

## Modified ZnO Thin Films for Visible and Solar Light Photocatalytic Degradation of Phenolic Pollutants in Wastewater

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**Abstract:** Nitrogen doped ZnO deposited with silver (N-Ag/ZnO) thin film was successfully prepared via simultaneous co-sputtering of ZnO and Ag in the presence of nitrogen gas. The structural, optical and photocatalytic properties of the N-Ag/ZnO were compared with the pure ZnO, N-doped ZnO (N-ZnO) and Ag deposited ZnO (Ag/ZnO) thin films. The prepared ZnO based thin films were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Field emission scanning electron microscopy (FESEM), UV-vis absorbance spectroscopy and photoluminescence (PL) spectra. The photocatalytic degradation efficiency of the prepared thin films were investigated for 2-chlorophenol (2-CP) in aqueous solutions under visible light and solar irradiation. Results obtained revealed that N-Ag/ZnO thin films have the higher absorption in visible region and highest photocatalytic activity compared to ZnO, N-ZnO and Ag/ZnO.

**Key words:** N-Ag/ZnO · Thin films · Visible light · Photocatalytic · Degradation · Wastewater

### INTRODUCTION

Chlorinated phenols discharged from various industries such as paper, pesticide, pharmaceuticals and so forth, belongs to the most toxic pollutants. The toxicity of these chlorophenols highly depends on the position of chlorine with respect to phenol group and degree of chlorination and pH [1]. Therefore, treatment of the wastewaters containing chlorophenols using advanced water treatment technologies is desired. Photocatalysis has gained considerable attention in recent years as an environment friendly technology for complete mineralization of organic contaminants present in wastewater.

Zinc oxide (ZnO) is a wide band gap semiconductor photocatalyst (3.37 eV) having electron mobility (200 – 300 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) and electron life time (>10s) comparatively higher than the traditional photocatalyst TiO<sub>2</sub> (0.1 - 4.0 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) [2]. Under the light illumination, ZnO absorb the large fraction of UV light and achieves

superior photocatalytic activity than the TiO<sub>2</sub> for organic pollutant decomposition. The valance band of ZnO is located considerably below TiO<sub>2</sub> VB, demonstrating that the •OH radical generated in the former (+3.06 V) has a higher oxidation potential compared to the latter (+2.7 V). Moreover, the electrons evolved from conduction band of ZnO are expected to be more negative charge than TiO<sub>2</sub> (at pH 0 vs. NHE) [2, 3]. Despite the superiority than TiO<sub>2</sub>, the photocatalytic properties of ZnO are reduced by its wide energy band gap (3.3 eV) which permits electronic excitations by absorption of UV light [4]. Commercial applications of ZnO photocatalysis are also hindered by fast recombination rates of the photogenerated electrons/hole (e<sup>-</sup>/h<sup>+</sup>) pairs while agglomeration of powder photocatalyst in aqueous medium also impedes the photocatalytic efficiency [5].

To overcome these obstacles, modification of surface and electronic structure of ZnO has been widely applied by tailoring the defect chemistry of ZnO to increase the photocatalytic activity under the visible light [2, 3].

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Doping/deposition of ZnO with noble metal such as Ag, Pt Au etc which not only act as electron sink but also help in altering the energy band gap considerably to promote visible light activity [6-9]. Another approach to widen the absorption window of ZnO to visible light may involve non-metal doping such as nitrogen [10, 11]. Nitrogen has been found to be a suitable dopant due to the O and N size compatibility and its lower ionization energy among other non-metal dopants [12]. Simultaneous cationic (Ag) and anionic (N) co-doping of ZnO can therefore be seen as a next logical step for improvement of the photocatalytic activity of ZnO in visible region and immobilization over transparent support as thin film could overcome the problem of catalyst agglomeration.

A number of chemical and physical deposition methods can be adopted for simultaneous doping/deposition of N and Ag over ZnO including chemical precipitation, hydrothermal synthesis, sol-gel method, molecular beam epitaxy, pulse laser deposition and chemical vapor deposition method [11, 13-16]. Radio Frequency Magnetron Sputtering (RF Sputtering) is a flexible deposition technique which provides high; reproducible deposition rates for nanocrystalline materials while preserving the optoelectronic properties of the deposited thin films [17]. In this work, RF sputtering method has been used for the preparation of ZnO, N doped ZnO, Ag deposited ZnO and N-Ag/ZnO thin films over the glass substrate. The photocatalytic activity of these films have also been investigated for the degradation of 2-chlorophenol in aquatic system.

## MATERIALS AND METHODS

**Materials:** ZnO, N-ZnO, Ag/ZnO and N-Ag/ZnO thin films were prepared on the glass substrate (UV grade). Prior to thin film deposition, the glass substrate was thoroughly clean with ethanol and acetone and N<sub>2</sub> flow was used to dry the substrate slides. High purity targets (99.999%) of ZnO and Ag were used as precursors in the RF system. 2-chlorophenol was purchased from Merck. A solution of the concentration 1000 mg/L was prepared by dissolving the appropriate amount of 2-CP in deionized water. The solution was further diluted for the photocatalytic experimental studies.

**Fabrication of Thin Films:** Radio frequency (RF) magnetron sputtering method was applied to prepare ZnO, N-ZnO, Ag/ZnO and N-Ag/ZnO thin films using DC/RF Magnetron Sputter System, Syskey Technologies,

Taiwan. The pure ZnO film was produced by generating plasma using Argon gas at RF power of 200 W while N-ZnO thin film was prepared by passing nitrogen gas at a flow rate of 10 SCCM. Ag deposited ZnO film was grown by co-sputtering ZnO and Ag targets at the RF power of 200 and 30 W, respectively. Similarly, N-Ag/ZnO thin film was grown at 200 and 30 W for ZnO and Ag targets respectively, in the presence of nitrogen gas at a flow rate 10 SCCM. The base pressure in the chamber was fixed to  $1 \times 10^{-6}$  Torr before introducing argon gas with fixed flow rate 20 SCCM. The operating pressure was maintained  $5 \times 10^{-3}$  Torr with substrate rotation at 15 RPM and deposition time 600 sec for the whole deposited films.

**Materials Characterization:** The surface morphology of the prepared thin films was studied by SEM using a field emission scanning electron microscopy (FESEM), JSM-7500 F (JEOL – Japan) operated at 10-15 kV. X-ray spectra of the thin films were recorded on X-ray diffractometer, Ultima-IV, Rigaku Corporation, Tokyo, Japan using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$  wavelength at 40 kV accelerating voltage and 30 mA current), Photoluminescence emission (PL) spectra of thin films were measured at room temperature using Fluorescence Spectro-fluorophotometer, model RF-5301 PC, Shimadzu, Japan. The films were excited by 325 nm at a slit width of 10 nm. UV-visible absorption spectra of prepared ZnO films were recorded using “UV-1650PC” UV-visible spectrophotometer (Shimadzu, Japan).

**Photocatalytic Experiments:** The photocatalytic activity of ZnO, N-ZnO, Ag/ZnO and N-Ag/ZnO thin films were investigated for the degradation of the 2-CP under the visible and solar light irradiation. Visible light (112 W cool white lamps) photocatalysis experiments were performed in Luzchem photochemical reactor (LZC4) system while the solar light experiments were carried out in open air on sunny days from 10 am to 2 pm with ample sunlight availability. The photocatalytic experiment were performed by taking 150 ml of 25 mg/L concentration of 2-CP in a quartz beaker at pH 5.5 under continuous aeration and light irradiation conditions. Thereafter, photocatalyst thin film was immersed into the solution and 3 mL sample was withdrawn after fixed time interval. The amount of the 2-CP remaining in supernatant solution was determined using HACH LANGE DR6000 UV-visible spectrophotometer at 270 nm.

## RESULTS AND DISCUSSIONS

**Thin Films Characterization:** The X-ray diffraction spectra of pure ZnO, Ag/ZnO, N-ZnO and N-Ag/ZnO thin films are provided in Fig. 1. The characteristic peak for hexagonal ZnO appeared at  $2\theta$  values of 31.51 (100), 34.15 (002) and 64.7 (103) (JCPDS card no. 80-0075). The peak appeared at 38.66 (111) belongs to face centered cubic Ag in Ag/ZnO thin film (JCPDS card no: 00-001-116) [18]. The strong peak at (002) plane support preferential c-axis orientation in all crystalline samples. N-Ag/ZnO thin film shows the lower crystallinity compared to pure ZnO, Ag/ZnO, N-ZnO. Doping of N and Ag deposition are the major factor for the poor crystalline nature of N-Ag/ZnO [18-19]. The peak of ZnO at  $34.15^\circ$  is perhaps could be shifted to  $36.13^\circ$  in the co-doped film (DB card number: 00-003-0888). It means that both N and Ag could induce significant defects or impurities in the lattice structure/surface of ZnO. The XRD spectra of N-ZnO showed no significant peak for nitrogen which may suggest nitrogen incorporation in the interstices and ZnO lattice without changing the ZnO structure. However a slight shift in the N-ZnO peaks was observed. Since the atomic radii of oxygen and N are almost equal; substitution of O with N in ZnO lattice and formation of O-Zn-N chemical bonds is also possible. The N-Zn bond length is smaller than O-Zn which may explain the XRD peak shifting in N-ZnO [21, 22]. Furthermore, the poor crystallinity of N-Ag/ZnO thin film may also be favored by low temperature deposition conditions and high degree of nitrogen incorporation into the ZnO matrix [23]. Increase in O vacancies and tensile stress in the thin films has also been reported to be the cause of decreased crystallinity [23].

XPS measurements were performed on the N-ZnO, Ag/ZnO and N-Ag/ZnO thin films as shown in Fig. 2. The XPS spectrum of the Zn  $2p_{3/2}$  for N-ZnO, Ag/ZnO and N-Ag/ZnO were observed at 1022.41, 1021.76 and 1021.82 eV, respectively. The positive shift of Zn  $2p_{3/2}$  in N-ZnO compared to the Ag/ZnO and N-Ag/ZnO is mainly due to presence of the higher O vacancies into the ZnO lattice also suggesting that N may be strongly attached to pure ZnO compared to Ag/ZnO hybrid film [24, 25]. The XPS analysis revealed that the amount of N (% atomic concentration) into N-ZnO and N-Ag/ZnO is 3.876 and 2.136, respectively. Fig. 2a shows the XPS N 1s spectra of N-ZnO and N-Ag/ZnO with the binding energy at 399.97 and 399.17 eV, indicating the formation of oxynitride ( $ZnO_{1-x}N_x$ ) due to substitution of O atoms of ZnO [24].

Fig. 2b show the XPS of O 1s peaks at 530- 533 eV obtained from N-ZnO has also been assigned to the O atoms bound to Zn in ZnO while other peaks are due to presence of moisture as OH (531.57eV) and H<sub>2</sub>O (533.17 eV) and N-Ag/ZnO. The O 1s peaks from Ag/ZnO and N-Ag/ZnO appear at binding energies 529.51- 531.99 eV respectively as demonstrated by other studies [24, 26]. Fig 2d displays the XPS Ag d 5/2 and Ag d 3/2 spectra at 366.91 and 372.73 eV with small shoulder at about 367.63 and 373.17 eV respectively, suggesting the presence of Ag in metallic state with very small amount of oxidized form of Ag [6]. These XPS measurements revealed the successful doping of N and deposition of Ag into/on the ZnO lattice.

The surface morphology and microstructure of ZnO, N-ZnO, N-Ag/ZnO and Ag/ZnO were studied by FESEM as shown in Fig. 3. In Fig. 3a, ZnO nanoparticles appear to be distinctly smaller than 20 nm range. The ZnO nanoparticles appear to be of slightly larger size range as a result of N doping (Fig. 3b). Fig. 3d shows the presence of Ag nanoparticles uniformly distributed within the ZnO layer. These silvery white assemblies are also reported by other studies at the ZnO grain boundaries [6, 27]. The silvery cluster of Ag nanoparticles however is slightly diminished by the N-co-sputtering and N-Ag/ZnO nanoparticles appear as larger less bright clusters (Fig. 3c).

The UV-visible absorption and diffuse reflectance spectra of the synthesized thin films measured by UV/Vis/NIR spectrometer showed significant increase in absorption values in the visible region as a result of Ag

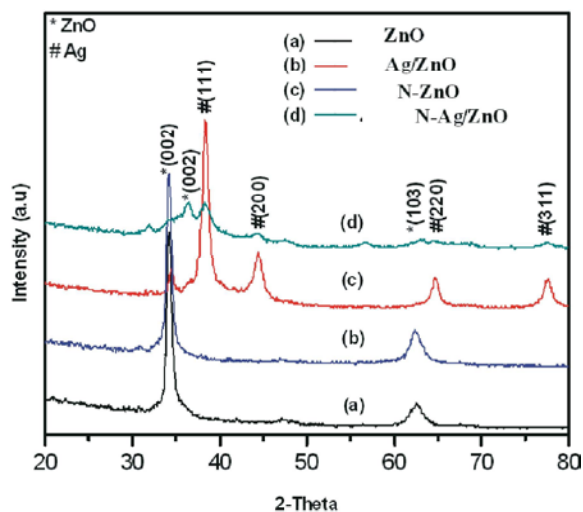


Fig. 1: XRD spectra of pure ZnO, Ag/ZnO, N-ZnO and N-Ag/ZnO thin films

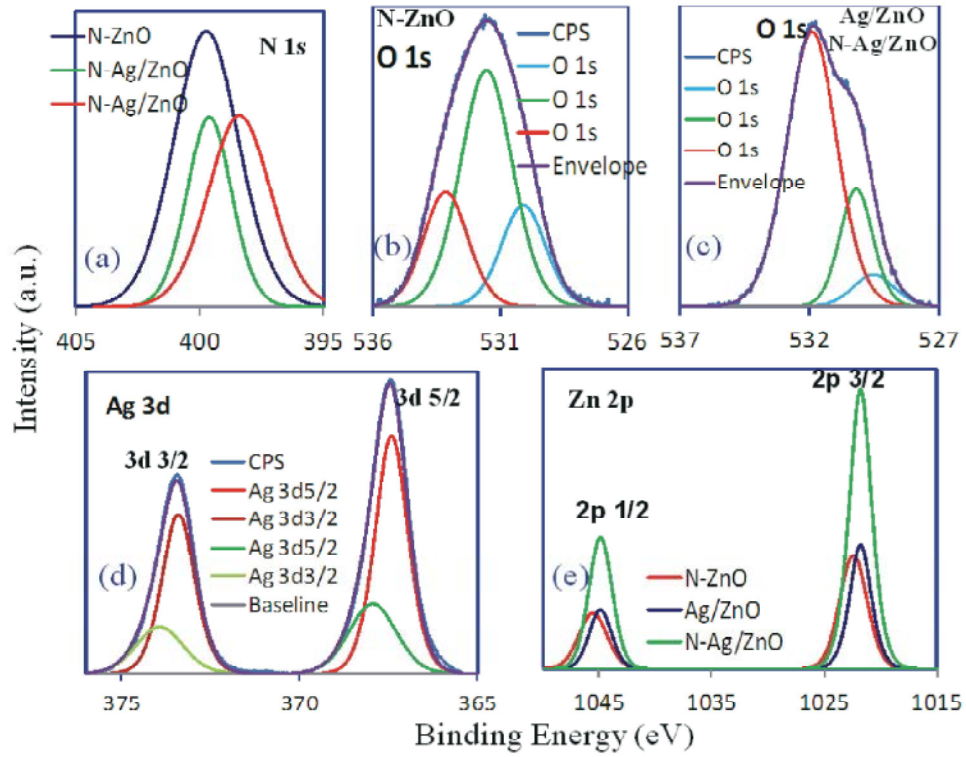


Fig. 2: XPS spectra of ZnO based thin films (a) N 1s (b) O 1s in N-ZnO (c) O 1s in Ag/ZnO and N-Ag/ZnO (d) Ag 3d and (e) Zn 2p

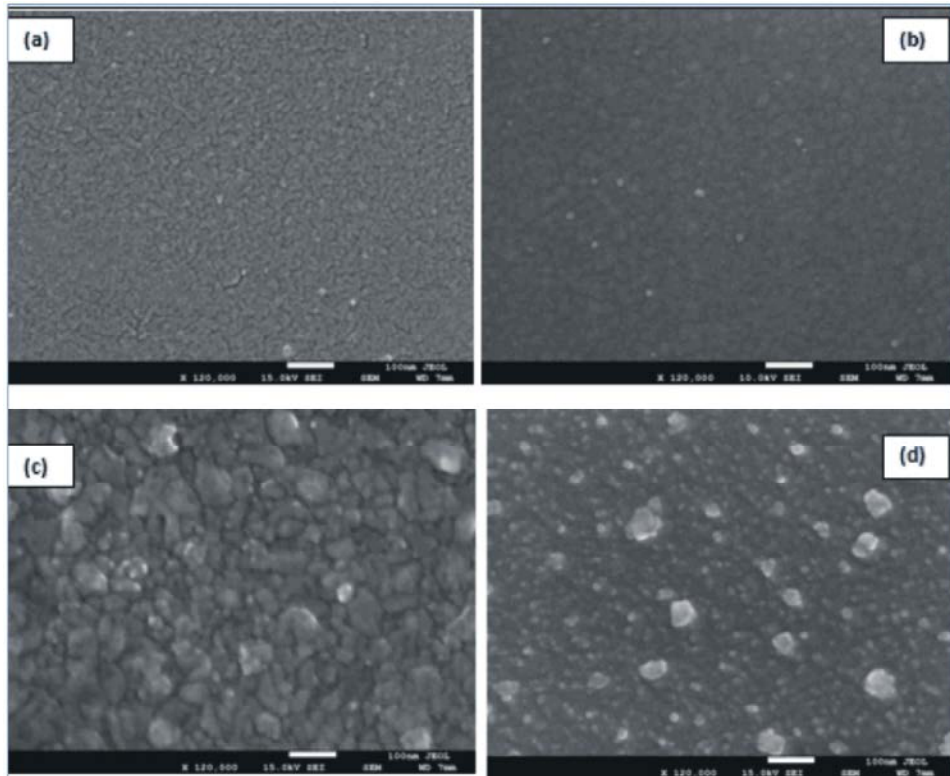


Fig. 3: SEM images of (a) pure ZnO, (b) N-ZnO, (c) N-Ag/ZnO and (d) Ag/ZnO

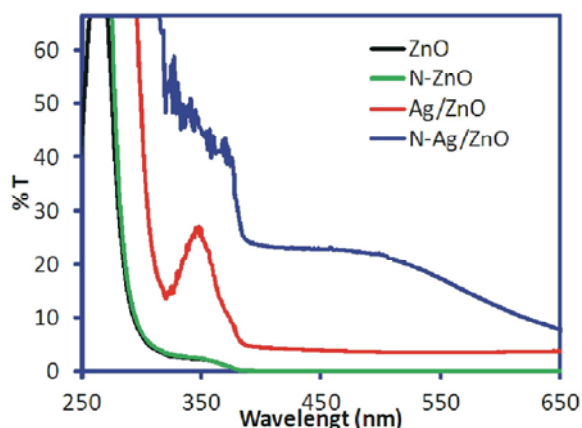


Fig. 4: UV-visible diffused reflectance spectra of pure ZnO, Ag/ZnO, N-ZnO and N-Ag/ZnO thin films.

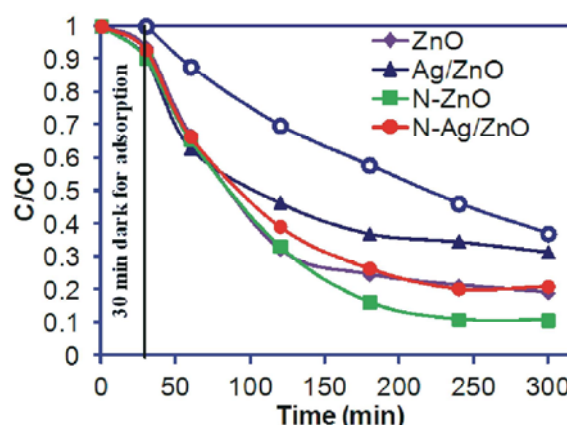


Fig. 6: Photocatalytic degradation 2-CP under solar light irradiation. (pH-5.5, V-150 mL, Conc.-25mg/L)

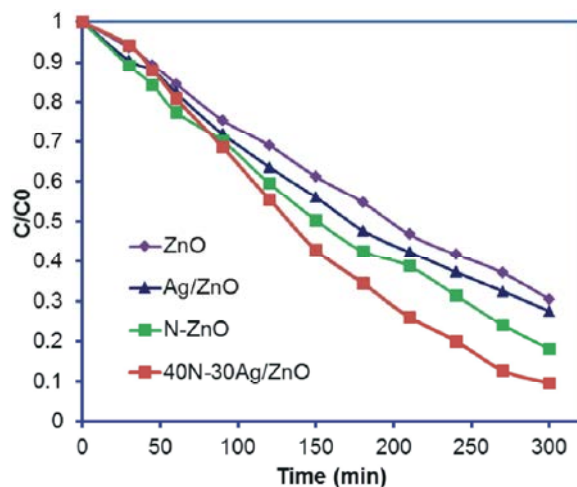


Fig. 5: 2-CP degradation under visible light irradiation. (pH-5.5, V-150 mL, Conc.-25mg/L)

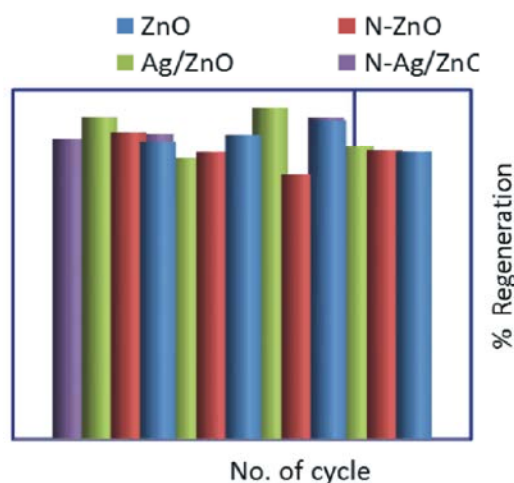


Fig. 7: Regeneration capacity of the ZnO based thin films for 2-CP photocatalytic degradation (pH-5.5, V-150 mL, Conc.-25mg/L)

and Ag-N co-sputtering. The diffused reflectance spectra of ZnO, N-ZnO, Ag/ZnO and N-Ag/ZnO nanoparticles thin films are shown in Fig. 4. The direct energy band gaps ( $E_g$ ) for all synthesized nano material thin films were calculated by plotting their respective  $(F(R?) \times h\nu)^2$  values against  $h\nu$ . The energy band gap values for these films are estimated from these plots. The direct energy band gap of ZnO, N-ZnO, Ag/ZnO and N-Ag/ZnO thin films were found to be 3.31, 3.30, 3.16 and 2.6 eV, respectively. N-ZnO thin films did not show any change in the energy band gap compared ZnO energy band gap. Previous studies also suggested that N doping did not make any reduction in the band gap energy [26, 28]. Nevertheless, N-Ag/ZnO thin film showed an additional narrower band gap of 2.6 eV. The change in the band gap may be

attributed to the Ag deposition. This may be the result of modification within the electronic levels of ZnO by doping with N. Interstitial ZnO sites can be occupied by the doped-N and the  $2p\delta$  electrons of nitrogen instead of O vacancies in the lattice sites can form new energy levels within the CB and VB of ZnO, thus, decreasing the band gap in zinc oxide [29-31]. Islam and coworkers observed optical band gaps 1.61 eV for the N-Ag/ZnO thin films synthesized by spray pyrolysis method and the shift in the band gap energy was attributed to silver oxide phase [32].

**Photocatalysis of Wastewater:** The photocatalytic activity of thin films has been evaluated for the degradation of 2-chlorophenol in wastewater under

synthetic visible light and natural solar light irradiation. The experimental results for the 2-CP degradation are displayed in Figures 5 and 6. The photocatalytic activity of N-Ag/ZnO thin films was found to be for 2-CP degradation is higher than the pure ZnO, N-ZnO and Ag/ZnO thin films.

Previous studies reported that the photocatalytic activity of semiconductor photocatalyst such as ZnO depends on the several factors i.e., crystallinity, surface structure, surface area, size of dopant, band gap energy and adsorption ability of adsorbate etc. [2]. The higher photocatalytic activity of the N-Ag/ZnO thin films can be discussed on the basis of crystallinity and surface structure. In contrast to cationic Ag deposition, N doping induced localized N 2p states within the band gap just above the valence band maximum of the metal oxide that increases the oxygen defects [28]. These O defects enhance the photon absorption ability and extend charge carrier life time. Upon the photo absorption, holes migrate to the interior of the ZnO and electrons move towards the semiconductor surface for the reduction process.

#### **Photocatalytic Reusability of ZnO Based Thin Films:**

The reusability of thin films is a very important parameter to assess the practical application of the thin films. All the synthesized thin films are subjected to four complete photocatalytic cycles under optimized conditions without any physical or chemical treatment for regeneration. The thin films were simply removed from the solution and thoroughly washed with de-ionized water and then dried at 50 °C. Thereafter, dried thin films were again introduced into a fresh batch of aqueous 2-CP solution for the next cycle. As shown in Fig. 7, all the ZnO based thin films were found to be highly stable and retained their characteristic photocatalytic activity in aqueous media upon subsequent reuse cycles, showing a mere 7-8% decrease in efficiency after 4<sup>th</sup> use.

#### **CONCLUSIONS**

Pure ZnO and Ag/ZnO, N-ZnO and Ag-N-ZnO thin films were prepared by radiofrequency (RF) co-sputtering technique for photocatalytic application. The SEM images and XRD spectrum clearly shows that doping of N and deposition of Ag alters the surface morphology and crystallinity of the ZnO based thin films. XPS analysis revealed that the Ag existed mainly as Ag<sup>0</sup> in Ag/ZnO and N-Ag/ZnO while the amount of N in N-ZnO and N-Ag/ZnO was 3.87 and 2.13 (% atomic concentration),

respectively. N-Ag/ZnO thin films showed superior photocatalytic activity for 2-CP degradation compared to pure ZnO, Ag/ZnO, N/ZnO films which can be attributed to the decreased band gap of Ag/ZnO and electron scavenging property of surface Ag. N doping on Ag/ZnO thin film results in highest sunlight and visible light photocatalytic activity for 2-CP degradation due to the tendency of N to form intermediate energy levels within the ZnO matrix narrowing the band gap and enabling the semiconductor to harness more photons of solar radiation. Therefore, N-Ag/ZnO thin films can be considered good candidates for visible and solar photocatalytic applications in wastewater treatment.

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