A study on Co doped SnO$_2$ loaded corn cob activated carbon for the photocatalytic degradation of methylene blue dye

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Research Article

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Abstract

SnO$_2$ with different Co$^{2+}$ doping concentrations (0.050, 0.075 and 0.10 M), and Co (0.075 M): SnO$_2$/corn cob activated carbon (Co: SnO$_2$/CCAC) were prepared, and are labelled CS1, CS2, CS3 and CS2/CCAC respectively. The CS2/CCAC showed that the particle size is reduced (16.29 nm) with Co$^{2+}$ doping and CCAC loading. Moreover, CS2/CCAC indicate that the decreased PL intensity and its lower value (2.156 $\Omega$) of impedance from EIS results and increased separation of the photogenerated e$^-$/h$^+$ pairs. Thus, the result showed that CS2/CCAC possesses improved photocatalytic efficiency (95.38 %) as compared to other samples. The photocatalytic mechanism of CS2/CCAC also is discussed.

1. Introduction

In recent years, organic and inorganic contamination due to population and industrial growth has been increased. Among these, organic contamination is a critical environmental problem in the world one. They are, organic pollutions occur due to more factories such as textiles, printing, rubber and etc [1]. To find a solution to this problem, the use of photocatalytic and adsorption process have recently are used [2, 3]. They are, semiconductor metal oxide have drawn much have been focus to the organic dye using UV or sunlight irradiation. The semiconductor materials in particular CuO [4], ZnS [5, 6], TiO$_2$ [7], ZnO [8], Fe$_2$O$_3$ [9], WO$_3$ [10], V$_2$O$_5$ [11], SnO$_2$ [12] etc., have suffered used as a photocatalyst for the removal of organic contamination. Among these, SnO$_2$ is the most promising n-type semiconductor with a wide band gap (3.6 eV), and its particular properties is magnetic, optical, electrical, and photocatalytic [13, 14]. Nowadays, research has been focused on the development of photocatalytic activities of SnO$_2$. It improves the photocatalytic efficiency of SnO$_2$, with metal [15] and non-metal [16]. They are, metal ions doped such as Mn, Zn, Ni, and Cu is also able to behave as an electron trapping which improves the SnO$_2$ photocatalytic activity due to the reducing of the e$^-$/h$^+$ recombination rate [17–21]. Finally, improved the photocatalytic efficiency of Co$^{2+}$ doping SnO$_2$ are also various researchers are reported. Toloman et al., [22] have reported that the photocatalytic activity of SnO$_2$ was enhanced due to cobalt doping and they observed the fast trapping of photogenerated electrons by the Co dopants. Chandran et al., [23] synthesized SnO$_2$ with different concentration of Co$^{2+}$ they observed a highest photodegradation of Co/SnO$_2$. Moreover, Mani et al., [24] prepared SnO$_2$ shows the band gap energy is reduced with the co-doping and they observed a highest photodegradation. Among these, non-metal is activated carbon (AC) is chosen. So, AC is a high surface area and large adsorption capacity [25]. They are SnO$_2$ loaded AC is supported. Furthermore, SnO$_2$/AC has been improved the adsorption and photocatalysts in the removal of organic dye [26]. In this work, pure SnO$_2$, CS1, CS2, CS3 and CS2/CCAC was produced and then, the photocatalytic activity of the CS2/CCAC was evaluated via the degradation of MB under the sunlight irradiation.

2. Experiment
2.1. Synthesis of Co doped SnO$_2$/CCAC

Co: SnO$_2$/CCAC [16] was prepared as follows, firstly, SnCl$_2$ H$_2$O (0.5 M) was added to 50 mL and stirred for 10 min. Secondly, (0.050 M) CH$_3$ COO)$_2$ Co (NO$_3$)$_2$ 6H$_2$O solution in 20 mL of DI was added to the mixture and solution was stirred for 30 min. Thirdly, (0.75 M) C$_2$H$_2$O$_4$ 2H$_2$O solution in 50 mL of DI was added drop wise under stirring for 60 min. Similarly, in the preparation, Co: SnO$_2$/CCAC, a 0.5 g of CCAC was added to an above solution was stirred for 4 h. The prepared solution was filtered, ethanol washed, and then dried at 110 °C for 2 h. The dried sample was then heated at 400 °C for 2 h to form the Co: SnO$_2$/CCAC. The same preparation technique was implemented for all concentrations of cobalt (0.075, and 0.1 M) and pure SnO$_2$. The products materials were indexed as pure SnO$_2$, CS1, CS2, CS3, and CS2/CCAC, respectively.

2.4. Characterization

The XRD patterns of the samples were recorded by X’PERT-PRO diffractometer with a Cu Kα (1.5406 Å) radiation. The binding-state of the CS2/CCAC were characterized with X-ray photoelectron spectroscopy (XPS) (HP 5950A, Hewlett-Packard firm using monochromatic AlK$_{α1,2}$). The photoluminescence (PL) emission spectra were indexed (Jobin Yvon, FLUOROLOG-FL3-11). The surface morphologies of the pure SnO$_2$, CS2 and CS2/CCAC were analyzed by FE-SEM (CARL ZEISS) with Energy-dispersive X-ray spectroscopy (Bruker). An electrochemical workstation (CHI 660C) was used for measuring EIS at an open circuit potential with (0.5 M Na$_2$SO$_4$) as the electrolyte solution. The pure SnO$_2$, CS2 and CS2/CCAC, Ag/AgCl and pt-wire were used as the working, reference, and counter electrodes, respectively.

2.5. Photocatalytic experiment

The photocatalytic degradation of MB using pure SnO$_2$, CS2 and CS2/CCAC was carried out. In the photocatalytic test, 0.20 g/L catalyst under stirring was added 100 mL of MB dye solution (60 mg/L) by under adsorption dark process for 1 h. Moreover, sunlight irradiation time (solar intensity 1250 x 100 Lu ± 100) and keeping dye solutions was immediately centrifuge to remove catalyst particles. After centrifuging for every 15 min, the absorption of the MB and the supernatant solution was measured by absorption spectrophotometer (UV-1800). Then, the photodegradation of the MB was calculated as [27].

3. Results And Discussion

3.1. XRD analysis

The XRD patterns of synthesized samples are shown in Fig. 1. It was clearly seen that all the diffraction peaks can be ascribed to the rutile tetragonal structure of pure SnO$_2$ phase (JCPDS No. 88–0287) [28, 29]. Further no traces of other phases were observed throughout the whole range of cobalt and CCAC contents considered. However, a peak at 2 theta approximately 26.51° (110) in the XRD pattern of CS2/CCAC, indicates all the intensity reduced peaks show that the decrease upon loading CCAC. XRD
pattern (Fig. 1b) for 2 theta range is 25–35°, it can be seen that (110) and (101) in the peaks at approximately 26.51° and 33.71° has slightly shifted all the doping and loading than the pure SnO2. Here, the ionic radius of Co2+ (0.58 Å) is smaller than that of Sn4+ (0.71 Å) and with the smaller amount of Co concentration used for doping [30]. Moreover, CS2/CCAC shows all the diffraction peaks indicate reduced compared to the other samples. The crystalline sizes of the pure SnO2, CS1, CS2, CS3, and CS2/CCAC were calculated by using Scherrer's equation [31]. The average crystalline size of pure SnO2, CS1, CS2, CS3, and CS2/CCAC is found to be 26.40, 24.80, 22.03, 23.41 and 18.76 nm respectively. This result suggests that the size growth is reduced due to the doping of cobalt and loading of CCAC.

3.2. XPS analysis

Surface charge states of elements show in the CS2/CCAC were analyzed using the XPS technique (Fig. 2a). On the other hand, high resolution XPS spectrums for Sn 3d, Co 2p, C 1 s and O 1 s of CS2/CCAC were observed. The peak around BE (Fig. 2b) of 486.78 and 496.24 eV represented Sn 3d5/2 and Sn 3d3/2, respectively, which confirms that the Sn ions possess intrinsic/native oxidation state of + 4 [32]. The peak around BE (Fig. 2c) of 780.15 and 786.24 eV were respectively corresponding to Co 2p3/2 and 2p1/2, which may be attributed to Co2+ ions [33]. The C 1 s BE (Fig. 2d) peak of CS2/CCAC was deconvoluted into three peaks at 284.18, 286.45 and 288.89 eV represented C-C, C-OH and C-O/C-O-C bonds respectively [16]. The O 1 s (Fig. 2e) BE broad peaks of CS2/CCAC revealed a single symmetrical peak at 531.28 eV which corresponds to the lattice oxygen of SnO2.

3.3. Photoluminance analysis

The PL emission spectra of pure SnO2, CS1, CS2, CS3, and CS2/CCAC were displayed in Fig. 3. It can be observed that, pure SnO2 exhibit the recombination emission peak at 399 nm. Moreover, the PL spectra intensity decreased for CS2/CCAC with respect to pure SnO2. The PL spectra intensity decreased for CS2/CCAC with respect to pure SnO2. It observed that the emission spectra exhibited a gradually decrease the UV and visible region upon cobalt doping and CCAC loading. Furthermore, cobalt doping SnO2/CCAC process, the excited e−/h+ is trapped by oxygen vacancies with the addition of Co2+ ions. Moreover, the excited e− can migrate from the VB to the new energy levels introduced nearer to the CB by cobalt doping, which may be due to the reduction of PL intensity. Finally, CS2/CCAC improves photocatalytic activity due to the lower e−/h+ recombination rate [34].

3.4. FE-SEM with EDAX analyses

The FE-SEM micrographs of the synthesized pure SnO2, CS2 and CS2/CCAC are shown in Fig. 4a-d along with their EDAX analysis. Figure 4a shows the spherical morphology with a size range of approximately 20–40 nm. Figure 4b shows the spherically shaped and less agglomerate with a size range of approximately 15–35 nm. Figure 4c shows the CS2 loaded on CCAC, further spherically shaped and agglomerate with a size range of approximately 10–25 nm. The chemical compositions of CS2/CCAC
(Fig. 4d) are analyzed by using EDAX. The presence of elements C, O, Sn, and Co was observed in CS2/CCAC indicated that CS2 was successfully loaded onto the CCAC.

### 3.5. Electrochemical impedance spectroscopy

The EIS measurements on synthesized samples are shown as Nyquist plots (Fig. 5). Meanwhile, CS2/CCAC show smaller radius in the EIS Nyquist plots than other samples, and especially, the resistance value is 3.328, 2.836 and 2.156 kΩ for the pure SnO$_2$, CS2 and CS2/CCAC. In addition, PL intensity of CS2/CCAC at 399 nm was much lower than that of pure SnO$_2$, also suggesting a faster charge separation (Fig. 3). Together with the EIS measurement, it was inferred that strong interfacial interaction between CCAC and CS2 in the accelerated the electron-hole separation and then benefit enhancement of photocatalytic activities of the as-prepared CS2 and pure SnO$_2$.

### 3.6. Photodegradation of MB dye

The UV–Vis absorption spectra of the MB dye under sunlight irradiation in the presence of pure SnO$_2$, CS2 and CS2/CCAC are shown in Fig. 6a-c. The intensity of the absorbance decreases with the increase of irradiation time. It can be observed that the absorption peaks (664 nm) is progressively reduced as the irradiation time (0-120 min) increase, indicative of the removal of MB dye solution. As observed in figure, CS2/CCAC removal of MB more rapidly than other sample.

Figure 7 shows the effects of contact time and % degradation of MB in the efficiency of the pure SnO$_2$, CS2 and CS2/CCAC. The removal efficiencies of MB at 120 min were 71.92, 83.07 and 95.38 % using pure SnO$_2$, CS2 and CS2/CCAC respectively. Table 1 show that the CS2/CCAC has a higher degradation percentage compared to the pure SnO$_2$ and CS2.

The degradation rates of the pure SnO$_2$, CS2 and CS2/CCAC were calculated by plotting $C_t/C_0$ versus irradiation time is shown in Fig. 8. As compared to pure and CS2 sample, the MB was degraded about 7.69% and 23.07% under the without sunlight, and MB was promote reduced under the photocatalytic process. Similarly, then Co$^{2+}$ doped and CCAC loaded, their MB removal efficiency reached 43.11% and 95.38% under the dark adsorption process and photocatalytic process. Finally, the adsorption of CS2/CCAC was improved from CS2, due to the CCAC loading. Herein, the highest degradation rate in the CS2/CCAC could be the creation of huge trapping sites and generation and consequent separation of $e^-/h^+$ pairs. The result is explained in PL and EIS study.

The photocatalytic performance of the pure SnO$_2$, CS2 and CS2/CCAC was calculated by using pseudo-first-order kinetics [35, 36]. Figure 9 shows that the plot of ln ($C_0/C_t$) with respect to irradiation time (min) such that by linear fit of the graph, the slope of the fitted line gives the value of the rate constant (k). They are, k value and the $R^2$ was calculated are given in Table 1. As shown in the table, cobalt doping and CCAC loading have a higher degradation rate (0.023 min$^{-1}$) compared to the pure and doping sample due to the lower crystalline size, lower resistance value, and lower recombination of charge carriers.
The photocatalytic mechanisms of CS2/CCAC are shown in Fig. 10. Firstly, the increase in the photocatalytic performance of the CS2/CCAC compared to SnO$_2$ is due to the effect of the Co$^{2+}$ doping and surface adsorption of the CCAC, but it also prevented the e$^-$/h$^+$ recombination. Secondly, CS2/CCAC under sunlight irradiation, the photogenerated e$^-$ can be transferred either to the CB of SnO$_2$ or to Co$^{2+}$ energy levels localized within the band gap of pure SnO$_2$. Co$^{2+}$ can trap e$^-$/h$^+$ pairs as a result they can increase the e$^-$/h$^+$ lifetime [22]. Another one, e$^-$ in CB can react with surface adsorbed O$_2$ to produce O$_2^-$ (Eqs. 2). Moreover, h$^+$ in VB can react with the surface adsorbed H$_2$O/ OH$^-$ to produce OH as well as attack and oxidize the MB (Eqs. 3,4). This mechanism can be described by the following equations.

$$Co : SnO_2/CCAC + h\nu \rightarrow e^- + h^+ \quad (1)$$  
$$e^- + O_2 \rightarrow O_2^- \quad (2)$$  
$$h^+ + H_2O \rightarrow H^+ + OH^+ \quad (3)$$  
$$h^+ + OH^- \rightarrow OH^- \quad (4)$$  
$$BG + OH^+ \rightarrow \text{degradation product} \quad (5)$$  
$$BG + O_2^- \rightarrow \text{degradation product} \quad (6)$$

Fig. 11 showed the reusability of CS2/CCAC (0.20 g/L) for the photodegradation of MB. The degradation rate of MB keep stable in the first and second, then slightly decreased after 3 cycles. At fourth cycles, the degradation rate of MB decreased at 93.57 %, respectively, due to the loss of photocatalytic activity of the CS2/CCAC. They are, recovered catalyst after each cycle was washed with water and ethanol, and then dried at 100 °C for 1 h and reused for next cycle. Finally, the finding supported that we can re-used CS2/CCAC for several times to reduce the treatment cost of MB.

4. Conclusion

In this study, CS2/CCAC was prepared and exhibited excellent photocatalytic degradation of MB under sunlight. The average crystalline sizes of the sample reduced (18.76 nm) with the doping and loading. Reduction of the emission peak (399 nm) with Co doping and CCAC loading into SnO$_2$ was observed in PL studies and its smaller value (2.156 kΩ) of impedance from EIS measurements revealing the faster transport and enhances separation of the charge carriers. They are CS2/CCAC showed a high removal efficiency of 95.38% compared to other samples. Moreover, Co$^{2+}$ doping, CCAC not only improved the adsorption capacity, but it also prevented the e$^-$/h$^+$ recombination. Thus, CS2/CCAC may be an efficient material for removal of the MB dye solution.

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### Table

**Table 1** Photocatalytic degradation efficiency (%), rate constant ($K_1$) values and regression coefficient ($R^2$) by different prepared samples.

| Samples      | PDE (%) | $K_1$ (min$^{-1}$) | $R^2$  |
|--------------|---------|--------------------|--------|
| Pure SnO$_2$ | 71.92   | 0.011              | 0.984  |
| CS2          | 83.07   | 0.014              | 0.987  |
| CS2/CCAC     | 95.38   | 0.023              | 0.986  |

### Figures
Figure 1

XRD patterns of (a) pure SnO$_2$, CS1, CS2, CS3 and CS2/CCAC, (b) (a) pure SnO$_2$, CS1, CS2, CS3 and CS2/CCAC enlarged view of (110) and (101).
Figure 2

(a) XPS full-survey-scan spectrum, (b) Sn-3d, (c) Co-2d, (d) C1s, and (e) O1s of CS2/CCAC.
Figure 3

PL spectra of pure SnO2, CS1, CS2, CS3 and CS2/CCAC.
Figure 4

FE-SEM images of (a) pure SnO2, (b) CS2 and (c) CS2/CCAC, corresponding EDAX spectra (d).
Figure 5

Nyquist plots of pure SnO$_2$, CS2 and CS2/CCAC photocatalysts in 0.5 M Na$_2$SO$_4$ electrolyte.
Figure 6

UV–Vis absorption spectra of the photodegradation of MB in the performance of (a) pure SnO2, (b) CS2 and (c) CS2/CCAC.
Figure 7

The effects of MB dye % degradation by pure SnO₂, CS₂ and CS₂/CCAC.
Figure 8

Photocatalytic degradation of MB dye using pure SnO$_2$, CS$_2$ and CS$_2$/CCAC.
Figure 9

Kinetic study of photodegradation of MB in the presence of pure SnO$_2$, CS2 and CS2/CCAC.
Schematic illustration of the photocatalytic mechanism of CS2/CCAC under sunlight irradiation.
Figure 11

Recycle efficiency of the CS2/CCAC for MB degradation dye.