Synthesis and Properties of visible light active novel $Ce_{0.5}Zr_{0.5}O_2$ for Photocatalytic decomposition of Organic dye from water

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Abstract: Due to the toxicity of organic compounds like dyes environmental pollution increases day by day. So it is essential to develop a technique which can decompose these toxic compounds effectively without creating any further toxicity. In this paper, we reported photocatalytic activity of $Ce_{0.5}Zr_{0.5}O_2$ for the bleaching of methylene blue under visible light irradiation. Photocatalyst $Ce_{0.5}Zr_{0.5}O_2$ was synthesized by Solid state calicination and Urea method. In Solid state calcination Reaction, highly photoactive powder of Cerium zirconate was obtained by heating a 1:1 molar mixture of Zirconyl oxychloride ($ZrOCl_2 \cdot 8H_2O$) and Ceric nitrate $Ce(NO_3)_2$ at 800 ^{0}c for 24 hrs. While in Urea method, Stoichiometric quantities of Zirconyl oxychloride ($ZrOCl_2 \cdot 8H_2O$) and Ceric nitrate $Ce(NO_3)_2$ were mixed with the required amount of urea and the mixture was heated on water bath for 1 hr . The yellowish precipitate was filtered, washed with distilled water, then baked at 100^{0}C in a hot air oven for 2 hrs. The prepared photocatalysts were then characterized by XRD, BET, SEM, TEM and UV-Vis diffuse reflectance analyses. The photocatalytic activity of $Ce_{0.5}Zr_{0.5}O_2$ was studied for bleaching of Methylene blue. After 180 min of visible light irradiation, we observed that 78% B was photo-degraded by CZ-SSR photocatalyst while degradation of MB was 92% over CZ-UM sample.

Key words: Cerium zirconate, photocatalysis, Photocatalytic activity, Methylene Blue

I. INTRODUCTION

The environment related problems become more and more complex due to the disposal of colored wastewater discharged into water bodies. Dyes widely used in textiles, paper, rubber and plastics industries often create severe water pollution. Azo dyes are the most important class of synthetic organic dyes used in the textile industry and are therefore common industrial pollutants[1-3]. Thus, for many years the main aim of researches have been targeted towards decolorization and mineralization of azo dye effluents. Conventional methods such as adsorption[4], flocculation[5], electrochemical methods[6], ozonation, advanced oxidation using UV/H_2O_2 or UV/TiO_2 [7,8] and biological oxidation for industrial wastewater can be used efficiently[9]. However many of them have some limitations, as we know traditional physical techniques just transfer organic compounds from waste water to another phase which can cause secondary pollution easily. Biological oxidation cannot degrade dyes under aerobic condition, while can reduce dyes into potentially carcinogenic compounds under anaerobic condition [10,11]. Thus, Due to the presence of many aromatic rings in dye molecules and stability of modern dye, there is a need to develop treatment methods that are more effective in eliminating dyes from the wastewater.

Among the various technologies developed for the removal of organic dyes in water, the photocatalytic oxidation process is considered to be a promising technology. The photocatalytic oxidation process can be effectively used at ambient temperature and pressure. The excitation source can be sunlight or low-cost fluorescent light source. Photocatalysts are generally nontoxic, inexpensive, and chemically and physically stable and final oxidation products are usually nontoxic and only oxygen from the air in presence of photocatalyst is required[12].

Conventionally, photocatalysis involves the use of semiconductor materials, which mainly included oxides like TiO_2, WO_3, ZnO and certain sulfides like ZnS and CdS [13]. Titanium Dioxide (TiO_2) is most commonly used photocatalytic material for the degradation of organics and dyes present in water, because it has excellent physical or chemical properties and has the ability to decompose organic species[14], but TiO_2 works under UV light due to its wide band gap and hence main part of solar spectrum cannot be used effectively. Several modifications of TiO_2 have been carried out to observe the changes in the photocatalytic activity. Recently, the modified composites of TiO_2 with other oxides, particularly with ZrO_2 have been used , which have much better photocatalytic activities for decomposition of organic pollutants than TiO_2 under the same reaction conditions[15].

Nowadays, CeO_2–ZrO_2 is one of the important catalytic supports due to its use in the three way catalysts [16]. It is applied in these systems due to its high oxygen

storage capacity. The incorporation of zirconium into the ceria lattice creates a higher concentration of defects improving, the O^{2-} mobility, such mobility would explain the excellent ability to store and release oxygen[17]. However, to our knowledge, Zhong et al, haave studied the effect of metal doping into $Ce_{0.5}Zr_{0.5}O_2$ on photocatalytic activity of $TiO_2/Ce_{0.45}Zr_{0.45}M_{0.1Ox}$ (M =Y, La, Mn) [18]. The catalytic activities of binary composite photo-catalysts CeO_2/TiO_2, ZrO_2/TiO_2 and the ternary composite photo-catalysts $H_3PW_{12}O_{40}$-CeO_2/TiO_2, $H_3PW_{12}O_{40}$-ZrO_2/TiO_2 were significantly higher than un-doped TiO_2 [19]. Fe-substituted $CeVO_4$ synthesized by solution combustion method has higher photocatalytic activity for degradation of dyes as compared to commercial Degussa P-25 TiO_2 and $CeVO_4$ [20]. Monophasic $Ce_{0.5}Zr_{0.5}O_2$ Solid solution synthesized by microwave induced combustion method has been used for various applications [21]. Omata et al, have studied photocatalytic degradation of methylene blue aqueous solution over a pyrochlore-related K-$CeZrO_4$ phase under irradiation with Xe discharge light within 8hrs.[22].

As we know, dyes widely used in textiles, paper, rubber and plastics industries often create severe environmental pollution in the form of colored wastewater discharged into environmental water bodies. Hence, the objective of this work is to synthesize $Ce_{0.5}Zr_{0.5}O_2$ by Solid state method and Urea method and investigate its photocatalytic activity, for the degradation of methylene blue.

II. EXPERIMENTAL

Synthesis of Photocatalyst

All reagents used during experiment are of A R grade. In Solid state calcination Reaction, highly photoactive powder of Cerium zirconate was obtained by heating a 1:1 molar mixture of Zirconyl oxychloride ($ZrOCl_2 \cdot 8H_2O$) and Ceric nitrate $Ce(NO_3)_2$ at 800 ^{0}C for 24 hrs. Both the fine powder reagents were mixed in mortar and grinded finely and then heated in oven at 100^{0}C for 24 hrs. During heating at 800^{0}C in muffle furnace, repeated grinding of the powder is carried out for the high agglomeration and compositional in homogeneity of the powders. In Urea method, reactive powder of Cerium zirconate was obtained by mixing stoichiometric quantities of 0.1 M Zirconyl oxychloride ($ZrOCl_2 \cdot 8H_2O$), 0.1 M Ceric nitrate $Ce(NO_3)_2$ and 0.1M Urea solution. During mixing there was no precipitation, as the pH of the solution was not varied. The molar ratio used was Ce/Zr/urea 1:1:30. Then the mixture was heated on a water bath for 1hr. and an yellowish precipitate was obtained. The precipitate was filtered, washed with distilled water and then baked at 100^{0}C for 2 hrs. in a hot air oven. These samples synthesized by solid state calcination and Urea method were labeled as CZ-SSR and CZ- UM respectively.

Apparatus and analysis

The crystalline phase structure was determined by Bruker D8 Advance X-ray diffractometer (XRD) using Cu K- radiation. The morphology of powder was studied by using scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) image which were recorded on a JEOL JEM-2100 transmission electron microscope. The BET surface areas were measured by the Brunauer – Emmett– Teller method using nitrogen gas as absorbent (BET, NOVA 4000) at 77 K. Optical Properties of synthesized material were studied by using UV- VIS diffuse reflectance spectroscopy (UV-1800, Shimandzu).

Photocatalytic activity of synthesized material

The setup for conducting the photocatalytic degradation of dyes consisted of a jacketed flask of capacity 150 ml in which the dye solution along with the catalyst and a magnetic pellet were placed. A Halogen lamp (40W/230V/36D, Phillips) was used as a visible light source, placed in a jacketed quartz tube. Both the flasks were circulated with cold water to remove the heat generated by the lamp. The Photocatalytic activity of synthesized material $Ce_{0.5}Zr_{0.5}O_2$ was studied by using cationic methylene blue. 100 ml of 50ppm dye solution was added with 0.1g of the catalyst and stirred using a magnetic stirrer. The solution was stirred in the absence of visible light for 1 hr. to observe the adsorption of the dye over the catalyst surface. The solution was then irradiated with visible light and the samples were taken for analysis at regular interval of time. The samples were then centrifuged and analyzed using UV–Vis spectrophotometer (UV 1800, Shimadzu, Japan). All the reactions were carried out at the natural pH of the dyes. In this paper, the conversion rate was calculated by $(C_0 - C)/C_0$, where C is the concentration of the reactant after irradiation as a function of reaction time and C_0 is the concentration of the reactant after adsorption equilibrium and before the irradiation in the presence of catalyst.

III. RESULTS AND DISCUSSION

XRD Analysis

The crystalline nature of the synthesized CZ-SSR & CZ-UM photocatalysts were studied by powder X-ray diffraction (XRD) as shown in Figure 1. The diffraction patterns match well with the diffraction pattern of Cerium zirconium oxide (Ref. No. 00-038-1439) which can be readily indexed as cubic type with the lattice parameters of a = 5.3049 Å [S. G. Fm3m]. The highest intensity of the (111) peak suggests that CZ-UM nano particles are growing along the (200) plane, providing active surface area for photocatalysis. The XRD patterns of the mesoporous CZ-UM nano particles show that the (111), (200) and (220) peaks are overlapping. The broadening of XRD peaks clearly indicates the nanocrystalline nature of CZ-UM. However in contrast to CZ-SSR, XRD pattern of Cerium zirconate synthesized by urea method (CZ-UM) has two

additional peaks at 2θ value of 22 and 25, which can be attributed to presence of impurities.

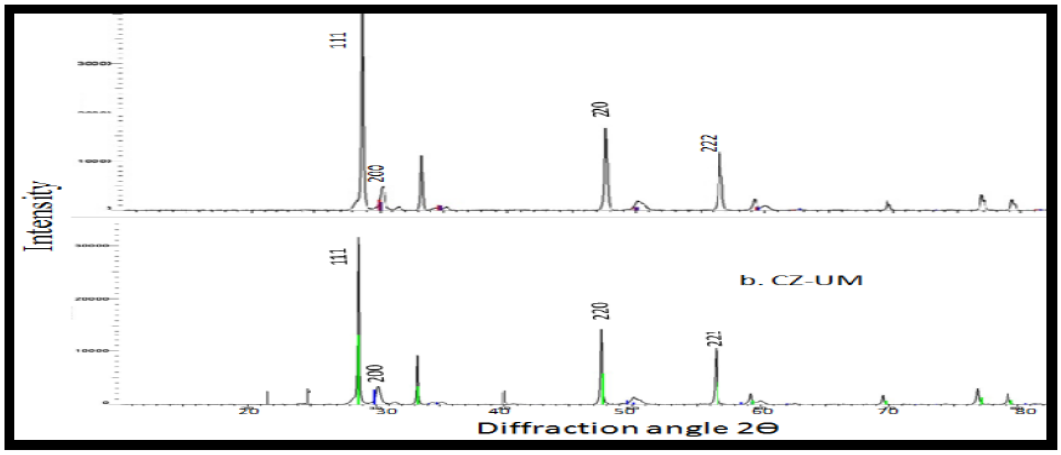

Figure 1. The XRD patterns of Cerium zirconate ($Ce_{0.5}Zr_{0.5}O_2$) a. CZ-SSR b. CZ-UM powders .

BET surface area, pore size, pore volume Analysis

The specific surface areas (SSA) of both the samples were analyzed by Brunauer-Emmett-Teller (BET) method based on the nitrogen adsorption/desorption isotherm and is provided in supplementary data (Table 1 and Figure 5). Compared with CZ-UM, BET surface area, pore volume and pore size of CZ-SSR decreases. Generally, after heating at 800^0C in CZ-SSR , particle size (particle diameter) decreased as well as pore size ,pore volume, and pore surface decrease. It was found that the specific surface area, pore size, and total pore volume (micro and mesopore volumes) slightly increased in case of CZ-UM at 100^0C and this increased surface area would be beneficial to the efficient photocatalytic performance of CZ-UM due to high surface adsorption of organic pollutants. Due to heating at high temperature, surface area of CZ-SSR decreases.

SEM and TEM of Ceric Zirconate ($Ce_{0.5}Zr_{0.5}O_2$) Analysis

The morphological evolution during calcination was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Micrographs of Cerium zirconate ($Ce_{0.5}Zr_{0.5}O_2$) CZ-SSR and CZ-UM powder calcined at 800^0C and 100^0C are shown in Figure 2. In general, the particles are agglomerated and basically irregular in shape, with a substantial variation in particle size, particularly in sample calcined at 800^0C. The results indicate that degree of agglomeration and roughness tend to increase with calcination temperature. Particle size of the powders are determined from TEM images by using the computer software program . The range of particle diameter was found to be about 61-70 and 21-30nm for the samples calcined at 800^0 C and 100^0C respectively, observed from the TEM image as shown in Figure 3. The results indicate that the average particle size and degree of agglomeration tend to increase with calcination temperature.

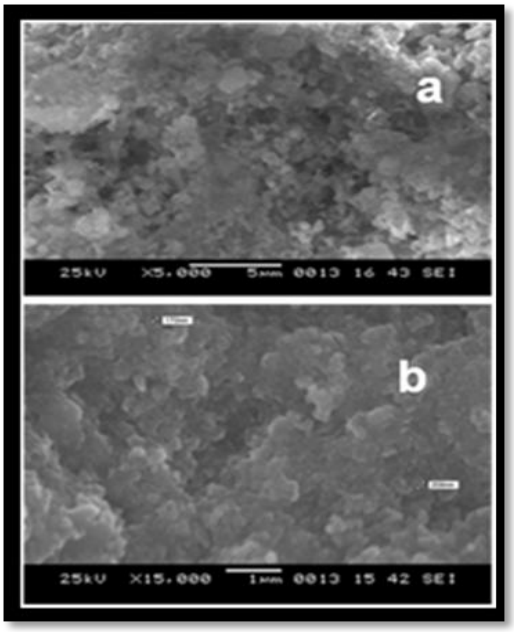

Figure 2. Micrographs(SEM) of Cerium zirconate ($Ce_{0.5}Zr_{0.5}O_2$) a. CZ-SSR b. CZ-UM owders.

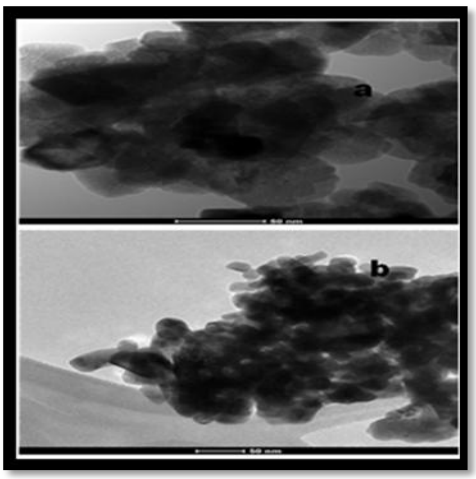

Figure3. Micrographs (TEM) of Cerium zirconate ($Ce_{0.5}Zr_{0.5}O_2$) a. CZ-SSR b. CZ-UM powders.

UV–Vis diffuse reflectance characterization

The UV-Vis diffuse reflective properties of synthesized material strongly influence photocatalytic activity. Diffuse reflectance spectra of CZ-SSR and CZ- UM indicates that both the materials absorb in 400nm – 600nm range. (DRS spectra of CZ-SSR and CZ-UM given in Figure 6) . This result is in good consentient with the result of photocatalytic activity. Cerium zirconate, CZ-SSR and CZ- UM absorb at 443nm and 457nm respectively which shows that these catalyst are visible light active. The band gap of the samples was determined by the equation Eg=1239.8/λ, where Eg the band gap (eV) is and λ (nm) is the wavelength of the absorption edges in the spectrum[23]. The band gap of CZ-SSR is found to be 2.79 eV at 443nm while the sample CZ- UM have band gap 2.71 eV at 457nm. This shows that band gap for CZ-UM is lower than CZ-SSR and hence it has better Photocatalytic activity than CZ-SSR.

Photocatalytic efficiency of photocatalyst

Photocatalytic activities of the Cerium zirconate samples (CZ-SSR & CZ-UM) were investigated on the degradation of methylene blue(MB) in aqueous solution. Blue color of the solution gradually diminished upon the visible light irradiation in the presence of photocatalysts, illustrating the degradation of MB. Total concentrations of all MB species were simply determined by the maximum absorption measurement. Figure 6. shows the decrease of the concentration of MB w.r.t. irradiation time in the presence of the as prepared Cerium zirconate samples (CZ-SSR and CZ-UM) and self-degradation under visible light irradiation. It was found that the self-degradation of MB under visible light irradiation was not obvious, indicating the stabilization of MB under visible light irradiation. The degradation of MB in the presence of CZ-SSR and CZ-UM under visible light irradiation can be attributed to a photosensitization pathway, where MB served as the sensitizer itself and catalyst served as electron-transfer mediator. However, for our synthesized photocatalysts CZ-SSR and CZ-UM , the photocatalytic activity of CZ-UM was superior. After 180 min of visible light irradiation, 78% MB was photo-degraded by the sample CZ-SSR while degradation of MB in the presence of the sample CZ-UM was 92%. As it is known, the photosensitization process and the direct photocatalytic reaction are the parallel pathways for the photodegeadation of MB in the presence of photocatalysts under visible light irradiation in aqueous solution. Therefore, besides the MB sensitized self-degradation processes on the surfaces of our visible light-responded photocatalysts, the processes of direct oxidation or indirect photodegradation by active hydroxide radicals ($OH^{\cdot}$) appear significant because the absorption edges of these photocatalysts showed clear absorption in the visible light region. Under visible light irradiation, charge separation will be induced for Cerium zirconate photocatalyst samples. The photogenerated holes on the valence band will then oxidize the MB either directly or indirectly via hydroxide radical generation.

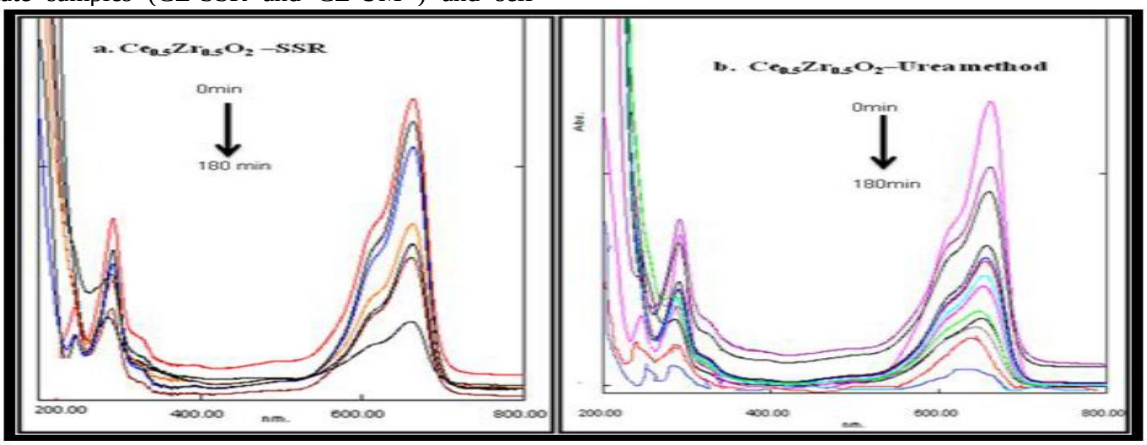

Figure 4. The changes in absorbance of MB solution (1 x 10^{-5} mols L^{-1}) by of Cerium zirconate ($Ce_{0.5}Zr_{0.5}O_2$) a. CZ-SSR b. CZ-UM powders. The conc. of the catalyst was 1 g/l.

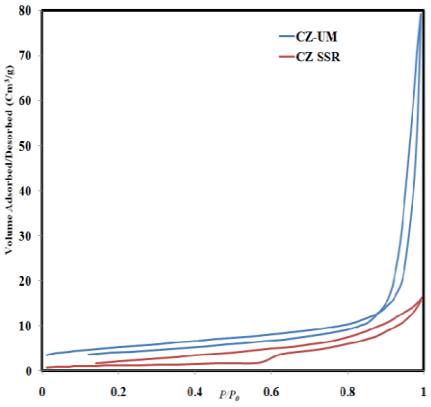

Figure 5 : The N_2 adsorption isotherms at -196 ^{O}C of Cerium zirconate a. CZ-SSR b. CZ- UM .

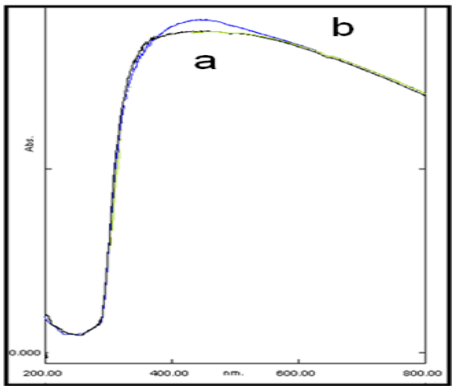

Figure 6. DRS of Cerium zirconate ($Ce_{0.5}Zr_{0.5}O_2$) a. CZ-SSR b. CZ-UM powders.

Table 1 : various surface textural parameters of CZ-SSR and CZ-UM photocatalyst calculated from N_2 adsorption isotherm at -196 ^{O}C.

Surface parameter	**Samples**	**CZ-UM**	**CZ-SSR**
Surface Area	Single point surface area at P/Po = 0.250169013: (m²/g)	18.28	4.109
	BET Surface Area: (m²/g)	18.57	4.225
	Langmuir Surface Area: (m²/g)	25.95	6.003
	t-Plot Micropore Area: (m²/g)	2.548	0.448
	t-Plot External Surface Area: (m²/g)	16.02	3.7588
Pore Volume	BJH Adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm width: (m²/g)	17.277	8.199
	t-Plot micropore volume: (cm³/g) (V micro)	0.0011	0.0002
	BJH Adsorption cumulative volume of poresbetween 1.7000 nm and 300.0000 nm width: (cm³/g)	0.1233	0.00252
Pore Size	BJH Adsorption average pore width (4V/A): (nm)	30.62	12.336

IV. CONCLUSIONS

Cerium zirconate, $Ce_{0.5}Zr_{0.5}O_2$-SSR and $Ce_{0.5}Zr_{0.5}O_2$-UM were synthesised via Solid state calcination and Urea method and their optical absorption spectra were recorded. The SEM and TEM of these materials indicate that surface of material has been rough and well agglomerated which help to enhance its photocatalytic activity. The low band gap of CZ-SSR (2.79 eV) and CZ-UM (2.71 eV) make it visible light active. The photocatalytic activity of these synthesized photocatalysts was studied for the photobleaching of methylene blue aqueous solution. After180 min of visible light irradiation, we observed, 78% MB was photo-degraded by CZ-SSR photocatalyst while degradation of MB was 92% over CZ-UM sample. The photocatalytic activity of CZ-UM was better than CZ-SSR for degradation of MB. The efficient degradation of methylene blue observed in this study suggest that Cerium zirconates are potentially useful material for removal of dyes from water under visible light irradiation.

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