Solar photocatalytic degradation of Bisphenol-A from industrial waste water over Cu-doped Zinc oxide

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ABSTRACT Frommental detoxification by semiconductor mediated solar photocatalysis is demanding area of research. $Cu_xZn_{1-x}O$ (x = 0.02 to 0.1) were synthesized by novel mechanochemical method and characterized with powder XRD, SEM, EDX, XPS, UV-Visible and Photoluminescence (PL) spectra.X-ray diffraction data suggests the hexagonal wurtzite structure for $Cu_xZn_{1-x}O$ crystallites and the incorporation of metal ion impurities expands the lattice constants of ZnO. UV-visible spectra propose the decrease in band gap of $Cu_xZn_{1-x}O$ with the extent of Cu increases up to 4.69%. The PL spectra suggest that, $Cu_{0.06}Zn_{0.94}O$ contains highest number of oxygen vacancies or defects in the form of O⁻. The XPS analysis supports the incorporation of Cu⁺ in Cu_{0.06}Zn_{0.94}O. Solar photocatalytic activity of $Cu_xZn_{1-x}O$ was evaluated by means of photocatalytic degradation (PCD) of Bisphenol A, an endocrine disruptor from industrial waste water. $Cu_{0.06}Zn_{0.94}O$ shows excellent solar photocatalytic activity due to greater cell volume, lower band gap and least electron-hole recombination. The detailed mechanism of PCD of BPA was proposed with the identification of intermediates such as hydroquinone, benzene-1, 2, 4-triol and 4-(2-hydroxypropan-2-yl) phenol.

Keywords: CuxZn1-xO, Mechanochemical, Photocatalysis, Bisphenol A, Sunlight

1. Introduction

Bisphenol-A (BPA) is a synthetic estrogen used in making many plastic products like plastic bottles, baby bottles, children's toys and even medical devices. It is also part of the epoxy resin that lines many metal cans, like those used for canned vegetables, fruits and meats. BPA is considered an "obesogen" because it can lead to obesity and as an "endocrine disruptor" because it disrupts the body's hormonal (endocrine) balance **[1]**.

Nowadays, environmental problems are becoming more and more serious with the development of industry and economy. Photocatalysis has been regarded as one of the most effective ways to solve these problems. Zinc oxide is one of the earliest discovered and most widely applied oxide photocatalytic materials. The application of ZnO as solar photocatalyst was limited due to its photo instability in aqueous solution. Nevertheless, ZnO can only absorb a small portion of solar spectrum in the UV region, which means that they do not allow the effective utilization of visible light. The low photocatalytic efficiency of ZnO is due to fast recombination rate for electron-hole pair photo generated on the semiconductors **[2]**. The presence of the doped metal ions in the ZnO crystalline matrix significantly affects the photocatalytic activity, charge carrier recombination rate and interfacial electron-transfer rate **[3]**. Recently, it was reported that oxygen defects were proposed to be active sites of ZnO. ZnO samples with a high concentration of oxygen defects exhibited excellent photocatalytic activity toward organic pollutants **[4]**. It means the doping of suitable metal ions in ZnO can lead to enhancement of optical properties and controlling the concentration of surface defects.

To significantly improve the photocatalytic efficiency of zinc oxide, lots of efforts have been made to tailor the band gap energies by modifying the host structures with various transition metal dopants, which shifts the threshold wavelength to the visible light region. Based on this inspiration, several metals have been doped in ZnO. Among various transition metals, Cu-doped ZnO was found to be good choice to achieve desired success in the area of visible light photocatalysis. Morphology and optical properties of Cu-doped ZnO depends upon size of particle, method of synthesis etc. Recently, silver and copper doped zinc oxide prepared by liquid impregnation methods was found to be active photocatalyst in the degradation of azo dye [5]. Synthesis of Cu doped ZnO by co-precipitation Method and their photocatalytic activity in the degradation of Crystal Violet (CV) dye in aqueous medium [6], Rhodamine B [7] and brilliant green dye under UV irradiation [8] was reported. The photocatalytic performance of Cu-doped zinc oxide microstructures synthesized by single step facile chemical method due to existence of (001) polar surfaces, oxygen vacancies, and increased optical absorbance at visible wavelengths, towards degradation of methylene blue (MB) and rhodamine B (RhB) dyes is also reported [9]. Bhuyan et al. [10] reported superior photocatalytic and antibacterial activity of Cu-doped ZnO nanorods synthesized by mech.-assisted thermal decomposition method. Cu-doped ZnO nanorods prepared by facial growth method were used for photocatalytic degradation of methyl orange [11] and photocatalytic degradation of methylene blue under 10 W UV light irradiation [12]. The photocatalytic degradation of diazinon over Cu-doped ZnO nanorods synthesized via a facile co-precipitation method [13] is also studied. Cu doped ZnO synthesized by facile and template free reflux method was found to bephotocatalytically active towards degradation of Methyl orange under UV light illumination [14] while, Sn and Cu doped ZnO hybrid nanoparticlesprepared bymicrowave assisted ultra-sonicated precipitation process has favorable photocatalytic activity in MB dye degradation [15]. Cu-ZnO/TiO₂ nanoparticles were prepared by sol-gel method found to be good photocatalyst in the degradation of methyl orange under visible light irradiation [16]. Though Cu-doped zinc oxide proved to be excellent photocatalyst for the degradation of various dyes, its activity was mainly decided by morphology, particle size etc. which basically depends upon method of synthesis.

The industrial waste water sample collected from polymer Industry area M.I.D.C. Mahad, Dist-Raigad, Maharashtra, (INDIA) was found to contain 49 to 143ppm Bisphenol A. This article reports solar photocatalytic degradation of Bisphenol A from industrial waste water over Cu-doped zinc oxide synthesized by eco-friendly, simple mechanochemical method.

2. Experimental

2.1. Materials

In present study, zinc acetate (assay \geq 98%) oxalic acid (assay 99.5%), Copper (II) acetate (assay 99%, Sigma-Aldrich), and other required chemicals are of analytical grade, obtained from Merck Limited, Mumbai, India and were used without further purification.

2.2. Collection of industrial waste water

The industrial waste water sample was collected from polymer Industry area M.I.D.C. Mahad, Dist-Raigad, Maharashtra, (INDIA) in the months of October, December (2017), February, April, June and August (2018). As soon as sample was collected from the source, it was kept under gravity settling for 24h. The entire sample was then filtered using vacuum filter to remove any suspended matter. The pH of water sample was recorded and then it was used for COD determination, GC-MS analysis and solar photocatalytic degradation study.

2.3. Synthesis of $Cu_x Zn_{1-x}O$ (x = 0.02 to 0.1)

Cu_xZn_{1-x}Owas prepared by a noveltwo step process. The first step is eco-friendly, solution free mechanochemical synthesis of zinc oxalate-copper oxalate precursor (ZOCO) and the second step is thermal decomposition of ZOCO to form Cu_xZn_{1-x}O. In a typical synthesis, 0.02mmol of copper (II) acetate monohydrate and 0.98mmol of zinc acetate dihydrate mixed with 1.2mmol of oxalic acid were taken in agate mortar and mixture was hand ground for 10 min at room temperature to obtain paste (semisolid) of Cu_{0.02}Zn_{0.98}C₂O₄.2H₂O and CH₃COOH. Then the mixture was allowed to stand for 30min. The driving force of the reaction is volatility of acetic acid byproduct. After 30min, most of the acetic acid byproduct goes off from the reaction mixture and semisolid gradually turns in to fine powder. Finally, Cu_{0.02}Zn_{0.98}O was obtained by calcination of Cu_{0.02}Zn_{0.98}C₂O₄.2H₂O precursor at 600°C. Similarly, Cu_{0.04}Zn_{0.96}O, Cu_{0.06}Zn_{0.94}O, Cu_{0.08}Zn_{0.92}O, and Cu_{0.1}Zn_{0.99}O were prepared by varying amounts of copper (II) acetate monohydrate and zinc acetate dihydrate. **2.4. Equipments**

Cu_xZn_{1-x}Ocrystallites were characterized by X-ray diffractometer (D-8 Advance Brukr AXS), UV-Visible Spectrophotometer(UV-1601, Shimadzu), Photoluminescence (PL) spectra (Shimadzu, RF-5301PC), Scanning Electron Micrograph (SEM JEOL JSM-6360A) and Energy dispersive X- ray spectra (EDXS). X-ray Photoelectron spectra (XPS) were recorded with a V.G. Microtech (UK) unit ESCA 3000 spectrometer equipped with Mg K α X-ray source (hu = 1253.6 eV) and a hemispherical electron analyzer. The X-ray source was operated at 150 W. The residual pressure in the ion-pumped analysis chamber was maintained below 1.0×10^{-9} Torr during data acquisition. The C_{1s} peak at a binding energy 284.6 eV was taken as an internal standard. The accuracy of BE values was within ± 0.2 eV. The photocatalytic reactions were carried out at ambient temperature under the irradiation of sunlight in batch photoreactor. The details of set up of photoreactor were already explained elsewhere **[17]**. The initial pH of suspension was recorded with the help of pH meter (EUTECH-pH510). The extent of photocatalytic degradation (PCD) of BPA at an interval of 30min sunlight irradiation was primarily checked by means of decrease in absorbance at 276nm (λ_{max} of BPA). Complete mineralization of BPA was confirmed by chemical oxygen demand (COD) reduction method. The COD determinations were performed with COD digester (SPECTRALAB 2015M). The PCD efficiency was calculated by using expression (1).

 $= (COD_i - COD_t / COD_i) \times 100$

(1)

Where, η = Photocatalytic degradation efficiency, COD_i = Initial chemical oxygen demand, COD_t = Chemical oxygen demand at time t. The intensity of sunlight was checked by ferrioxalate actinometry **[18]**. The average photon flux calculated for sunlight was found to be 1.7×10^{-7} Einstein s⁻¹cm⁻². The PCD intermediates were identified by HPLC and GC-MS analysis.HPLC analysis was performed with a Shimadzu 20A instrument equipped with C18 column. Acetonitrile/water (40:60) was used as mobile phase at a flow rate of 1mL min⁻¹. The sample injection volume of 10 µL and UV wavelength of 254 nm were employed. GC-MS analysis was done with Shimadzu GCMS-QP5050 instrument equipped with DB-5 capillary column and Quadrapole detector. Helium was used as a carrier gas. The GC injection volume of 2µL and the split ratio of 25:30 were used. The reusability of the photocatalyst was evaluated by reclaiming the photocatalyst after PCD reaction in the batch mode, washing, drying in electric oven at 110°C and using it for BPA degradation under identical experimental conditions.

2.5. Photocatalytic degradation experiments

Solar photocatalytic degradation of Bisphenol A from industrial waste water was investigated over Cu_xZn_{1-x}Oin comparison with zinc oxide (ZO). All the PCD experiments were carried out in duplicate and at an ambient temperature, without external supply of oxygen. In all the PCD experiments, 100ml of industrial waste water containing Bisphenol A and 200mg of photocatalyst was taken in batch photocatalytic reactor vessel and agitated for 5 min in an ultrasonic bath to obtain uniform suspension. Initial pH of suspension was recorded and whole setup was then placed in sunlight with constant stirring for specific period of time between 9:00 a. m. to 5:00 p.m. during the months of December to March. The effect of fluctuation of sunlight intensity was eliminated by simultaneous run of PCD experiments. After the specific sunlight irradiation time PCD reaction was stopped and whole suspension was centrifuged at a speed of 3000 rpm for 5 min (Remi, India) and then filtered. The liquid portion was used for absorbance and final COD measurement. The 150ppm solution of Bisphenol A (BPA150) was prepared by using double distilled water and its results of solar photocatalytic degradation were compared with that of industrial waste water sample. The extent of degradation of Bisphenol A from industrial waste water and BPA150 was also studied under similar experimental conditions in dark as a control experiment.

3. Results and Discussion

3.1 Characterization of $Cu_xZn_{1-x}O$ (x = 0.02 to 0.1)

The Cu_xZn_{1-x}Osamples were characterized by XRD, SEM, EDX, XPS, UV-Visible and Photoluminescence (PL) spectra. The optimization of lowest possible calcination temperature to obtain Cu_xZn_{1-x}OfromCu_xZn_{1-x}C₂O₄.2H₂O was done by TG-DTA analysis.

3.1.1Thermal analysis of Cu_{0.06}Zn_{0.94}C₂O₄.2H₂O

Fig. 1 shows typical TG-DTA curve of Cu_{0.06}Zn_{0.94}C₂O₄.2H₂O. The thermal decomposition curves in the temperature range 20–210°C shows a single step dehydration process. The measured weight loss for this decomposition stage is about 18.87% of the total weight (calculated loss: 19.03%) indicating the elimination of two water molecules. Corresponding to this dehydration step, there is only one endotherm in DTA. In the second stage (210-500°C), dehydrated oxalate is converted to oxide and DTA confirms the oxide formation by the exothermic peak. The weight loss for second decomposition step is 38.73% of the total weight (calculated loss: 38.64%) attributed to the formation of Cu_{0.06}Zn_{0.94}O. Above 550°C there was no any kind of weight loss, indicating the existence of stable oxide ($Cu_{0.06}Zn_{0.94}O$) at this temperature. Hence ZOCO precursors are calcined at 600°C to obtain Cu_xZn_{1-x}O samples.

3.1.2 XRD analysis

Fig. 2 shows the stepwise changes is XRD pattern of $Cu_xZn_{1-x}O$ (x = 0.02 to 0.1) with the increase in extent of copper. The XRD data of bare ZnO, Cu_{0.02}Zn_{0.98}O (1.56% Cu), Cu_{0.04}Zn_{0.96}O (3.12% Cu)and Cu_{0.06}Zn_{0.94}O (4.69% Cu) exactly matches to that of JCPDS card No. 36-1451 for hexagonal wurtzite structure of ZnO. The absence of Cu related peaks rules out the existence of Cu-based clusters within the detection limit of XRD. This indicates the incorporation of copper ion in to the Zn lattice site rather than interstitial ones. Additionally, the peaks related to CuO have been observed in the XRD pattern of $Cu_{0.08}Zn_{0.92}O$ (6.25% Cu) and $Cu_{0.1}Zn_{0.9}O$ (7.82% Cu) but they are very weak due to the low concentration and poor crystallinity of CuO. This result is in agreement with the report of Liu et al., who believed that a secondary phase would appear when the Cu-doping concentration in ZnO exceeds to 5 at.% [19]. The XRD pattern of $Cu_{0.02}Zn_{0.98}O$, Cu_{0.04}Zn_{0.96}Oand Cu_{0.06}Zn_{0.94}O was found to be broader and slightly (0.18) shifted towards lower Bragg angle than that of bare ZnO. This shift is attributed to the shrinkage of ZnO crystal lattice due to the substitution of Zn ion(0.06 nm) by smaller Cu ion(0.057 nm) [20]. This implies an increase in lattice constant c of the ZnO crystal, which is attributed to incorporation of copper ions into the Zn lattice site, leading to increase of cell volume. The intensity of XRD peaks was found to decrease with the increase in extent of incorporated copper up to Cu_{0.06}Zn_{0.94}O, indicating the decrease of the crystallinity of Cu_xZn_{1-x}O. It is further to be noted that the intensity of XRD peaks of Cu_{0.08}Zn_{0.92}O and Cu_{0.1}Zn_{0.9}O increases as the doped Cu exist as CuO in the interstitial position of ZnO. The Cu_{0.06}Zn_{0.94}O with Cu occupying lattice sites of ZnO shows excellent solar photocatalytic activity, as discussed in **section 3.2**.

3.1.3 XPS analysis

The composition of Cu_xZn_{1-x}Owas investigated by XPS. The full scan XPS of Cu_{0.06}Zn_{0.94}O are shown in Fig. **3a.**Cu_{0.06}Zn_{0.94}Oshows prominent asymmetric XPS peak in O1s region (Fig. 3b). Regarding this, two contributions can be found: low energy component located at 529.7eV and the high energy component at 531.1eV which can be evaluated by peak fitting. The former is associated with photoemission in O^{2-} ions with valence state of lattice oxygen in ZnO and the latter is for lower valence oxygen i.e. surface adsorbed oxygen and 0⁻ [21]. This suggests that, besides surface oxygen, Cu_{0.06}Zn_{0.94}O contains additional lower valence oxygen sites. In the Zn 2p region, peaks situated at 1021 and 1044 eV of $Cu_{0.06}Zn_{0.94}O$ are assigned to $Zn 2p_{3/2}$ and $Zn 2p_{1/2}$ electrons respectively, which supporting the Zn^{2+} state of ZnO (Fig. 3c). The high-resolution scan of Cu 2p region of Cu_{0.06}Zn_{0.94}O is depicted in Fig. 3d. It shows peaks located at 932.6 eV (Cu $2p_{3/2}$) and 952.3eV (Cu $2p_{1/2}$). The characteristic XPS peak of Cu²⁺species usually located at 933 eV (Cu $2p_{3/2}$) together with the shake-up feature at 942 eV [22], while slightly lower binding energy (932.6 eV) and the absence of shake-up peak is indication of doping of Cu^+ in zinc oxide [23]. Thus, XPS data suggests the incorporation of Cu^+ (d^{10}) in ZnO, despite the fact that Cu^{2+} (d⁹) ions were added during the synthesis of $Cu_{0.06}Zn_{0.94}O$. The conversion of Cu^{2+} in to Cu^{+} is because of abstraction of e- from either lattice O²⁻ or conduction band, which helps to prevent electron-hole recombination in zinc oxide.

3.1.4 SEM-EDX analysis

The morphology of Cu_xZn_{1-x}O was studied by SEM analysis. Fig. 4a displays SEM-EDX investigation of $Cu_{0.06}Zn_{0.94}O$. SEM micrograph of $Cu_{0.06}Zn_{0.94}O$ show hexagonal crystallites, homogeneous phase and granular morphology; which in principle should be of more interest for photocatalysis. Furthermore, incorporation of copper ion into ZnO was also proved by EDX analysis. In addition to peaks related to Zn and O, Cu0.06Zn0.94O shows peaks for Cu (Fig. **4b**). No trace amount of other impurities could be seen in the detection limit of the EDX.

3.1.5 UV-Visible spectral studies

The UV-visible absorption spectra of bare ZnO, Cu_{0.02}Zn_{0.98}O, Cu_{0.04}Zn_{0.96}Oand Cu_{0.06}Zn_{0.94}Osamples dispersed in absolute alcohol are shown in Fig. 5. All the four samples showed well defined exciton band at 375-386nm, which corresponding to the bulk ZnO absorption. When ZnO doped with copper, red-shift trend was observed. The longer wavelength range (386nm) absorption suggests the existence of more absorption states or defect energy bands in Cu_{0.06}Zn_{0.94}O. The band gap (eV) calculated from corresponding λ_{max} (nm) values, decreases as the amount of copper in ZnO increases, bare ZnO (3.301), Cu_{0.02}Zn_{0.98}O (3.295), Cu_{0.04}Zn_{0.96}O(3.243), and Cu_{0.06}Zn_{0.94}O (3.212).The lowering of band gap energy helps to absorb more photons which lead to generation of more electron-hole pairs.

3.1.6 Photoluminescence studies

The photoluminescence (PL) spectra of undoped and Cu_xZn_{1-x}Owith the excitation wavelength of 300 nm are shown in Fig. 6. In general, PL spectrum of

ZnO exhibits a near-band-edge (NBE) UV emission (390 nm) and a broad defect related deep level emission in the visible region. The PL spectra of Cu_xZn_{1-x}O show a red shift as compare to bare ZnO. It is well known that the green yellow emission band between 450-480 nm originates from deep level (DL) defect emission associated with oxygen vacancies in ZnO lattices. Larger the content of oxygen vacancy or defect, stronger is the PL signal [24]. The green emission bands of Cu_xZn_{1-x}O samples were found to be stronger than that of pure ZnO. This suggests the existence of more number of oxygen vacancies or defects in these samples than that of bare ZnO. The green emission band of Cu_{0.06}Zn_{0.94}O was found to be strongest indicating maximum number of oxygen vacancies or defects in this sample. It is further to be noted that oxygen vacancies occur in three different charge states: the neutral oxygen (O), the singly ionized oxygen (O⁻), and the doubly ionized oxygen (O²⁻) **[25].** Vanheusden et al. **[26]** reported that the singly ionized oxygen vacancies (O⁻) are responsible for the intense green luminescence in the ZnO. Thus, Cu_xZn_{1-x}O must contain additional oxygen vacancies or defects in the form of O⁻, which is generated due to conversion of Cu²⁺ in to Cu⁺. The evidence of Cu⁺ is supported by XPS analysis. On the other hand the UV NBE band of Cu_xZn_{1-x}O were found to be weaker than that of pure ZnO, which supports the fact that in Cu_xZn_{1-x}O less electron-hole recombination than that in bare ZnO. It is further to be noted that, the weakest UV NBE band of Cu_{0.06}Zn_{0.94}O is attributed to least electron-hole recombination.

3.2. Photocatalytic degradation of Bisphenol A over CuxZn1-xO

The industrial waste water sample collected in the month of April was found to contain highest content of Bisphenol A (143ppm) **(Table 1)**. Hence, 150ppm solution of Bisphenol A (BPA150) was prepared by using double distilled water as a standard and its results of solar photocatalytic degradation over pure and Cu doped ZnO were compared with that of industrial waste water sample.

Blank experiments were carried out without photocatalyst to examine to what extent the BPA150 undergoes 'photolysis' if photocatalyst was not used. There was no evidence of degradation in the absence of pure or modified ZnO. In the dark (zero time irradiation) when BPA150 containing pure or $Cu_xZn_{1-x}O$ magnetically stirred for 7h, 4% degradation was observed. When BPA150 containing pure or $Cu_xZn_{1-x}O$ was irradiated with sunlight, substantial PCD was observed. The optimization of photocatalyst loading, concentration of Bisphenol A and initial pH of suspension for maximum solar PCD was separately studied. The solar PCD efficiency was found to be highest at 200 mg/100 ml of photocatalyst loading without adjustment of pH (Natural pH of suspension). It is observed that with increase in sunlight irradiation time, PCD efficiency increases. With increase in irradiation time, the absorbance of BPA150 at 276 nm (λ_{max}) was found to be decreases and it becomes lowest after 7 h irradiation of sunlight (Fig. 7). PCD efficiency was found to enhance with the extent of copper in $Cu_xZn_{1-x}O$ (Fig. 8) and $Cu_{0.06}Zn_{0.94}O$ (4.69% Cu) shows highest PCD efficiency (94.9%). This is due to fact that, up to $Cu_{0.06}Zn_{0.94}O$ copper gets incorporated in lattice position which increases the cell volume and oxygen vacancies in the form of O⁻ at the same time decreases band gap. As the extent of copper exceeds 5% the PCD efficiency drastically decreases to 60% for $Cu_{0.08}Zn_{0.92}O$ (6.25% Cu) and 43% for $Cu_{0.1}Zn_{0.90}O$ (7.82% Cu).

 $Cu_{0.06}Zn_{0.94}O$ was also found to be excellent solar photocatalyst for the degradation of Bisphenol A from industrial waste water samples **Table 2**.

3.3. Photocatalytic degradation mechanism

The excitation of photocatalyst by solar energy leads to the formation of an electron-hole pair **(Scheme 1a)**. The hole combines with water to form OH radicals while electron converts the dissolved oxygen to super oxide radical (O_2), a strong oxidizing species **(Scheme 1b, c)**. The O_2 radicals are further converted into HO₂ and OH radicals **(Scheme 1d - f)**. These photoexcitation reactions **(Scheme 1a to f)** are contending the electron-hole recombination in photocatalyst. The PL study reveals that the extent of chemisorbed oxygen vacancies is found to be highest in Cu_{0.06}Zn_{0.94}O therefore it consumes photo-generated electrons more effectively and there is least electron-hole recombination. This leads to maximum generation of OH radicals. The OH radicals thus formed during photo excitation shows electrophilic character and attack the electron rich C4 or C4' positions in the phenyl groups of BPA [I], which results in the formation of 4-isopropyl phenol radical forms cyclohexa-1, 4-diene-1, 2, 4-triol radical [IV], which is converted in to benzene-1, 2, 4-triol [V] (m/z = 125 + proton) by reaction with dissolved oxygen. The 4-isopropyl phenol radical gets converted in to 4-(2-hydroxypropan-2-yl) phenol [VI] (m/z = 151 + proton) by reaction with OH radicals. The species [V] and [VI] are finally oxidized in to CO₂ and H₂O. The existence of [III], [V] and [VI] intermediates was also confirmed by HPLC analysis.

4. Reuse of photocatalyst

The reuse of Cu_{0.06}Zn_{0.94}O was separately studied, by keeping all other parameters constant. During this study, after sunlight irradiation for 7h, photoreaction mixture was centrifuged and filtered. Filtrate was used for COD determination and residue was washed several times with double distilled water in ultrasonic bath followed by filtration and drying at 110°C in an electric oven. Recovered photocatalyst was then reused for new PCD batch, without any further treatment such as heating in any kind of furnace. The activity of recycled Cu_{0.06}Zn_{0.94}O was found to retain even after fifth photo degradation experiment.

5. Conclusions

In present study $Cu_xZn_{1-x}O$ (x = 0.02 to 0.1) was synthesized by novel solution free mechanochemical method. The incorporation of Cu ion in to ZnO was supported by broadening and lower Bragg angle shift in XRD pattern of these samples as compare to that of pure ZnO, which indicates the incorporation of metal ion into the Zn lattice sites. The XPS study supports the existence of Cu⁺ in Cu_{0.06}Zn_{0.94}O, which is responsible for inhibition of photogenerated electron-hole recombination. The PL spectra of Cu_xZn_{1-x}O show a red shift in comparison to bare ZnO. The excellent solar photocatalytic activity of Cu_{0.06}Zn_{0.94}O is due to its greater cell volume, lower band gap, highest number of oxygen vacancies or defects in form of O⁻ and least electron-hole recombination. Activity of recycled modified ZnO was found to retain even after fifth PCD experiment.

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Figures

Fig.1. TG-DTA of $Cu_{0.06}Zn_{0.94}C_2O_{4.2}H_2O$



Fig. 2. XRD pattern of Cu_xZn_{1-x}O (x = 0.02 to 0.1)



Fig.3. XPS of Cu_{0.06}Zn_{0.94}O



Fig.4. SEM-EDX analysis of Cu_{0.06}Zn_{0.94}O



Fig. 5. UV-visible absorption spectra of pure and Cu_xZn_{1-x}O



Fig.6. The photoluminescence spectra of pure and Cu_xZn_{1-x}O







Fig. 8. Comparative solar photocatalytic activity of Cu_xZn_{1-x}O (x = 0.02 to 0.1)



 $[Bisphenol A] = 150 ppm; [Cu_{0.06}Zn_{0.94}O] = 200 mg/100 ml; Initial pH of the suspension = Natural 6.8 (without adjustment); Sunlight irradiation time 7h, Intensity of sunlight = <math>1.7 \times 10^{-7}$ Einstein s⁻¹cm⁻².

Table 1.

Sample code	Initial	Extent of
	pH	Bisphenol A
		(ppm)
OCT97	6.88	97
DEC112	6.79	112
FEB131	6.64	131
APR143	6.80	143
JUN49	6.85	49
AUG65	6.75	65
BPA150	6.37	150
	Sample code OCT97 DEC112 FEB131 APR143 JUN49 AUG65 BPA150	Sample code Initial pH OCT97 6.88 DEC112 6.79 FEB131 6.64 APR143 6.80 JUN49 6.85 AUG65 6.75 BPA150 6.37

Table 2.

Sample code	Initial COD _i	Final CODt	PCD
	(ppm)	(ppm)	(%)
ОСТ97	444	21	95.3
DEC112	482	26	94.6
FEB131	530	28	94.7
APR143	560	37	93.4
JUN49	323	7	97.8
AUG65	363	18	95
BPA150	490	25	94.9

[Cu_{0.06}Zn_{0.94}O] = 200mg/100ml; Initial pH of the suspension = Natural (without adjustment); Sunlight irradiation time 7h,

Intensity of sunlight = 1.7×10^{-7} Einstein s⁻¹cm⁻².

Scheme 1





Photocatalytic degradation mechanism of Bisphenol A