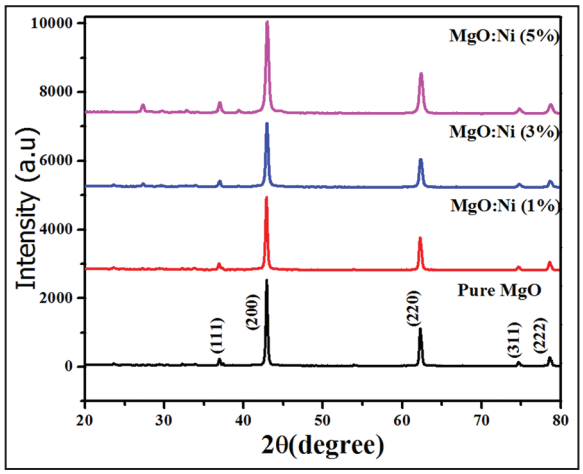

Figure 1: Powder X-ray diffraction spectra.

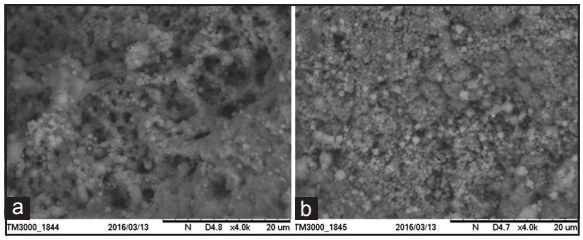

Figure 2: Scanning electron microscopy images.

Table 1: Crystalline size and cell parameters calculation.

Sample	A (A°)	C (A°)	c/a	Volume V $(A°)^3$	D-S method	W-H method (nm)	Strain, $\varepsilon \times 10^{-3}$
Pure MgO	10.02	3.323	0.306	290.73	29.22	28.57	2.720
MgO:$Ni_{1\ mol\ \%}$	10.07	3.324	0.330	291.00	27.11	28.06	3.044
MgO:$Ni_{3\ mol\ \%}$	10.08	3.321	0.330	291.06	24.14	25.63	3.267
MgO:$Ni_{5\ mol\ \%}$	10.13	3.319	0.329	291.88	20.54	21.88	3.732

MgO=Magnesium oxide

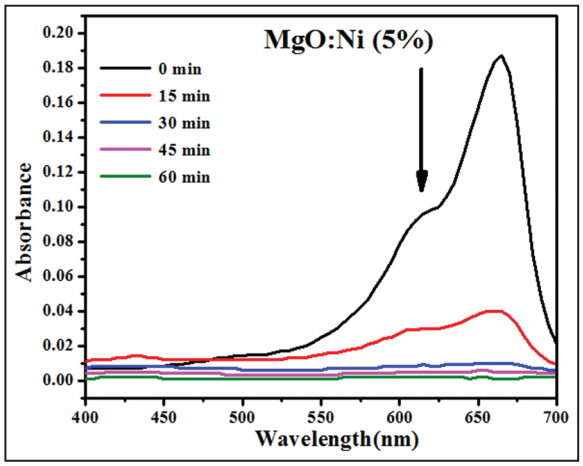

Figure 3: Absorbance spectra for 5% Ni-doped magnesium oxide.

MB, respectively. The catalyst of 60 mg was dissolved in 250 ml of 20 ppm MB dye and allowed for UV light illumination. Then, 5 ml of the solution was pipette out at different time intervals till 60 min. Finally, the collected samples were analyzed for absorbance in UV-visible spectrophotometer. The undoped MgO shows a very low degradation percentage of 85% while Ni-doped MgO (5 mol %) shows an enhanced photocatalytic activity of 94%.

4. CONCLUSION

In the present work, undoped MgO and MgO: Ni^{2+} (1-5 mol %) NPs were prepared by simple, facile, eco-friendly green mediated solution combustion method at low temperature (500°C). The PXRD patterns confirmed single phase, cubic structure, and the crystalline size decreases from 29 to 20 nm proving the important role played by dopant. Photocatalytic studies were carried out by choosing MB as hazardous dye. The photocatalytic activity of the MgO NPs increases by Ni doping and thereby incurs the increased surface area. The reaction between conduction-band electrons and oxygen in the solution could generate the reactive oxygen species which is responsible for the color decolonization and its value increases with Ni doping. As a result, the increase of nickel doping improves the photocatalytic activity of the MgO NPs.

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***Bibliographical Sketch**

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