Effective Photo degradation of Solochrome Black Using Efficient Photo catalytic Nano Ceria

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Abstract. Photocatalytic dye degradation of Solochrome black was analyzed using synthesized Cerium oxide (CeO_2) (ceria) nanoparticles (NPs). Herein, we have synthesized hydrothermal CeO_2 NPs (HYNP) and Co-precipitation CeO_2 NPs (CONP). The synthesized NPs were characterized using UV-Vis spectrometer, here the absorption maxima (λ_{max}) obtained at 379 nm with energy band gap (E_g) of 2.62 eV for HYNP and the λ_{max} 359 nm with energy band gap (E_g) of 3.02 eV for CONP. E_g was calculated by the Tauc's plot. Further, from Transmission electron microscopy (TEM), the particle sizes were confirmed that are about ~11.18 nm for HYNP and ~5.77 nm for CONP. The elemental composition was examined by Energy dispersive X-ray diffraction (EDX). The photocatalytic activities of HYNP and CONP were evaluated using Solochrome black under UV irradiation condition for different time interval. The results showed that the HYNP are having higher photocatalytic degradation value as compared to CONP.

INTRODUCTION

In the most recent years the researchers, scientists and industries are focused on synthesis and characterizations of nanomaterials because of their wide usage and attractive worthy results. Industries are using around 8000 chemicals and more than 3600 dyes manufacturing for the textiles and printing [1]. These industries dispose harmful organic molecules through the water which are very toxic and hazardous to all living organisms [2]. So now the real challenge on the world is wastewater treatment. Only 2.5% of the total water on the earth is fresh water. Therefore the waste water treatment is a serious concern around the world. It is our pivotal work to eliminate the dyes from the water capitals, for that there are many conventional methods to remove or degrade the dye from the water such as adsorption, biodegradation, electrochemical, photochemical and ultrafiltration methods [3-4]. As a recent development, nanotechnology & nanocatalysis playing important role because of their small particle size and the large surface to the volume ratio. For this, the photocatalytic degradation is a promising technique. Hence, NPs used as nanocatalysts to remove the toxicity from the water [5-7]. Among many metal nanoparticles, cerium oxide NPs are very promising & significant because of their unique properties & several applications in photo luminescent devices, complex ceramics, photocatalysis and nonlinear optical semiconductors [8].

Previously we reported co-precipitation synthesized CeO_2 NPs. Currently, we reported the hydrothermal synthesized CeO_2 NPs and doing a co-relative study of both HYNP & CONP in optical, morphology, chemical composition and the photocatalytic activity of the both HYNP & CONP using Solochrome Black dye under the illumination of UV lamp.

EXPERIMENTAL SECTION

Materials and methods

The commercial Dye Solochrome Black ($C_{20}H_{12}N_3O_7SNa$; 461.38 g/mole; 99% pure) purchased from Fisher – Scientfic, India and used as supplied. Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$; 434.2 g/mole; 99% pure) and sodium hydroxide pellets (NaOH, 40.0 g/mole; 98% pure) obtained from the Himedia Laboratories Pvt. Ltd. Mumbai, India, and Ethanol (CH_3CH_2OH: 46.06 g/mole; 99.9% pure) purchased from CHF Chemical co.Ltd, China city, China. For the preparation of all solutions Double distilled water was used.

CeO_2 NPs were synthesized by the Hydrothermal method and Co-precipitation method using $Ce(NO_3)_3.6H_2O$ as starting material and NaOH as a reacting agent. For the typical hydrothermal process initially, 8.68 gm of cerium nitrate hexahydrate of 1 M concentration is dissolved in 15 ml of distilled water. Similarly, 8 ml of NaOH solution is prepared by dissolving 0.2 M of 0.08 gm NaOH crystal in distilled water. To form aqueous solution both solutions were mixed by constant stirring for the 20 min with 4000 rpm. Then the mixture is poured to Teflon – lined stainless steel autoclave and the kit is heated at 180 °C for 180 minutes in an oven. After cooling down naturally the product is centrifuged, washed with distilled water finally once with ethanol and dried for 2 hours at 60 °C. Finally, the CeO_2 NPs used for further studies. For the Co-precipitation method, we followed our previous report [9]. To study photocatalytic studies the Solochrome black dye solution is prepared in 20 ml distilled water with 0.0001 M.

Instrumentations

a) UV-Vis spectroscopy: For the optical studies, UV-Visible spectrometer (model: V-670 Jasco) is used at the wavelength range of 200 nm – 800 nm at USIC, K.U. Dharwad, Karnataka, India.
b) Surface morphology & particle size: The particle size of the synthesized NPs are examined by TEM (Model: Jeol/JEM 2100) at STIC, Cochin, Kerala, India.
c) Elemental analysis: Elemental composition of the synthesized samples were analyzed using EDX (model: JED 2300) at STIC, Cochin, Kerala, India.
d) Photocatalytic studies: The dye degradation is performed by the UV-Vis spectrophotometer (model: V-670 Jasco) at the wavelength range of 200 nm – 800 nm at USIC, K.U. Dharwad, Karnataka, India.

RESULTS AND DISCUSSION

Optical studies

The UV-Vis spectra of the both HYNP & CONP were recorded for the optical studies. The absorption maxima (λ_{max}) and with the help of Tauc's plot the energy gap also calculated. UV-Vis spectroscopy produced absorption maxima at 379 nm for the HYNP and 359 nm for CONP respectively. Which is shown in **FIGURE 1** (a). The appearance of these peaks confirms the presence of CeO_2 NPs [10]. According to the Kubelka-Munk transformation [11],

$$\boldsymbol{\alpha h\nu = A\left(h\nu - E_g\right)^{1/2}} \text{ ----} \quad (1)$$

[Where α: optical absorption coefficient; h : energy of the photon; E_g: band gap energy; A: constant depends on the transition probability] we have calculated the band gap energy and the graph of $(\alpha h\nu)^{1/2}$ Vs $h\nu$ (Tauc's plot) resulted E_g = 2.62 eV & E_g = 3.02 eV for HYNP and CONP respectively as shown in FIGURE 1 (b).

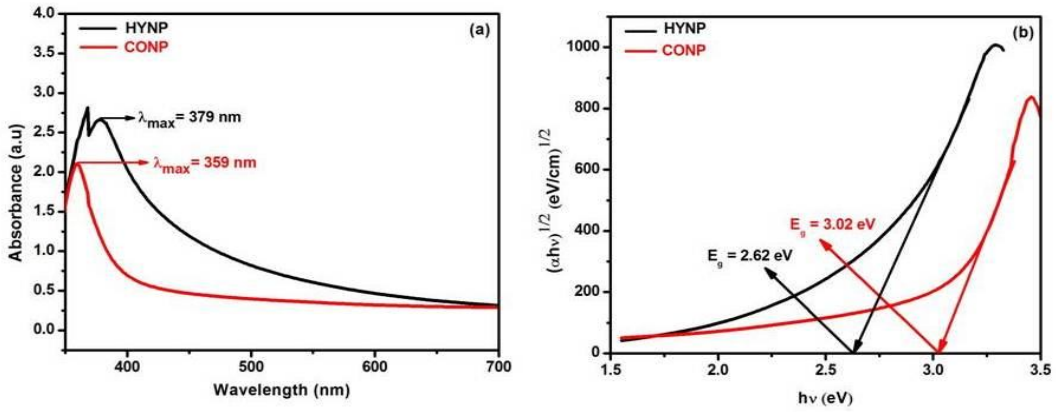

FIGURE 1. (a) UV-Vis spectrum for HYNP & CONP and (b) the corresponding Tauc's plot for HYNP & CONP.

Particle size and Elemental composition studies

FIGURE 2 (a) & (b) shows the TEM images of HYNP and CONP respectively with the resolution of 50 nm. The HYNP image revealed that the NPs are ultra fine and crystal in nature. The crystallite sizes were found to be around 11.18 nm. The CONP image revealed that there is agglomeration in the particles and the sizes were found to be around 5.77 nm. **FIGURE 2** (c) & (d) shows the EDX spectrum of the HYNP & CONP which ensures the presence of Ce & O. The weight content of Ce is 72.31% for HYNP and 72.58% for CONP. The weight content of O is 27.69% for HYNP and 27.42% for CONP. The atomic content of Ce is 22.97% for HYNP and 23.17% for CONP. The atomic content of O is 77.03% for HYNP and 76.83% for CONP. This reveals that the obtained NPs are pure and are in a proper stoichiometry of cerium and oxygen only.

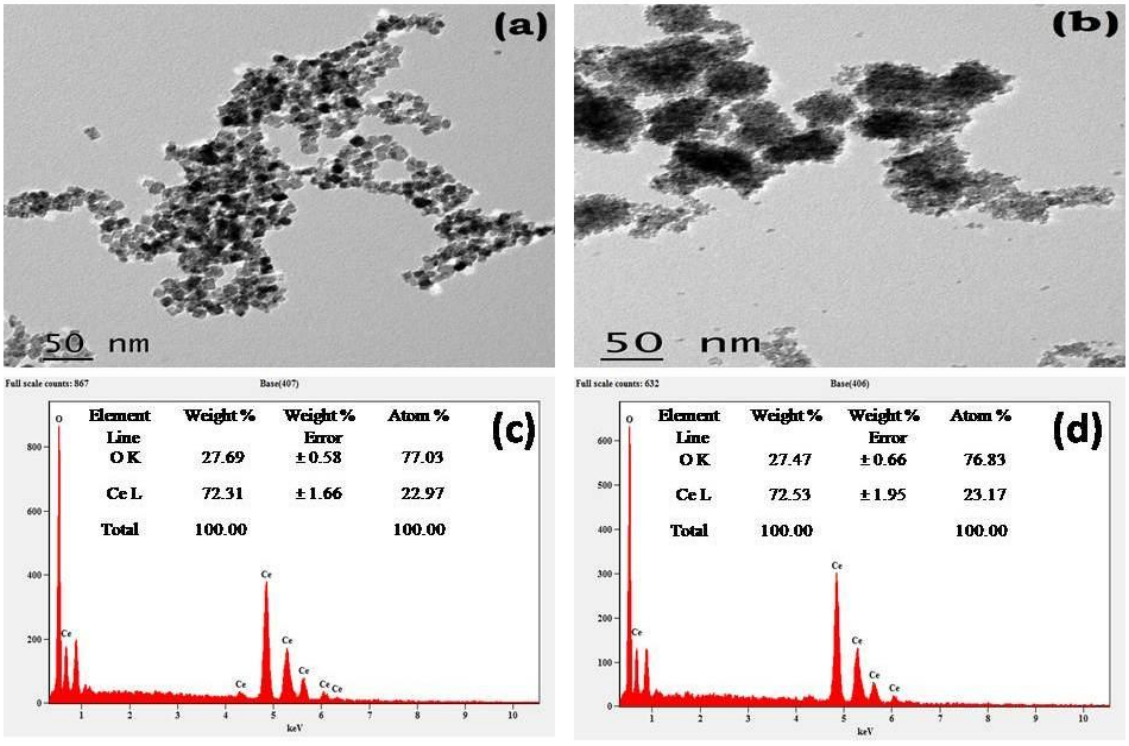

FIGURE 2. (a) TEM image of HYNP (b) TEM image of CONP (c) EDS graph of HYNP (d) EDS graph of CONP.

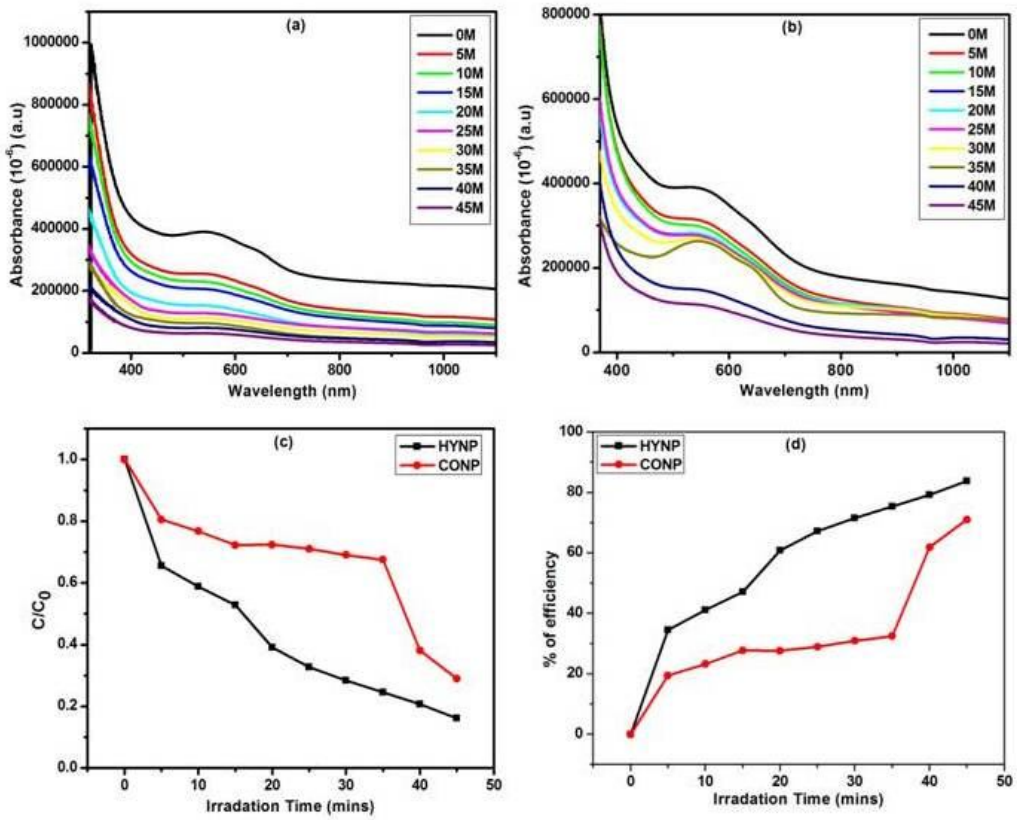

FIGURE 3. (a) Photo degradation of dye by HYNP (b) Photo degradation of dye by CONP (c) Photo catalytic activity of HYNP under UV light, plotted as a function of time (d) Photo catalytic activity of CONP under UV light, plotted as a function of time.

Effect of CeO_2 NPs on Solochrome black

The photocatalytic tests were carried out in UV light chamber of an area 2025 cm^2 using UV lamp of Philips TUV 16W. The light is placed inside the top of the chamber. The Solochrome black dye solution is prepared for 20 ml with 0.0001 M and irradiated to the UV lamp for the degradation with respect to time. The maximum absorbance of Solochrome black is observed at 540 nm for HYNP and 544 nm for CONP. The absorbance gradually decreases with the increasing irradiation time which is shown in **FIGURE 3** (a) for HYNP & in **FIGURE 3** (b) for CONP. The photocatalytic efficiency (η) of synthesized CeO_2 NPs and the normalized residual concentration of dye was calculated by [8, 12]

$$\eta = \left(1 - \frac{C}{C_0}\right) \times 100 = \left(1 - \frac{A}{A_0}\right) \times 100 \quad (2)$$

[Where C_0 : Initial concentration of dye; C: Residual concentration of the dye with respect to time ; A: Intensity of absorption band with respect to time : A_0: Intensity of absorption band at 0 minutes]. **FIGURE 3** (c) indicates the concentration degradation of dye with time in the presence of HYNP & CONP. **FIGURE 3** (d) indicates the percentage efficiency of degradation of dye for HYNP & CONP. The efficiency of HYNP is ~15% better than the efficiency of CONP.

CONCLUSION

In summary, the CeO_2 NPs were synthesized by two different chemogenic routes, namely hydrothermal and co-precipitation methods. The synthesized HYNP & CONP were characterized for optical studies and energy band gap also calculated by Tauc's plot. Particle size and elemental composition were examined by TEM & EDX respectively. The photocatalytic behavior of synthesized HYNP & CONP was studied over Solochrome black dye

under different irradiation time of UV lamp. Finally it is proved that CeO_2 NPs are efficient catalysts. Particularly HYNP showed superior photocatalytic activity with higher efficiency than CONP.

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