



# Sunlight-enhanced catalytic degradation over Ag–CuO nanoparticles thin films prepared by DC/RF sputtering technique

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**Abstract.** Herein, we report sunlight-activated photo-catalysis response of direct current radio frequency (DC/RF)-sputtered Ag–CuO nanoparticles thin films. We have adopted this approach for facile removal and easy recovery of thin films after use. Ag was incorporated at 2.5 and 5.4 wt% with reference to pure CuO. Structural analysis through X-ray diffraction showed successful incorporation of Ag into the CuO lattice. Surface morphological observation was carried out using a field emission scanning electron microscope, which showed a uniform deposition of the subjected thin films. The surface composition and change in the chemical state of pure and incorporated thin films were studied by X-ray photoelectron spectroscopy. In addition to structural and surface analysis, optical band gap evolution was also studied through UV–visible spectroscopy. The obtained results reflected that optical band gap decreased from 1.84 to 1.77 and 1.61 eV for 0, 2.5 and 5.4 wt% Ag, respectively. Methylene blue dye was used to investigate the photo-catalytic degradation response of deposited thin films in sunlight. Furthermore, the effect of pH and dye concentration was also taken into account. The degradation results indicate the acceleration of degradation process with the Ag incorporation into CuO lattice. Moreover, the pH also contributes positively to the degradation progression. This research study could provide a platform to understand and develop metal oxide thin films with an efficient photo-catalytic response in sunlight.

**Keywords.** CuO; silver nanoparticles; photo-catalysis; thin films; Methylene blue.

## 1. Introduction

With the passing of every minute, the world population is increasing with amassed daily life needs. Clean and pure water is one of the basic needs and rights of every human. The rapid and fast growth of industries is reducing the opportunities for clean water as well as environment. In this context, many strategies have been adopted to provide more viable clean water resources. Hence, the treatment of wastewater is the most vital solution for this problem. The treatment of wastewater has two main impacts on the life of human: reducing environmental pollution and secondly providing clean and safe water for the human.

Various techniques such as ultrafiltration, employing ion exchange adsorbents, adsorption, etc. have been used for pollutants removal [1–3]. However, in these mentioned methods, the pollutants are only transferred from water to the adsorbent material but still exist as auxiliary pollutants, which need further treatment.

Degradation of dyes in industrial wastewaters has therefore got expanding consideration in the field of wastewater treatment. Semiconductor materials are being considered as

a green technology to convert the harmful organic dyes into inorganic materials through photo-catalytic degradation [4,5]. Sunlight is being used as a natural source for the photo-degradation process, which is considered as a cost-effective advantage [6]. The photo-catalytic degradation process starts with the absorption of photons (with sufficient energy that equals or exceeds the band-gap energy of the catalyst) through light [7]. This excites an electron ( $e^-$ ) from the valence band (VB) to the conduction band (CB). This transformation generates a hole ( $h^+$ ) in the VB. The photo-excited electrons attack an oxidant to produce a reduced product; also, the generated holes react with a reductant to produce an oxidized product. The dye can be reduced by the photo-generated electrons or electron acceptors such as  $O_2$  adsorbed on the surface of the semiconductor or dissolved in water by reaction with photo-generated electron, reducing it to active species (superoxide radical anion  $O_2^{\cdot-}$ ) [1]. The photo-generated holes can attack the organic molecule (dye), forming  $R^+$ , or react with  $OH^-$  or  $H_2O$ , producing  $OH^\bullet$  radicals. These species are good oxidants and cause the heterogeneous photo-decomposition of organic molecules on the surface of the semiconductor [8].

Cupric oxide (CuO) thin film is a p-type semiconductor with low band gap ranging from 1.2 to 2.1 eV, non-toxic in nature and chemically stable. Photo-catalysis with nanostructured copper oxide (CuO) promises to be a new solution to the water problem. Umadevi and Christy [9] reported the methyl orange (MO) degradation using CuO nanoflowers under UV irradiation, which is considered as harmful light and needs special precautions during the measurements. Both Tamuly *et al* [10] and Tadjarodi *et al* [11] used a photo-catalyst of CuO nanoparticles for degradation of methyl red (MR) and Rhodamine B (RhB) in visible light, respectively. However, there are numerous issues that result from using such powder catalysts such as difficulty in separation and producing environmental risks. Thin films development has gained attention for the photo-catalytic activities due to cost-effectiveness and enhanced biomedical and antibacterial activities. These properties of thin films photo-catalysts would provide an ideal solution for avoiding the problems of powder photo-catalysts [12–14].

To the best of our knowledge, there are very limited reports on Ag–CuO nanoparticles thin films photo-catalytic dye degradation. Ag plays a significant role in enhancement of the photo-catalytic degradation of dyes because it works as surface traps, which can capture the electrons from the CB of metal oxide and minimize the electron–hole recombination [15]. In this work, we have successfully deposited Ag simultaneously with CuO as a thin film on glass substrate using DC/RF sputtering technique. Compositional, optical and surface properties were investigated. The degradation efficiency of deposited thin films was checked at various concentrations of Methylene blue (MB) dye. Furthermore, we have also investigated the effects of dye pH in sunlight.

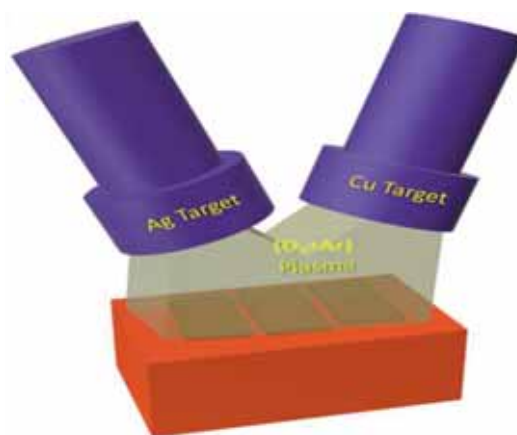
## 2. Experimental

### 2.1 Thin films deposition

Thin films of Ag–CuO nanoparticles have been deposited on a cleaned glass substrate using a DC/RF magnetron sputtering system (see scheme 1) (Syskey Technologies, Taiwan) as described in our previous work [16]. Prior to deposition, the glass substrate was cleaned by acetone, followed by drying in pressurized nitrogen gas. The targets of Cu ( $3 \times 0.6 \text{ inch}^2$ ) and Ag ( $3 \times 0.6 \text{ inch}^2$ ) metals used were of high purity (99.991%). The deposition parameters for Ag–CuO thin films are completely listed in table 1.

### 2.2 Characterization techniques

An X-ray diffractometer (XRD; Ultima-IV, Rigaku, Japan) with Cu K $\alpha$  radiation of wavelength ( $\lambda$ ) = 1.5418 Å at accelerating voltage of 40 kV and 30 mA current was used for phase and crystal structure analysis of the deposited thin films. The surface morphology of the deposited films was



**Scheme 1.** Simultaneous multitarget DC/RF sputtering.

**Table 1.** Deposition parameters of Ag–CuO nanoparticles thin films.

Deposition parameters	Value
Base pressure	$9 \times 10^{-6}$ Torr
Operating pressure	$5 \times 10^{-3}$ Torr
Deposition time	500 s
Substrate temperature	25°C
DC power for Cu target	200 W
RF power for Ag target	0.20 and 30 W
Oxygen flow rate	15 SCCM
Argon flow rate	20 SCCM
Target–substrate distance	14 cm

examined using a field emission scanning electron microscope (FESEM-JSM—7600F; JEOL, Japan). The optical properties were measured using a UV–visible spectrophotometer (Perkin Elmer, Lambda 750). X-ray photoelectron spectroscopy (XPS PHI 5000VersaProbe II, ULVAC-PHI Inc, Japan) was used for investigating the surface and chemical states of the deposited thin films nanoparticles.

### 2.3 Photo-catalytic experiments

MB dye was used as a model for evaluating the photo-catalytic activity of the deposited thin films in natural sunlight. First, MB solution with concentration of 10, 20 and 30 ppm was prepared in distilled water. Then, the deposited films were fixed inside a glass reactor having 100 ml of MB solution. To get accurate results, all investigations were completed in daylight without pressure and temperature control and the solar power was measured using a solar power meter (TENMARS). It was found to be about 1000–1100 W.

We have also investigated the pH effect on the photo-degradation efficiency. The dye solution pH was first adjusted using hydrochloric acid (HCl) and sodium hydroxide (NaOH)

before degradation experiment. At certain time intervals of 30 min, 3 ml of dye solution was withdrawn and the change in its concentration was determined using the UV-visible spectrophotometer.

The degradation percent is estimated by the following equation:

$$\text{Degradation\%} = \frac{C_o - C_t}{C_o} \times 100, \quad (1)$$

where  $C_o$  and  $C_t$  are the initial and residual concentration of MB ( $\text{mg l}^{-1}$ ), respectively.

### 3. Results and discussion

#### 3.1 Structural analysis

XRD diffraction patterns of the prepared Ag–CuO films on a glass substrate are shown in figure 1. The deposited films have polycrystalline nature with tenorrite phase (JCPDS 00-005-0661). The diffraction planes were identified as (110), (–111), (111), (–113), (002), (–311) and (–222). The diffraction planes (–111) and (111) reveal the monoclinic CuO thin films. It is clearly seen that the diffraction planes (–111) and (111) shift to lower diffraction angle with successive addition of Ag. The shifting of these diffraction planes to lower angle reflects that Ag atoms are successfully incorporated to CuO atoms. Das and Alford [17] also noticed a similar behaviour in the diffraction planes (–111) (111) with Ag nanoparticles. The variation in each diffraction plane is calculated by the following equation [18]:

$$\text{TC}_{\text{hkl}} = \frac{I_{\text{hkl}}/I_{0\text{hkl}}}{(1/n) \sum I_{\text{hkl}}/I_{0\text{hkl}}}, \quad (2)$$

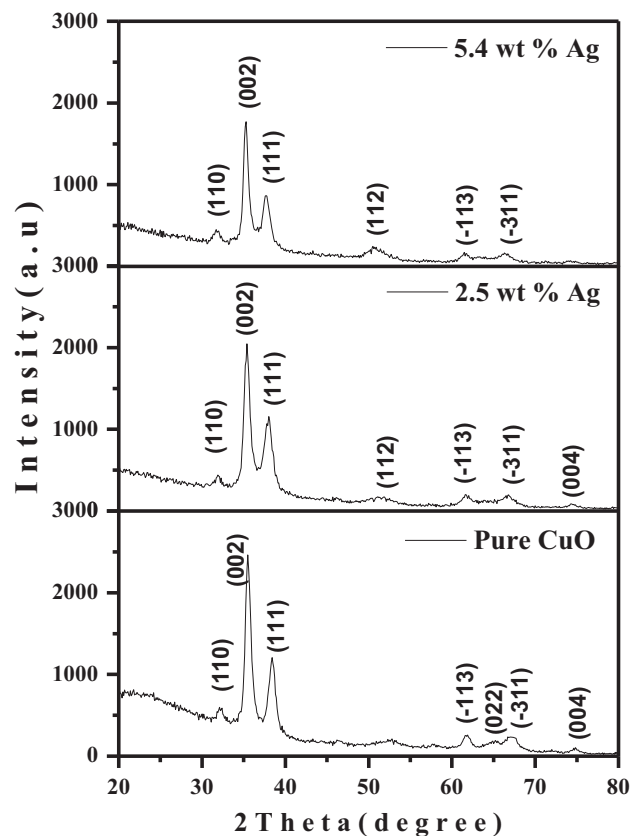
where  $I_{\text{hkl}}$ ,  $I_{0\text{hkl}}$  refer to the intensities of the obtained diffraction planes of the deposited films and the intensity of the planes as reported in JCPDS (00-005-0661) card, respectively;  $n$  is the number of diffraction planes. From equation (3) [18], the dislocation density of Ag–CuO nanoparticles films is investigated:

$$\delta = \frac{1}{D^2}, \quad (3)$$

where  $D$  represents the grain size of the deposited films. We have applied equation (4) [19] for calculating the lattice strain in the deposited films:

$$\varepsilon = \beta \cos \theta / 4, \quad (4)$$

where  $\beta$  represents the full-width at the half-maximum. The values of all parameters dislocation density, crystallite size, texture coefficient and strain are tabulated in table 2.



**Figure 1.** XRD patterns of Ag–CuO nanoparticles thin films.

#### 3.2 Surface morphology

Thin films surface morphologies of Ag–CuO nanoparticles have been scrutinized using the FESEM as shown in figure 2. The surface analysis indicates growth of a very uniform thin layer via DC/RF sputtering technique. Moreover, an increase in the particle size was clearly observed with increasing Ag nanoparticles percentage. The change in particle size of Ag–CuO nanoparticles may be due to the electropositive nature of the silver ions. Hence, by changing the Ag content in CuO nanoparticles films, the aggregation and particles growth can be controlled [20]. Energy-dispersive X-ray spectroscopy (EDS) was employed for the cross-verification of surface analysis of Ag–CuO nanoparticles thin films. Figure 2 shows the detected elements at each thin film sample.

#### 3.3 Optical properties

The optical response of the Ag–CuO nanoparticles films was examined through transmittance spectra. The transmittance spectra were measured in the wavelength range 300–2400 nm as presented in figure 3. The maximum transmittance of the pure CuO nanoparticles film was noticed to be about 75%

**Table 2.** XRD structural parameters of Ag–CuO nanoparticles thin films.

Material	$2\theta$ (°)	(hkl)	Crystallite size (nm)	Dislocation density	Lattice strain	Texture coefficient
Pure CuO	32.14	(110)	11.17	8.01E–03	3.10E–03	0.68
	35.46	(002)	11.00	8.26E–03	3.15E–03	1.71
	38.39	(111)	8.78	1.30E–02	3.95E–03	0.74
	61.67	(–113)	9.47	1.12E–02	3.66E–03	0.62
	65.17	(022)	5.30	3.57E–02	6.55E–03	1.03
	67.02	(–311)	5.14	3.78E–02	6.74E–03	1.69
	74.68	(004)	10.09	9.83E–03	3.44E–03	0.50
Mean value			<b>8.70</b>	<b>1.77E–02</b>	<b>4.37E–03</b>	
2.5 wt% Ag	32.04	(110)	12.55	6.35E–03	2.76E–03	0.62
	35.34	(002)	10.00	1.00E–02	3.47E–03	1.46
	38.03	(111)	7.43	1.81E–02	4.66E–03	0.99
	51.14	(112)	3.01	1.10E–01	1.15E–02	0.87
	61.49	(–113)	4.59	4.74E–02	7.55E–03	1.78
	66.70	(–311)	6.97	2.06E–02	4.97E–03	0.68
	74.44	(004)	9.29	1.16E–02	3.73E–03	0.60
Mean value			<b>7.69</b>	<b>3.20E–02</b>	<b>5.52E–03</b>	
5.4 wt% Ag	31.78	(110)	9.27	1.16E–02	3.74E–03	0.73
	35.16	(002)	12.33	6.58E–03	2.81E–03	0.96
	37.71	(111)	8.29	1.45E–02	4.18E–03	0.63
	50.73	(112)	3.57	7.86E–02	9.72E–03	0.88
	61.45	(–113)	2.01	2.49E–01	1.73E–02	2.15
	66.41	(–311)	5.81	2.96E–02	5.96E–03	0.64
Mean value			<b>6.88</b>	<b>6.51E–02</b>	<b>7.29E–03</b>	

while Ag–CuO nanoparticles films transmittance spectra were decreased.

A swing in the transmittance spectra of incorporated thin films was observed as compared with pure CuO thin film. Further, it also revealed the change in the absorption edge of the incorporated thin films. This change in the absorption edge is attributed to surface plasma resonance (SPR) as reported by Chervinskii *et al* [21]. This SPR is highly desirable for the harvesting of light photons into the material, which increases the conduction of electrons; as a result, it can enhance the photocatalytic efficiency of the subjected material [22].

The following equation is applied to calculate the absorption coefficient  $\alpha$  for Ag–CuO nanoparticles thin films [23]:

$$\alpha = \ln(1/T)/d, \quad (5)$$

where  $d$  is the thickness of the film and  $T$  is the film transmittance. The well-known Tauc's equation is used to determine the optical band gap of deposited films [24]:

$$(\alpha h\nu) = A(h\nu - E_g)^n, \quad (6)$$

where  $h\nu$  is the energy of the incident photon,  $\alpha$  is the absorption coefficient,  $A$  is a constant and  $n = 0.5$  for direct band gap, while in the case of indirect band gap  $n = 2$ . In our case, we have used  $n = 2$  because it gives an excellent linear fit curve in the band-edge region. The band gaps of pure CuO and

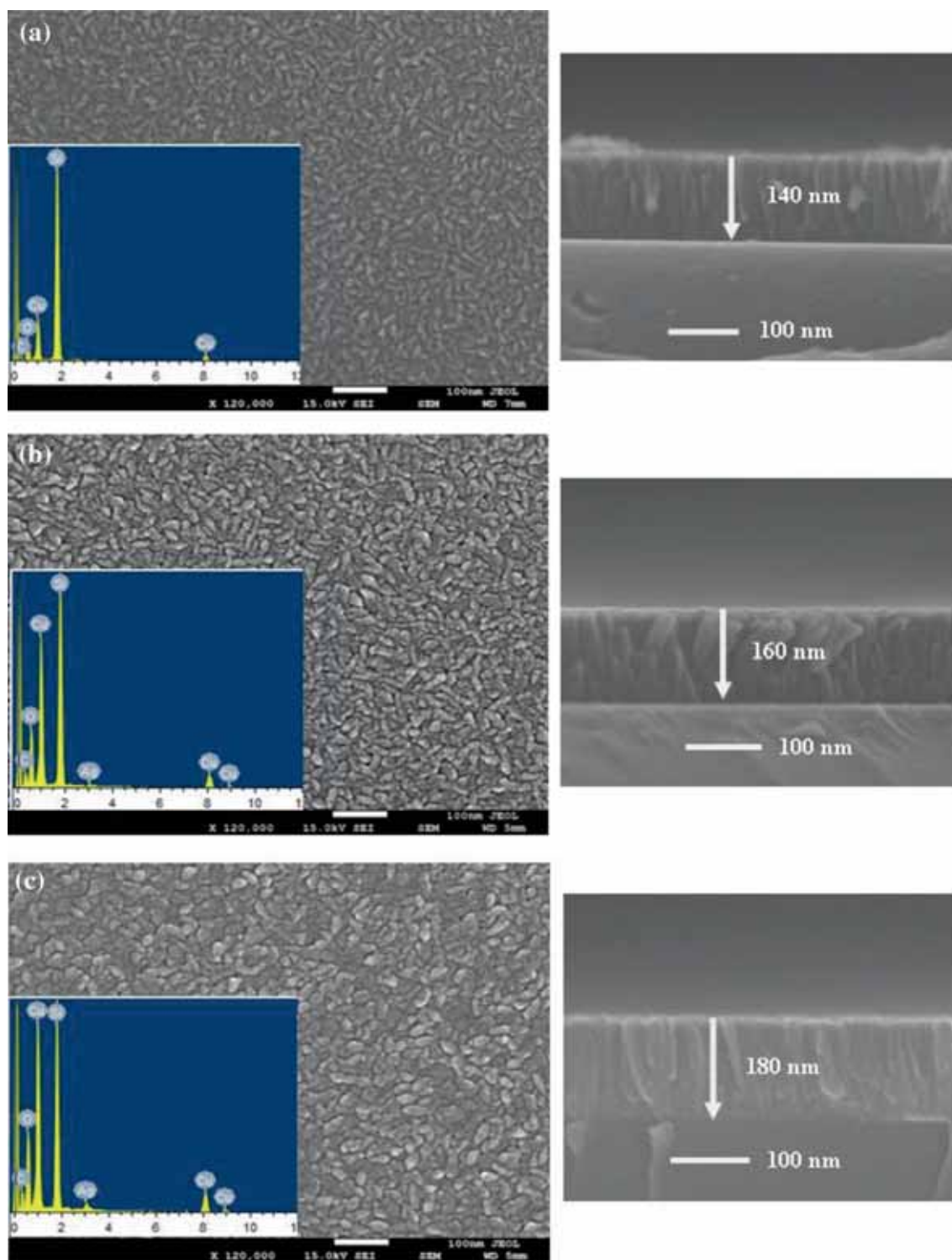
Ag–CuO films are given in figure 4. The band gap was found to decrease from 1.84 to 1.61 eV on increasing Ag content.

### 3.4 Surface chemical state analysis

Surface composition and chemical state of the deposited films were determined using XPS analysis. Figure 5 shows the survey scan of the Ag–CuO nanoparticles thin films. The detected elements through survey scan of each sample are tabulated in table 3.

The high-resolution spectrum of Cu 2p<sub>3/2</sub> is recorded for Ag–CuO nanoparticles thin films for the possible change in the chemical state. Figure 6 presents the chemical state analysis Cu 2p<sub>3/2</sub> of the CuO and Ag–CuO nanoparticles films. Peaks have been observed at ~933.5, ~935.13, ~941.3, 943.5 and 943.3 eV. The main peak at ~933.5 eV results from the final configuration of the CuO (d<sup>10</sup>) while the border shake-up satellite peak from 941 to 943.5 eV is related to the d<sup>9</sup> configuration. With the Ag nanoparticles the shifting of shake-up satellite to higher binding energy has been seen. This shifting revealed that there is the availability of excess Cu<sup>+</sup>(d<sup>8</sup>) [25]. This d<sup>8</sup> available in excess has more attraction for Ag metal during the sputtering process. It can be seen from our XRD data that Ag content affects the diffraction planes, i.e., (–111) and (111), moving it to lower diffraction angle. So, the chemical state analysis of Cu 2p<sub>3/2</sub> is in good agreement with our XRD observation.

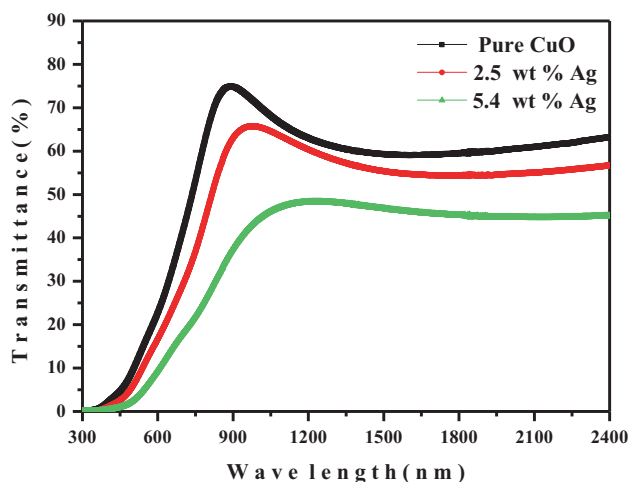




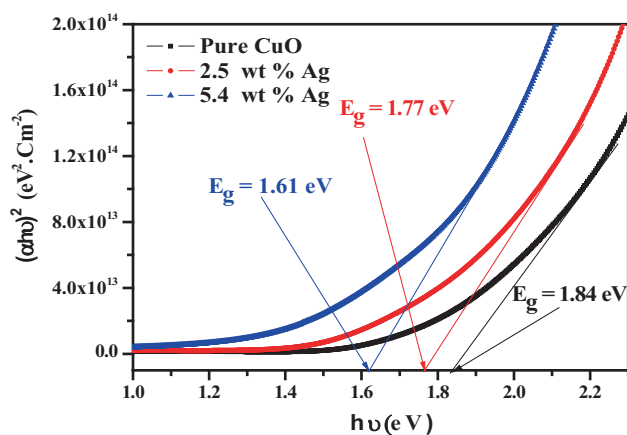
**Figure 2.** SEM surface images, cross-section and EDS spectrum of Ag–CuO nanoparticles thin films: (a) pure CuO, (b) 2.5 wt% Ag and (c) 5.4 wt% Ag.

Figure 7 shows the high-resolution spectra of O1s for Ag–CuO nanoparticles films. The peaks were observed at about 529.5 and 531.5 eV. The peak at 529.5 eV is attributed

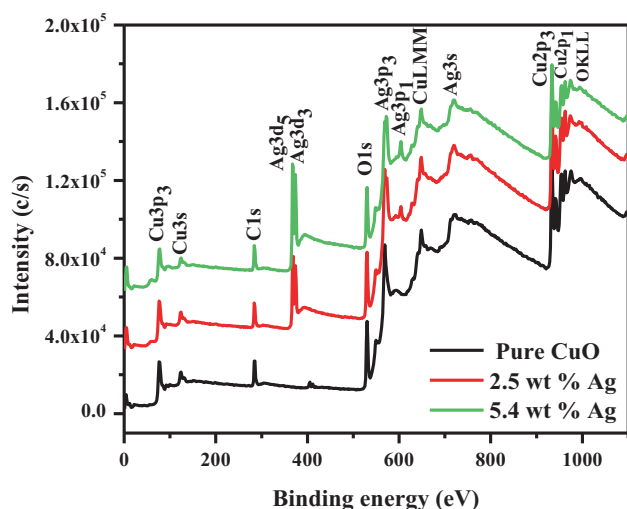
to CuO and the peak at 531.5 eV is related to the surface-chemisorbed  $\text{O}^-$  species [26]. It is seen that with increasing Ag content, the area (%) of higher binding energy, i.e.,



**Figure 3.** Transmittance spectra of Ag–CuO nanoparticles thin films.



**Figure 4.** Variation of optical band gap for Ag–CuO nanoparticles thin films.



**Figure 5.** XPS survey scan of Ag–CuO nanoparticles thin films.

**Table 3.** XPS survey scan of Ag–CuO nanoparticles thin films.

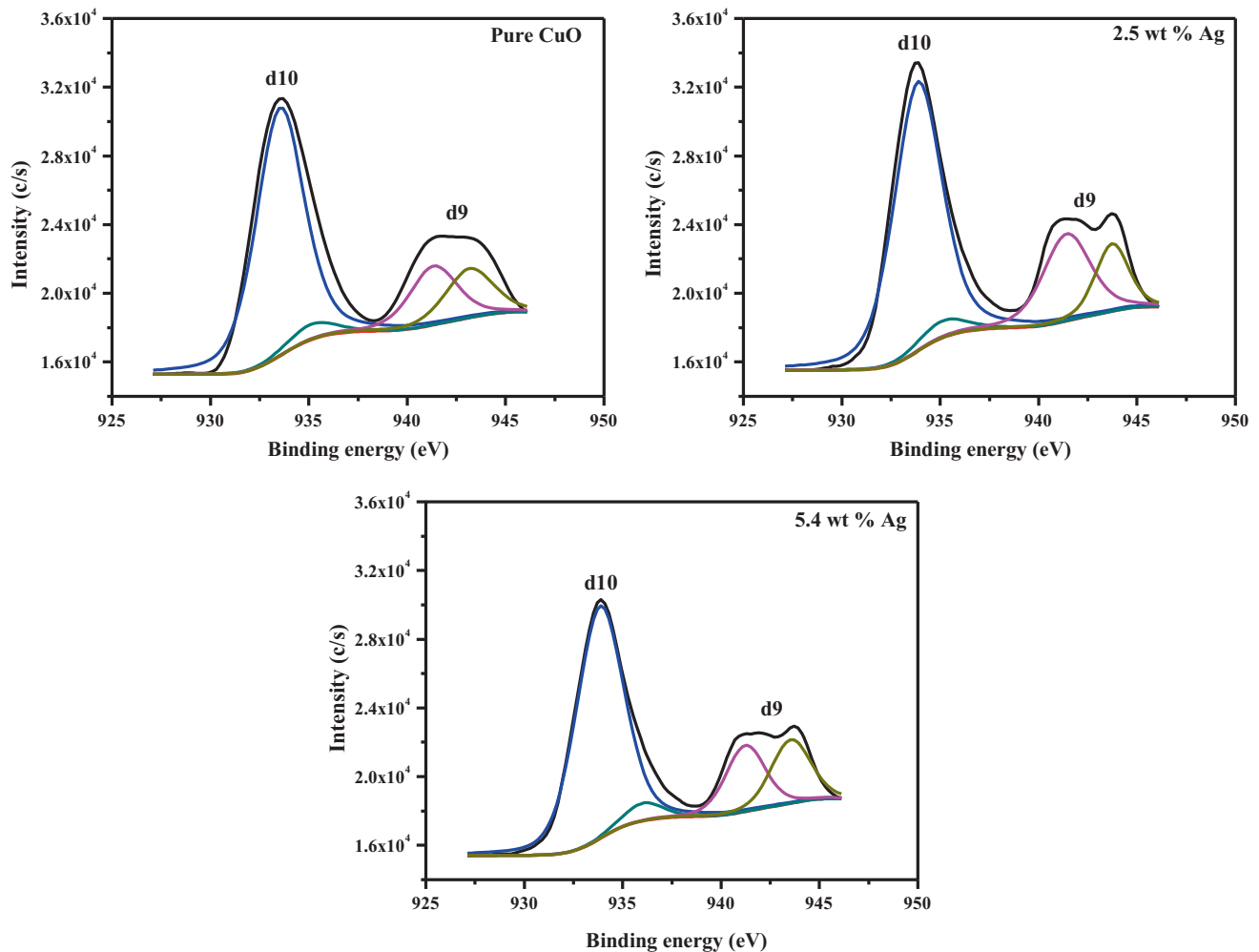
Sample details	C1s	O1s	Cu2p <sub>3</sub>	Ag3p <sub>3</sub>	Ag3d
Pure CuO	10.1	54.8	35.1	0	0
2.5 wt% Ag	9.8	42.3	24.5	20.9	2.5
5.4 wt% Ag	10.2	40.5	23.4	20.5	5.4

531.5 eV, increases. The increase in chemisorbed  $O^-$  species attributed to Ag content and maximum was observed at 5.4% Ag, therefore, the maximum photo-catalytic response was found at 5.4 wt% Ag. Zhang *et al* [27] and Zhao *et al* [28] documented the enhancement in photo-catalytic activity of the material with increasing surface defects oxygen  $O^-$  species. Hence, our finding through O1s analysis also agrees with reported data, where they have correlated the photo-catalytic activity of the material with the surface oxygen.

The high-resolution Ag3d spectra in Ag–CuO films are analysed as presented in figure 8. The peaks were found at about 368.1 and 374.1 eV; these observed peaks correspond to  $Ag3d_{5/2}$  and  $Ag3d_{3/2}$ , respectively. Furthermore, the separation between  $Ag3d_{5/2}$  and  $Ag3d_{3/2}$  was noticed to be 6.0 eV, which indicates the presence of silver as zero-valent  $Ag^0$  [29].  $Ag^0$  is not sensitive to oxygen [30]. Hence, based upon the XPS and XRD findings, it may be concluded that the silver has been perfectly incorporated to CuO nanoparticles, which leads to the increase of  $O^-$  species on the thin films surfaces, which are responsible for enhancing the photo-catalytic activity of the Ag-containing films.

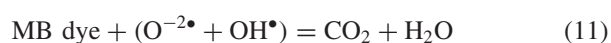
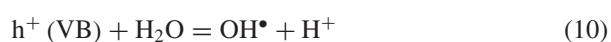
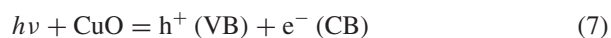
### 3.5 Photo-catalytic behaviour

**3.5a Effect of Ag content:** The photo-catalytic activity of CuO films with different Ag contents was evaluated by degrading 10 ppm solution of MB dye of pH 6.5 for 4 h of sun exposure; the results are shown in figure 9. The rates of degradation were 65, 83 and 100% with respect to Ag content at 0, 2.5 and 5.4 wt%, respectively. As mentioned previously, the photo-degradation of organic dyes on the surface of semiconductor catalysts depends on the photo-generated electron–hole pairs. For enhancing the photo-catalytic properties of a semiconductor catalyst, more light must be harvested by the semiconductor and the photo-generated electrons and holes should be separated for increasing its lifetime. Hence, Ag content plays a vital role in enhancing the photo-catalytic properties of CuO; deposited Ag nanoparticles have the SPR property, which has a direct effect in increasing the electron–hole pairs lifetime and also in enhancing light harvesting. When photons of sunlight fall on the surface of CuO thin film, some electrons are excited from VB (equation 7) to CB, creating holes in the VB; the excited electron in CB is trapped by the Ag nanoparticles (equation 8) on the surface of CuO (figure 10); thus, the recombination process is



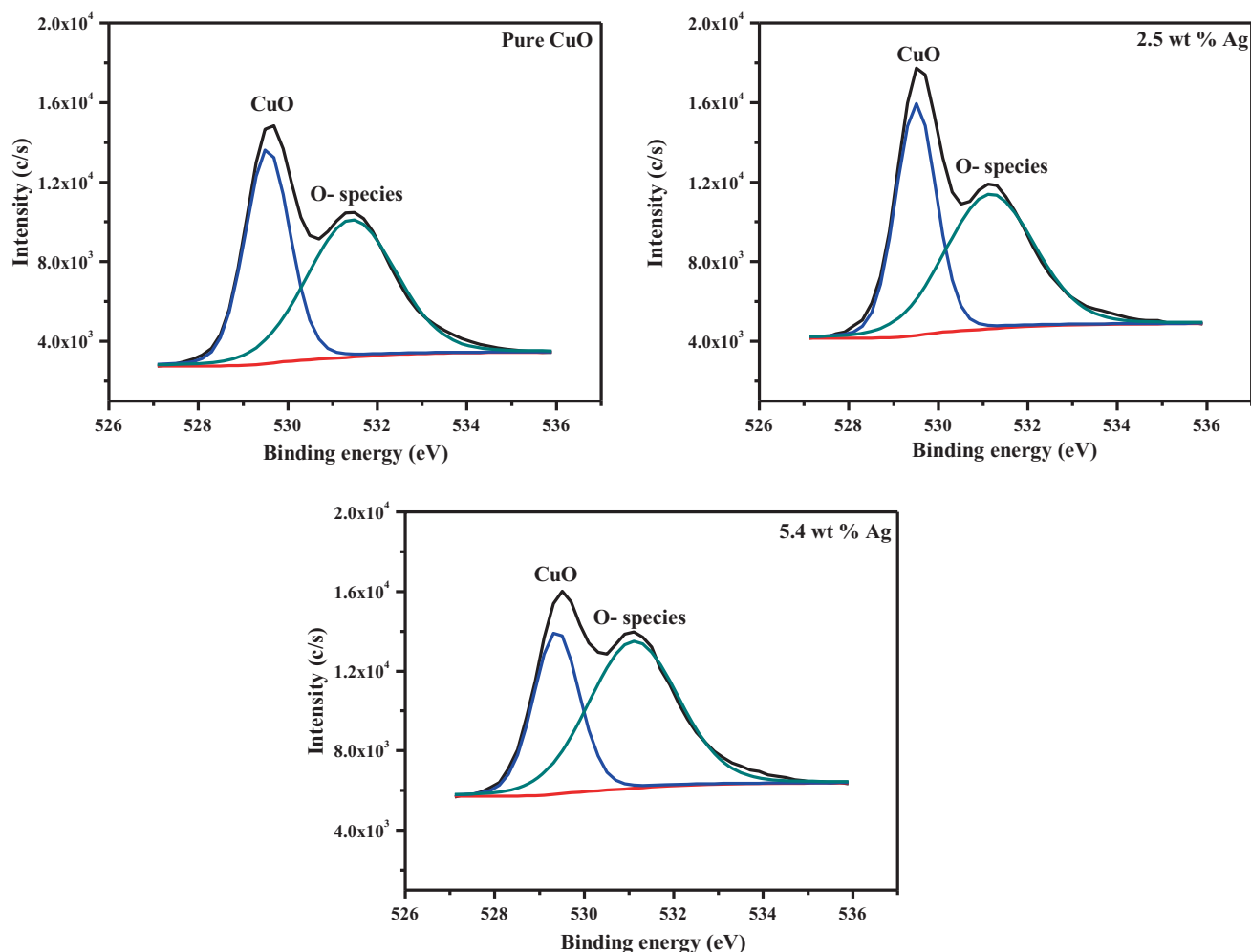
**Figure 6.** Chemical state of Cu 2p<sub>3/2</sub> spectra of Ag–CuO nanoparticles thin films.

delayed. After this, the electron trapped by Ag nanoparticles can interact with the dissolved O<sub>2</sub>, forming O<sup>−2•</sup> (equation 9) and the created holes can oxidize the adsorbed H<sub>2</sub>O molecules, forming the active species OH<sup>•</sup> (equation 10), responsible for attacking the MB molecule and starting the degradation process (equation 11). Moreover, due to the SPR of Ag nanoparticles, it increases the light scattering inside CuO film; thus, the light passage will be prolonged inside the photo-catalyst, leading to increasing of the electron–hole pairs generation. Hence, increasing Ag content results in enhancing the photo-catalytic degradation properties of CuO films [15].



where OH represents hydroxyl radicals while O<sup>−2•</sup> represents the superoxide anion radicals.

**3.5b Effect of MB initial concentration:** For optimizing the photo-degradation condition, different concentrations of MB dye were used in the degradation experiments. Ag–CuO nanoparticles film with 5.4 wt% Ag was selected for these experiments, while the pH was adjusted at 6.5. Direct sunlight exposure duration was 4 h in all experiments. Three concentrations of MB were selected (10, 20 and 30 ppm). MB degradation percentage was noticed to be 100, 73 and 55% with respect to 10, 20 and 30 ppm, respectively (see figure 11). The decrease in degradation percentages with increasing MB concentration can be explained by the fact that the surface of the deposited film has a fixed number of active sites while the number of dye molecules increased on increasing the dye concentration. However, from another point of view, the amount of MB dye degraded was increased as the initial dye concentration increases. This is because with increasing number of dye molecules in solution, there



**Figure 7.** Chemical state of O1s spectra of Ag–CuO nanoparticles thin films.

will be a driving force from the MB molecules on the active sites of CuO film catalyst; thus, the total number of MB molecules attacked by the formed active species will be high.

**3.5c Effect of initial pH:** For identifying the ideal condition at which Ag–CuO films can be used for the photo-degradation of MB, more investigation has been done. The MB solution was initially adjusted and its effect was evaluated. The initial pH of MB solutions was 5, 6.5 and 9 and the MB concentration was 10 ppm. Ag–CuO sample with 5.4 wt% of Ag was used, and sunlight exposure duration was fixed at 4 h. Figure 12 presents the initial pH effect on the photo-catalytic degradation activity. It is clear that the degradation of MB dye increases as the initial pH increases. At the highest pH (i.e., 9 in our case) the time of degradation was reduced to 3 h instead of 4 h (see figure 12).

The alkaline medium induces a negative charge on the film surface, which helps igniting the dyes of cationic nature, and MB has a cationic nature; hence, on increasing the pH of

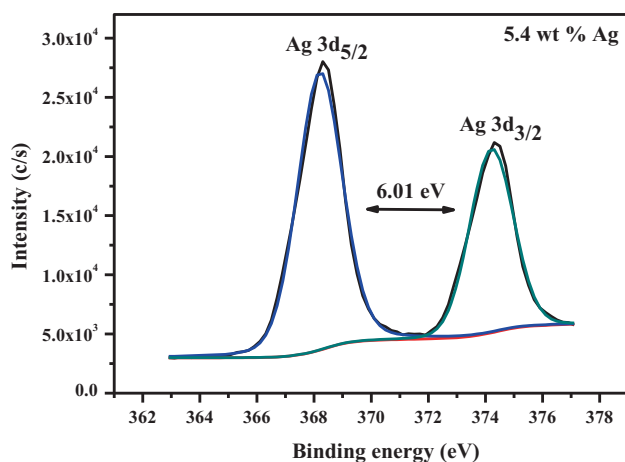
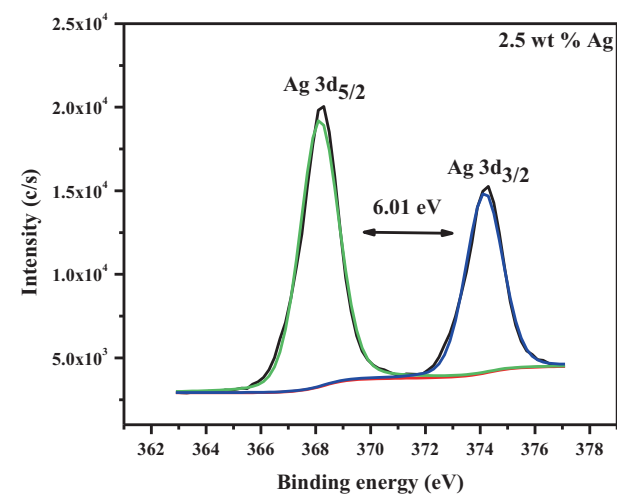
the solution more negative charge accumulates on the thin films surface, which results in enhancement of photo-catalytic behaviour. On the contrary, on decreasing the pH value of the solution, positive charges accumulate over the thin films, which hinder the attachment of the cationic MB dye, resulting in decrease of photo-catalytic activity [31,32].

The kinetics of the decolourization reaction was studied using the Langmuir–Hinshelwood kinetics model as presented in figure 13a–c [33]:

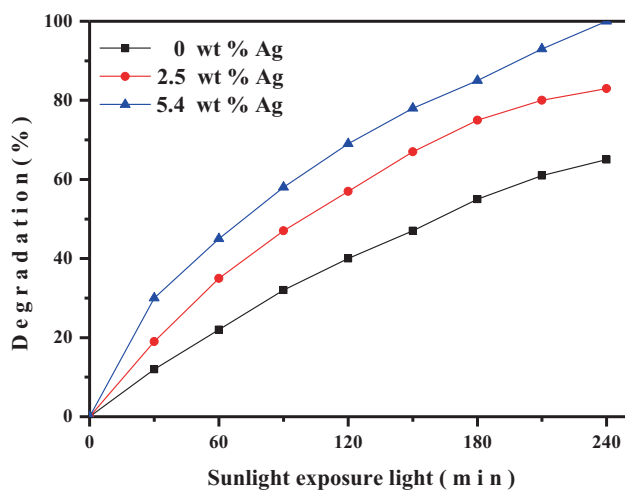
$$\ln \left( \frac{C_0}{C_t} \right) = k_{app} t, \quad (12)$$

where  $C_0$  and  $C_t$  are the MB concentration ( $\text{mg l}^{-1}$ ) before degradation and after time  $t$ , respectively, whereas  $k_{app}$  represents apparent rate constant ( $\text{min}^{-1}$ ). Table 4 shows that the rate of degradation depends on the reaction conditions such as Ag wt%, MB concentration and initial MB solution pH. It is clear from the results that MB dye photo-degradation process obeys a pseudo-first-order reaction kinetics.

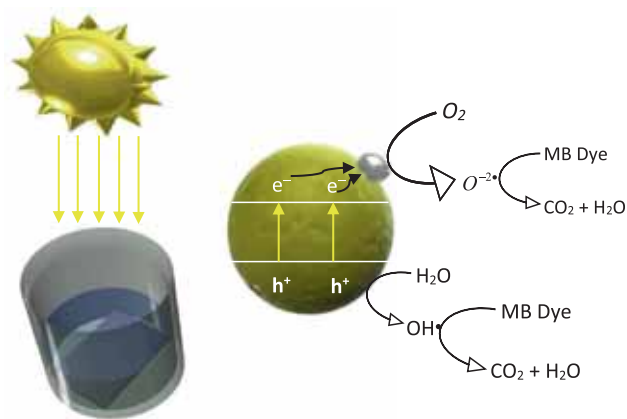




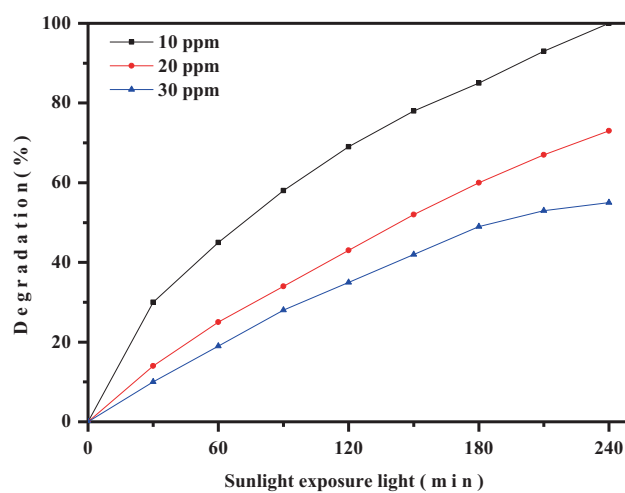
**Figure 8.** Chemical state of  $\text{Ag}3d_{5/2}$  and  $\text{Ag}3d_{3/2}$  spectra of Ag–CuO nanoparticles thin films.



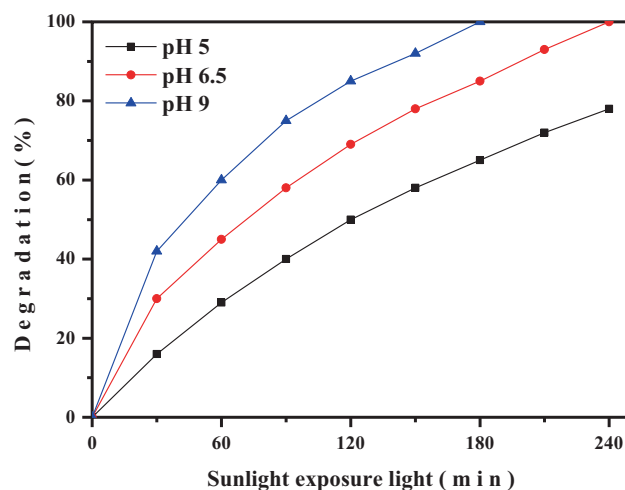
**Figure 9.** Effect of Ag content on photo-catalytic degradation of MB (MB concentration = 10 ppm, pH = 6.5 and sunlight exposure duration = 4 h).



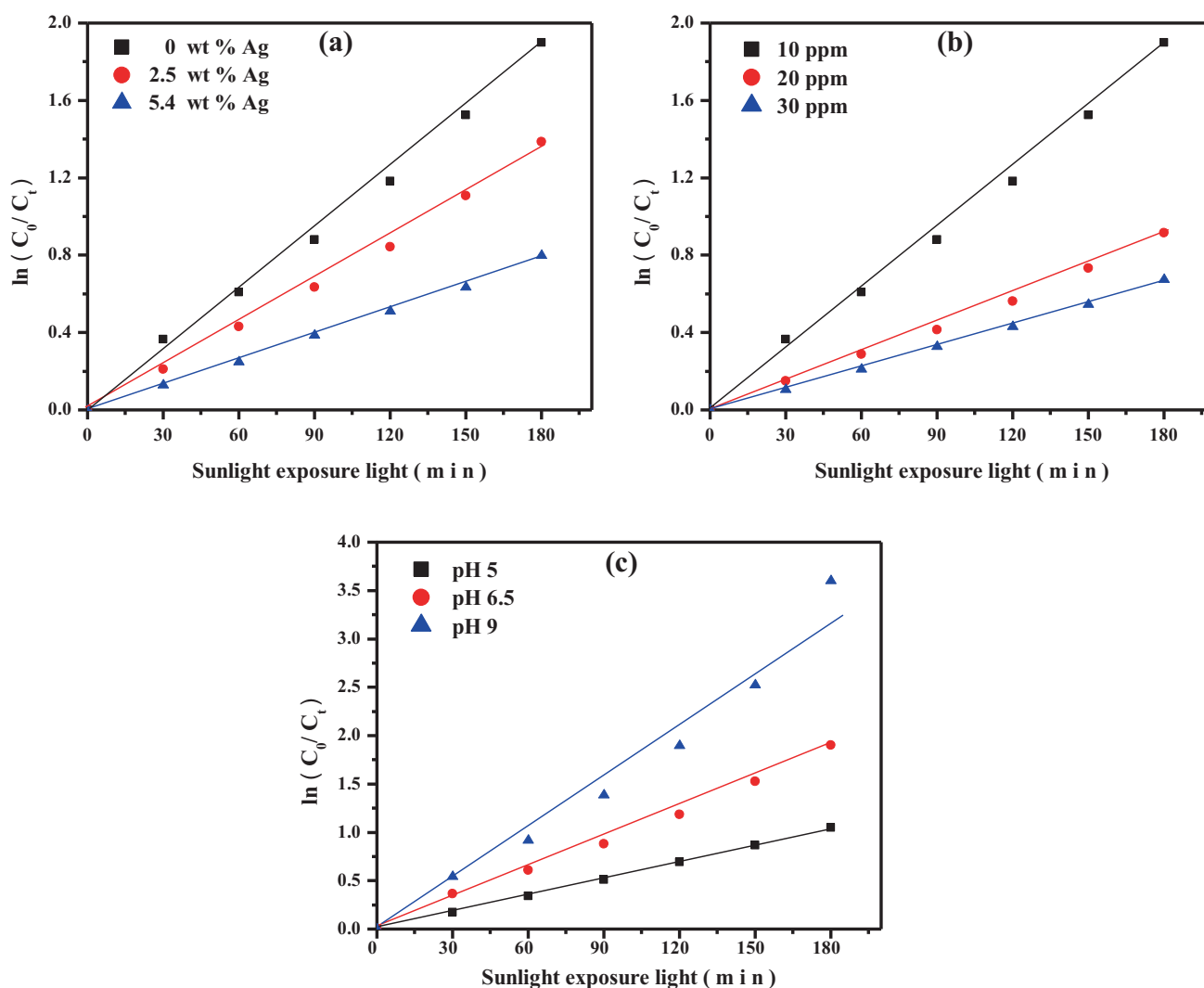
**Figure 10.** Mechanism of degradation of MB by Ag–CuO nanoparticles thin films.



**Figure 11.** Effect of MB concentration on photo-catalytic degradation of MB (5.4 wt % Ag, pH = 6.5 and sunlight exposure duration = 4 h).



**Figure 12.** Effect of pH on photo-catalytic degradation of MB (5.4 wt % Ag content, MB concentration = 10 ppm and sunlight exposure duration = 4 h).



**Figure 13.** The pseudo-first-order rate constant of MB dye at different (a) Ag wt%, (b) MB concentration and (c) pH.

**Table 4.** The apparent rate constant ( $K$ ) and correlation factor ( $R^2$ ) of the Methylene blue dye decomposition reaction.

Ag conc. (wt%)	$k_{app}$ ( $\text{min}^{-1}$ )	$R^2$	MB conc.	$k_{app}$ ( $\text{min}^{-1}$ )	$R^2$	pH	$k_{app}$ ( $\text{min}^{-1}$ )	$R^2$
0	0.0043	0.998	10	0.01023	0.995	5	0.0058	0.999
2.5	0.0075	0.996	20	0.0049	0.996	6.5	0.01023	0.995
5.4	0.01023	0.995	30	0.00371	0.998	9	0.0187	0.964

#### 4. Conclusion

In summary, a physical deposition method (DC/RF sputtering technique) has been used for preparing thin films of Ag–CuO nanoparticles with different wt% of Ag on glass substrates. XPS surface analysis revealed that Ag nanoparticle was deposited in its metallic form.  $\text{Ag}^0$  plays a significant role in increasing the surface defects oxygen  $\text{O}^-$  species in the Ag–CuO films, which results in the enhanced photo-catalytic process. The grain size of the incorporated thin films was

decreased with increasing  $\text{Ag}^0$  percentage. The reduction of band gap was noticed from 1.84 to 1.61 eV with the rise in  $\text{Ag}^0$  percentage. The chemical state analysis of O1s reveals that the surface-chemisorbed  $\text{O}^-$  species increase with  $\text{Ag}^0$  content. The incorporated amount of Ag has positive effect on enhancing the photo-catalytic activity of CuO in sunlight. The plasmonic nature of Ag helps in increasing the lifetime of the photo-generated electron–hole pairs and also helps in harvesting more light photons; thus the catalytic degradation activity of CuO was increased with increasing Ag content.

The degradation condition of MB using Ag–CuO films in sunlight was optimized by studying the effects of different factors on degradation efficiency. The combination of higher pH value with the lower concentration of dye is the best condition for degrading MB on Ag–CuO films. This research could provide a platform to study the Ag–metal oxide nanoparticles thin films for degradation of organic dyes in sunlight.

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