Influence of Cd, Mn, and Co addition on the structural and optical properties of TiO$_2$ crystal

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**Abstract.** Synthesis of TiO$_2$-M (M = Cd, Mn, Co) has been done by the sol gel method. Solution of titanium (IV) isopropoxide was hydrolyzed using a solution of glacial acetic acid at a temperature range of 10-15 °C to obtain a sol, subsequently heated to form a white gel. Ion solution Cd (II), Mn (II) and Co (II) each added to the gel TiO$_2$ with Ti:M mole ratio (M= Cd, Mn, Co) = 3:1 (mol/mol). After calcination process at a temperature of 400 °C, we have obtained TiO$_2$ and TiO$_2$-M (Cd, Mn, Co). Characterization of the samples with XRD showed TiO$_2$-M (M = Cd, Mn, Co) produces crystalline of anatase TiO$_2$ phase. SEM-EDX results showed differences in the amount of metal contained within TiO$_2$-M (M= Cd, Mn, Co) that is equal to 8.62% (w/w) Cd; 3.26% (w/w) Mn; 0.721% (w/w) Co. The addition of transition metals ion as impurities as Cd (II), Mn (II), or Co (II) have inhibited the growth of TiO$_2$ crystals. The insertion of metal ions in the TiO$_2$ were also affected the optical properties shown by the energy band gap (E$_g$) shift in order of E$_g$ TiO$_2$ (3.35 eV)$>$TiO$_2$-Cd (3.10 eV)$>$TiO$_2$-Co (3.00 eV)$>$TiO$_2$-Mn (2.5 eV). The electronic structures of TiO$_2$ doped 3d transition metals showed that an electron occupied level energy occurs. Electron from dopand are somewhat delocalized, thus significantly contributing to the formation of the valence band with O p and Ti 3d electrons. Based on a comparison with the absorption data, we show that t$_2g$ state of the dopand plays a significant role in the photoresponse of TiO$_2$ under visible irradiation.

1. **Introduction**

Photocatalytic degradation for waste treatment has been widely practiced. Commonly degradation methods was used as photocatalyst, electrocatalyst and photoelectrocatalyst [1,2,3,4]. Wastewater treatment with filtration, adsorption and biological degradation has also been carried out, but the physical method usually still leaves waste elsewhere [5]. Adsorption process using zeolites and chitosan still produce waste of adsorbent-filled adsorbent [6] so that the effort to convert waste into harmless environmental compounds less optimal.

The photocatalytic process by the TiO$_2$ photocatalyst was performed by exposure a photon source that capable to excite their electrons for the initiation of oxidation and reduction pollutant processes. TiO$_2$ with a high gap value (E$_g$) (~3.2-3.4 eV) requires photon energy in the ultra violet region ($\lambda$<380 nm). Efforts to increase the uptake of photon energy above 380 nm, it can be performed on the TiO$_2$ semiconductor through insertion of transition metal ions into TiO$_2$ structure. The insertion of transition
metal ions to the TiO$_2$ crystal can be carried out by means of hydrogenation, metal doping [7,8,9], and nonmetallic doping [10,11].

The insertion of Cd$^{2+}$ metal ions into the TiO$_2$ structure can decrease the band gap energy [12] and increase photocatalytic activity in visible light [13]. The decreasing of TiO$_2$ band gap by the addition of Co have increased photocatalytic activity on visible light was also reported [14,15] and Mn metals [8,9,16,17]. The effect of the insertion of Fe$^{3+}$ metal ions on TiO$_2$ was capable influence the electronic level caused by the reduction potential of Fe$^{3+}$ lying below the reduction potential of the excited state TiO$_2$ (TiO$_2$(e$^-$)). In this study, we carried out the insertion of metal ions Cd$^{2+}$, Co$^{2+}$ and Mn$^{2+}$ through a sol gel process. The growth of TiO$_2$ crystals have inhibited by metal ions dopand. The character of the structure and optical properties were studied to discern the effect of metal insertion of Cd$^{2+}$, Co$^{2+}$ and Mn$^{2+}$ on the crystal structure and the ability of TiO$_2$-doped semiconductors to absorb a visible light.

2. Experimental

2.1. Materials

The materials used in this study were titanium tetraisopropoxide (TTIP) (E Merck), CdSO$_4$.8H$_2$O, MnSO$_4$.H$_2$O, CoSO$_4$.7H$_2$O (E merck), glacial acetic acid, aquades, and 98% ethanol (E Merck). Calcination of TiO$_2$ and TiO$_2$-M (M = Cd, Co, Mn) was performed by Furnace Thermo. Meanwhile, the analysis and characterization of materials were done by XRD (Bruker D8 Advantage), SEM-EDX (SEM 250 Quanta), UV Vis Spectrophotometer Pelkin Elmer Lambda 25, and FTIR (Shimadzu Prestige 21).

2.2. Synthesis of TiO$_2$-M (Cd, Mn, Co)

The titanium (IV) isopropoxide solution was hydrolyzed using a glacial acetic acid solution (temperature of 14 ºC) at a ratio of 1: 10 (v/v) and then stirred continuously using a magnetic stirrer until a white sol gel was obtained, then stirred and heated at 90ºC until obtained white gel [18]. After the gel obtained, the metal ions of Cd$^{II}$, Co$^{II}$ and Mn$^{II}$ in the aquades solvent were added to the TiO$_2$ sol gel until a stoichiometric ratio of Ti:M (M= Cd, Mn, Co)= 3:1 (mol/mol). The mixtures were subsequently cooled to room temperature for a perfect gelation process. The resulting gel were heated at 150 ºC for ± 24 hours. The obtained TiO$_2$ xerogels were calcined at 400 ºC for 2 hours. The resulting TiO$_2$-M ( M= Cd, Mn, Co) crystalline powder were then analyzed by XRD, UV Vis, FTIR spectrophotometer and SEM-EDX.

3. Results and Discussion

Synthesis of TiO$_2$ with the insertion of metal (Cd, Mn, Co) was carried out using the sol-gel method. The insertion of metals was expected to replace several positions of Ti atoms in TiO$_2$. The calcination process was carried out at 400 ºC for 2 hours to obtain TiO$_2$ crystals with an anatase phase. X-ray diffractograms of TiO$_2$ and TiO$_2$-M are shown in Figure 1.
Figure 1. X-Ray Diffractogram of (a) TiO$_2$-Co (3:1) (b) TiO$_2$-Mn (3:1) (c) TiO$_2$-Cd (3:1) (d) TiO$_2$ (e) JCPDS TiO$_2$ No 78-2486

TiO$_2$-M synthesized using the sol-gel method shows the anatase phase crystals at $2\theta = 25.49^\circ$, $2\theta = 37.79^\circ$ and $2\theta = 48.04^\circ$. In Figure 1, A is a symbol of anatase phase formed in TiO$_2$-M and TiO$_2$. Based on the XRD spectra of TiO$_2$-M (3:1) (Figure 1), it can be seen that the main peaks are A (101), A (004), A (200) at $2\theta = 25.49^\circ$, $2\theta = 37.79^\circ$ and $2\theta = 48.04^\circ$ which is the characterization of TiO$_2$. The XRD data is compatible with JCPDS No. 78-2486 after being processed with Jade MDI Program. The insertion of metal ions Cd, Mn and Co shows the characteristics of TiO$_2$ Anatase. The diffractogram of TiO$_2$-Cd (3:1), TiO$_2$-Mn (3:1) and TiO$_2$-Co (3:1) only shows the peak of anatase at $2\theta = 25.607^\circ$ ($d_{101}$), $38.010^\circ$ ($d_{004}$) and $48.190^\circ$ ($d_{200}$). The insertion of Cd, Mn and Co in TiO$_2$ semiconductors inhibits the growth of TiO$_2$ crystals and causes a decrease in TiO$_2$-M crystal size (M = Cd, Co, Mn).

Table 1. Crystal sizes of TiO$_2$ and TiO$_2$-M (M = Cd, Co, Mn)

| Material    | Crystal Size (nm) |
|-------------|-------------------|
| TiO$_2$     | 15.622            |
| TiO$_2$-Cd  | 6.907             |
| TiO$_2$-Co  | 7.223             |
| TiO$_2$-Mn  | 7.404             |

Figure 2. Morphology of (a) TiO$_2$-Cd (b) TiO$_2$-Mn (c) TiO$_2$-Co
SEM-EDX results showed that the percentage of $M$ ($M = \text{Cd, Mn, Co}$) in TiO$_2$ is equal to 8.62%, 3.26% and 7.21%, respectively. The insertion of $M$ ($M = (\text{Cd, Co, Mn})$ in TiO$_2$ crystallites affects the electronic properties showed by changes in band gap energy (Figure 3). The band gap energy from the calculation result is shown in Table 2.

![Figure 3. Tauc Plot Graph of (a) TiO$_2$-Co (b) TiO$_2$-Cd (c) TiO$_2$ (d) TiO$_2$-Mn](image)

**Table 2.** Band gap energy and wavelengths of TiO$_2$-$M$ (3:1)

| Material       | Band Gap (eV) | $\lambda$ (nm) |
|----------------|---------------|-----------------|
| TiO$_2$        | 3.35          | 370.15          |
| TiO$_2$-Cd     | 3.15          | 393.65          |
| TiO$_2$-Co     | 3.00          | 413.33          |
| TiO$_2$-Mn     | 2.5           | 496.00          |

The insertion of metal to TiO$_2$ causes a decrease in band gap energy as shown in Table 2 with the band gap energy of TiO$_2$ > TiO$_2$-Cd > TiO$_2$-Co > TiO$_2$-Mn. The wavelength is calculated using the equation $\lambda = \frac{1240}{E_g}$. Visually, the insertion of the metal affects the band gap energy ($E_g$) result as in Figure 4.

![Figure 4. Scheme of insertion metal ions Cd$^{2+}$, Co$^{2+}$, and Mn$^{2+}$ in TiO$_2$.](image)

Infra red spectra of TiO$_2$ showed characteristic absorptions at 3405.47 cm$^{-1}$, 1627.99 cm$^{-1}$, and strong wide absorption band at 576.74-421.46 cm$^{-1}$. Absorption band at 3405.47 cm$^{-1}$ showed the stretching vibration from H$_2$O in TiO$_2$ [19]. While the absorption band at 1625-1650 cm$^{-1}$ showed the
bending vibration of trapped water molecules in TiO$_2$ structure, and absorption band at 609.5-420.5 cm$^{-1}$ represent O-Ti-O vibration [18]. The presence of Cd is showed at 1115-1057 cm$^{-1}$ and 540-425 cm$^{-1}$ which can be associated with the formation of Ti-O-Cd bonds. Two absorption bands at 1100 cm$^{-1}$ and 980 cm$^{-1}$ are the characteristic stretching vibration of the Ti-O-Cd in accordance with Ge et al. [20]. Both absorption bands show different intensities in the mole ratio of TiO$_2$: Cd, where the absorption intensity looks sharp with the more addition of Cd. This observation is also occur at absorption band in the range 619.18–618.21 cm$^{-1}$ as bending vibration of Cd.

![Figure 5. IR spectra of TiO$_2$-Cd, synthesized with mole ratio of TiO$_2$: Cd (a) 1:3 (b) 1:2 (c) 1:1 (d) 2:1 (e) 3:1, and (f) TiO$_2$](image)

Similar characters are also showed in the absorption of TiO$_2$-Co (Figure 6). Weak wide absorption at 2840 cm$^{-1}$ getting stronger with the increase of Co bonded, indicating absorption from OH on Co-O (bounded to H$_2$O). Absorption peak at 1000-1250 cm$^{-1}$ is characteristic of Co, as evidenced by the increase absorption with the increasing of mole of Co [21].

![Figure 6. IR spectra of TiO$_2$-Co, synthesized with mole ratio of TiO$_2$: Co (a) 1:3 (b) 1:2 (c) 1:1 (d) 2:1 (e) 3:1, and (f) TiO$_2$](image)

TiO$_2$-Mn spectra (Figure 7) show the characteristic absorption at 660 cm$^{-1}$ which is a vibration of $\beta$-MnO$_2$. In addition, absorption band at 620 cm$^{-1}$ and 530 cm$^{-1}$ is indicated as vibrations of O-Ti-O
and Mn-O-Ti. Absorption band at 1140–997 cm$^{-1}$ is estimated to be characteristic of Mn-O because the intensity of the peak looks sharp within the addition of more Mn.

![Figure 7](image_url)

**Figure 7.** IR spectra of TiO$_2$-Mn, synthesized with mole ratio of TiO$_2$:Mn (a) 1:3 (b) 1:2 (c) 1:1 (d) 2:1 (e) 3:1, and (f) TiO$_2$

If we compare the FTIR spectra of the TiO$_2$-M (M = Cd, Co, Mn) (Figure 7), then the difference is seen in the M-O-Ti stretch vibration area at 1100-990 cm$^{-1}$. Absorption band in the area is characteristic of the insertion different dopants, and distinguish dopants added to TiO$_2$ crystal.

4. Conclusion

Synthesis of TiO$_2$ with the insertion of M (M= Cd, Co, Mn have been done using the sol-gel method. The insertion of Cd, Co, Mn decreases the crystallinity of TiO$_2$ as indicated by the decreasing in crystal size about ± 54%. The insertion of M (M=Cd, Co, Mn) in TiO$_2$ lattice were also affect the electronic properties of TiO$_2$ as a semiconductor with the band gap energy (E$_g$) was decrease as E$_g$ TiO$_2$ > E$_g$ TiO$_2$-Cd > E$_g$ TiO$_2$-Co > E$_g$ TiO$_2$-Mn.

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