



MODIFICATION OF TITANIUM DIOXIDE NANOPARTICLES WITH COPPER OXIDE CO-CATALYST FOR PHOTOCATALYTIC DEGRADATION OF 2,4-DICHLOROPHENOXYACETIC ACID

(Nanozarah Titanium Dioksida Terubahsuaikan Ko-Mangkini Kobalt Oksida untuk Degradasi Asid 2,4-diklorofenoksiasetik)

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Abstract

2,4-dichlorophenoxyacetic acid (2,4-D) is a common herbicide that has been used widely. Due to its excessive usage, the 2,4-D herbicides can cause contamination over agricultural land and water bodies. In the present work, a simple impregnation method was used to modify the commercial titanium dioxide (P25 TiO₂) nanoparticles with the copper oxide. The prepared samples were characterized by X-ray Diffraction (XRD), reflectance UV-visible and fluorescence spectroscopies. It was observed that the incorporation of copper oxide did not significantly affect the crystal structure of P25 TiO₂. On the other hand, the presence of copper oxide was confirmed by reflectance UV-visible and fluorescence spectroscopies. The activity of the prepared sample was evaluated for photocatalytic removal of the 2,4-D. The photocatalytic activity of the TiO₂ increased with the increase of copper oxide loading up to 0.5 mol%. Unfortunately, the higher loading amount of copper oxide resulted in the lower photocatalytic activity. This study suggested that the higher photocatalytic activities obtained on the low loading samples were due to the lower electron-hole recombination.

Keywords: P25 TiO₂, copper oxide, impregnation, photocatalyst, 2,4-D herbicide

Abstrak

Asid 2,4-diklorofenoksiasetik (2,4-D) adalah herbisid biasa yang telah digunakan secara meluas. Oleh kerana penggunaan yang berlebihan, herbisid 2,4-D boleh menyebabkan pencemaran di kawasan pertanian dan sistem air. Dalam kajian ini, satu kaedah pengisitepuan yang mudah telah digunakan untuk mengubahsuaikan nanozarah titanium dioksida komersial (P25 TiO₂) dengan kuprum oksida. Sampel yang disediakan telah dicirikan dengan XRD, spektroskopi pantulan serakan ultra lembayung-cahaya nampak, dan spektroskopi pendarfluor. Didapati pengubahsuaian P25 TiO₂ dengan kuprum oksida tidak memberi kesan yang signifikan kepada struktur kristal P25 TiO₂. Sebaliknya, kehadiran kuprum oksida telah disahkan oleh spektroskopi pantulan serakan ultra lembayung-cahaya nampak. Aktiviti sampel telah diuji untuk penyingkiran 2,4-D. Aktiviti fotomangkini TiO₂ meningkat dengan peningkatan jumlah kuprum oksida kepada 0.5 mol%. Malangnya, jumlah kuprum oksida yang lebih tinggi menghasilkan aktiviti fotomangkini yang lebih rendah. Kajian ini mencadangkan bahawa aktiviti fotomangkini yang tinggi diperolehi pada sampel loading rendah adalah disebabkan oleh penggabungan elektron-lubang yang lebih rendah.

Kata kunci: P25 TiO₂, kuprum oksida, pengisitepuan, fotomangkini, 2,4-D herbisid

Introduction

The 2,4-dichlorophenoxyacetic acid (2,4-D) is one of the most used herbicides in the world and has been used since the 1940s. The 2,4-D is used widely to control broadleaf weeds in a variety of settings from crops, rights-of-way, lawns, forests to aquatic settings. In 1986, the International Agency for Cancer Research (IARC) classified the chlorophenoxy herbicides as a Group 2B (possible) carcinogen. Since then, various studies have been done on the toxicity and carcinogenicity of the 2,4-D. Recently, the 2,4-D epidemiology literature has been qualitatively reviewed [1]. Even though no convincing evidence for any chronic adverse effect of 2,4-D in human, studies in the removals of the 2,4-D in order to prevent the negative effects of the 2,4-D towards human and environment are still in progress.

One of the simple methods to remove the 2,4-D from water is by adsorption process. Some adsorbents have been reported to give good performance to adsorb the 2,4-D, such as the layered double hydroxides (LDH) [2 –5] and mesoporous materials [6] due to the large surface area, high anion capacity, and good thermal stability. However, rather than removing the 2,4-D by an adsorption process, degradation of the 2,4-D would be a great advantage to solve the environment problems. Degradation of the 2,4-D could be achieved by introducing the electrochemical assistance to a microbiological reduction system [7], and photooxidation via Fenton reaction and in the presence of strong oxidant such as hydrogen peroxide [8]. However, from the point of view of sustainability and environmentally safe process, photocatalytic reaction would be the promising method to degrade the 2,4-D herbicide [9 – 13]. Some studies also reported the combined method to degrade 2,4-D by the photocatalytic reactions with the use of strong oxidants and microwave [9, 10].

In general, photocatalytic removal of environmental pollutants has been a topic of great interest over the years [14]. One of the most widely used materials for photocatalytic degradation of environmental pollutants is titanium dioxide (TiO_2). As a photocatalyst, TiO_2 has a range of useful features, including high photocatalytic activity, stability, low toxicity, ready availability and low cost [15]. While TiO_2 is one of the most active catalysts for the degradation of a wide range of organic compounds, its catalytic activity should be further improved. Hence, there have been a great number of studies to modify the TiO_2 based photocatalysts. It has been reported that the TiO_2 bound with TiO_2 sol with the help of polymeric bonds showed better photocatalytic activity for degradation of 2,4-D than the unmodified TiO_2 , owing to the better distributions of photons [11]. Another study reported that the addition of reduced graphene oxide and CuInS_2 the TiO_2 improved its activity for degradation of the 2,4-D [12]. The addition of Ag/reduced graphene oxide was also reported increasing the activity of TiO_2 for the 2,4-D degradation [13]. The improved activity was closely related to the effective carriers separation and large adsorption capacity for the 2,4-D [12, 13].

While several studies have been reported to modify TiO_2 with noble metals, transition metal oxides and non-metal ions [15-18], in particular, it has been shown that transition metal oxides such as copper oxide have the potential of enhancing the photocatalytic activity of TiO_2 [19 – 21]. When applied to TiO_2 on the optimal composition, phase and size, these transition metal oxide nanoparticles can act as effective co-catalysts that improve the efficiency of TiO_2 photocatalysis. In the present work, a simple impregnation method was used to grow copper oxide nanoparticles on the surface of commercial P25 TiO_2 particles. The amount of copper incorporated on the surface of the P25 TiO_2 particles was varied in the range of 0.1 to 5 mol%. The effect of Cu loading on the photocatalytic activity of TiO_2 to degrade the 2,4-D was investigated.

Materials and Methods

Preparation of photocatalysts

P25 TiO_2 (Evonik) and copper(II) nitrate trihydrate (Aldrich, 99 – 104%) were used as received without any treatments. The required amount of copper(II) nitrate trihydrate was dissolved into 20 ml of distilled water. Then, P25 TiO_2 (1 g) was dispersed in the copper nitrate solution by sonicating the mixture for 10 minutes. Under vigorous stirring, the resultant mixture was heated at 80 °C until the solvent was removed. The dried mixture was ground to a fine powder and calcined at 500 °C for 4 hours. The resultant powder was ground and stored under ambient conditions. The samples were labeled as x mol% Cu/P25 TiO_2 , with x showed the ratio of Cu to Ti (mol%) and varied in the range of 0.1 – 5 mol%. For comparison, the P25 TiO_2 was also treated in the same manner to the samples, except for the addition of the copper(II) nitrate trihydrate.

Characterizations

X-ray Diffraction (XRD, Bruker AXS Difract plus release 2000) was used to identify the structure of the prepared photocatalysts. The optical properties of the samples were analyzed by an Avantes spectrophotometer AvaSpec-ULS2048 using a reflection probe holder with angle of 45° and PTFE-coated white material as the reference sample. The emission spectra were measured at room temperature on a Fluorescence Spectroscopy JASCO FP-8500. The spectra were monitored at excitation wavelength of 218 nm. The morphology and particle size of the samples were investigated by a transmission electron microscopy (TEM, JEM-2100) at an accelerating voltage of 200 kV. The sample was dispersed well in ethanol and then, put on a carbon-coated copper grid.

Photocatalytic activity test

The prepared samples were evaluated for removal of 2,4-D at room temperature under UV light irradiation. Prior to the irradiation, the sample (50 mg) was dispersed in 2,4-D solution (50 mL, 0.5 mM) and stirred in the dark condition for 1 hour to achieve the adsorption-desorption equilibrium. The reaction was carried out for 1 hour under irradiation by a 200 W Xe-Hg lamp, which light intensity was 15 mW cm^{-2} and it was equipped with an IR cut off filter. The remaining amount of 2,4-D after each reaction was determined by UV-Visible spectrophotometer using a Thermo Scientific Genesys 10S. The monitored wavelength was 283 nm. The percentage of 2,4-D removal was then calculated from the ratio of concentrations between the reacted and the initial 2,4-D.

Results and Discussion

Properties of Cu/P25 TiO₂ samples

Figure 1 shows the XRD patterns of P25 TiO₂ and the prepared Cu/P25 TiO₂ samples. All samples showed the diffraction peaks at 25.30° and 27.43° , corresponding to the (101) plane of anatase TiO₂ and (110) plane of rutile TiO₂, respectively. These XRD patterns clearly suggested the presence of both anatase and rutile phases in the samples. However, no appreciable diffraction peak of copper oxide phase was observed on all of the Cu/P25 TiO₂ samples. This was mostly likely due to the small amount of copper oxide present in the sample. In addition, a high degree of dispersion of copper oxide on the TiO₂ support would result in the small particle size of the metal oxide, which would be beyond the detection limit of XRD.

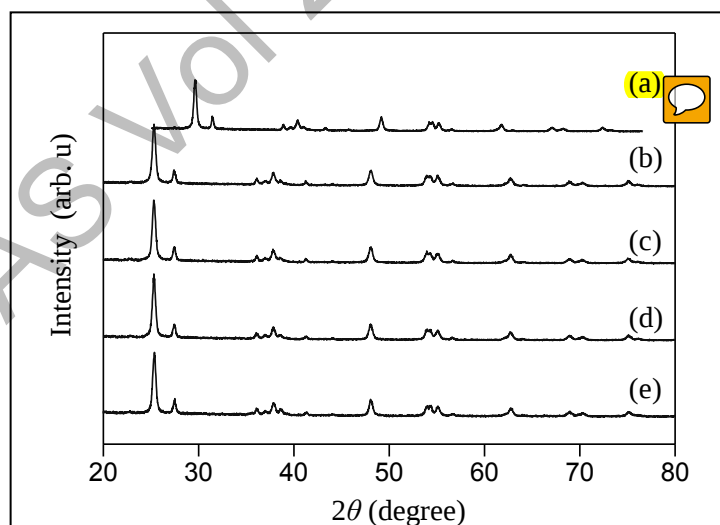


Figure 1. XRD patterns of (a) P25 TiO₂, (b) 0.1 mol% Cu/P25 TiO₂, (c) 0.5 mol% Cu/P25 TiO₂, (d) 1 mol% Cu/P25 TiO₂, and (e) 5 mol% Cu/P25 TiO₂ samples

As shown in Figure 1, the XRD patterns of the Cu/P25 TiO₂ samples were very similar to that of the P25 TiO₂ sample. This result showed that the incorporation of copper oxide did not affect significantly the crystal structure of P25 TiO₂. Table 1 shows the crystallite size of anatase and the anatase to rutile ratio of the P25 TiO₂ and the prepared Cu/P25 TiO₂ samples. The crystallite size for anatase and rutile phase was determined by a Scherrer equation shown in Equation 1, using the most intense peak of anatase (101) around 25.3° and rutile (110) around 27.4°, respectively.

$$t = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where t is the average crystallite size in nm, while K is dimensionless shapes factor generally taken as 0.89, λ is the wavelength of the X-ray equals to 1.542 Å, β is full width at half maximum (FWHM) at 2θ of 25.3 or 27.4° and θ is Bragg's angle. The anatase to rutile ratio was also calculated based on the intensity of the most intense peaks at around 25.3 and 27.4° for anatase (101) and rutile (110), respectively, as shown in Equation 2.

$$A(\%) = \frac{100 \times I_A}{I_A + 1.265 \times I_R} \quad (2)$$

where $A(\%)$ is the percentage of anatase, I_A and I_R correspond to the intensity of the anatase (101) and rutile (110) reflections, respectively.

As listed in Table 1, the crystallite size of P25 TiO₂ for both anatase and rutile phase was only slightly increased upon the addition of copper oxide. The average crystallite size for anatase phase was in the range of 17-21 nm, while for rutile phase was in the range of 60-72 nm. In addition, the anatase to rutile phase ratio of P25 TiO₂ likewise was not much affected by the incorporation of copper oxide. In order to support the crystallite size data, TEM images for the P25 TiO₂ and 0.5 mol% Cu/P25 TiO₂ are shown in Figure 2. The P25 TiO₂ showed irregular polyhedral shape nanoparticles (Fig. 2(a)). Most of the particles have size in the range of 15-25 nm due to the presence of anatase phase, while larger particles in the range of 50-70 nm were due to the presence of rutile phase. On the other hand, Figure 2(b) showed that no remarkable change in morphology and particle size could be observed on the 0.5 mol% Cu/P25 TiO₂. These results are in good agreement with the calculated average crystallite size from the XRD patterns shown in Table 1.

Table 1. Crystallite size and anatase to rutile ratio for P25 TiO₂ and Cu/P25 TiO₂ samples

Entry	Sample	Crystallite size (nm) ^a		Anatase to rutile ratio (%) ^b
		Anatase	Rutile	
1	P25 TiO ₂	17.1	60.2	72:28
2	0.1 mol% Cu/P25 TiO ₂	18.1	67.8	74:26
3	0.5 mol% Cu/P25 TiO ₂	18.5	71.9	74:26
4	1 mol% Cu/P25 TiO ₂	18.7	59.9	76:24
5	5 mol% Cu/P25 TiO ₂	20.3	62.0	74:26

^aEstimated by the Scherrer equation shown in the Eq. 1.

^bEstimated by the formula shown in the Eq. 2.

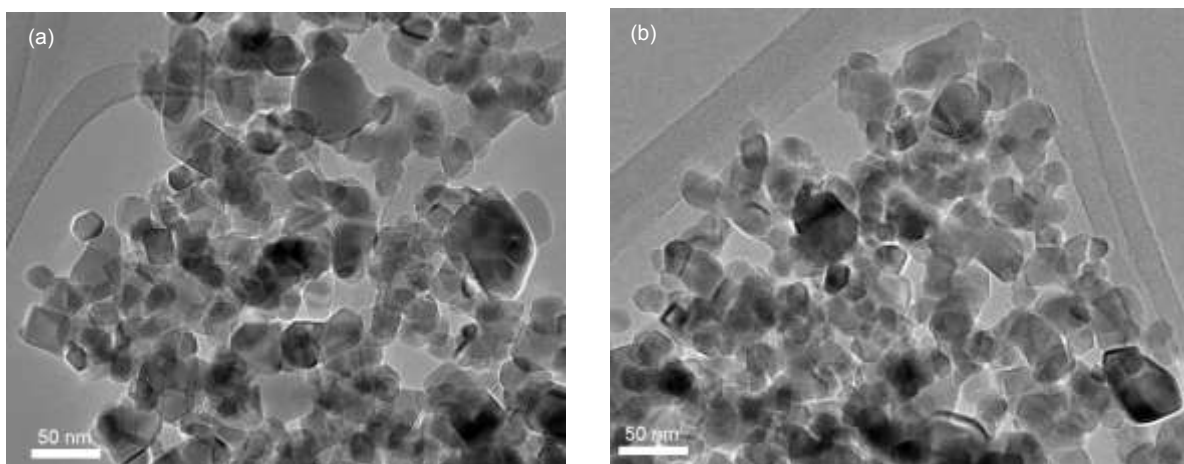


Figure 2. TEM images of (a) P25 TiO₂ and (b) 0.5 mol% Cu/P25 TiO₂ samples.

Figure 3 shows the reflectance UV-Vis absorption spectra of the P25 TiO₂ and Cu/P25 TiO₂ samples. The unmodified P25 TiO₂ sample has white colour as can be reflected in its UV-Vis absorption spectrum that displayed very low absorption intensity in the visible region of the spectrum (Fig. 3(a)). The addition of copper oxide resulted in the colour change from white to green. The colour became darker with the increase of the copper oxide loading. These changes could be observed in Figure 2, in which the Cu/P25 TiO₂ samples gave additional absorption in the visible light region and the absorbance increased with the increase of the copper oxide loading amount. The absorbance in the visible light region would be originated from the d-d transitions of the Cu²⁺ system [19], which were present on the surface of copper oxide modified TiO₂. While the Cu/P25 TiO₂ samples with low loadings of copper oxide did not much influence the band gap of the TiO₂, sample with high loading 5 mol% Cu/P25 TiO₂ slightly shifted the band edge absorption of P25 TiO₂ to longer wavelength. The shift indicated that some copper metal ions might alter the band gap of TiO₂ [16, 17].

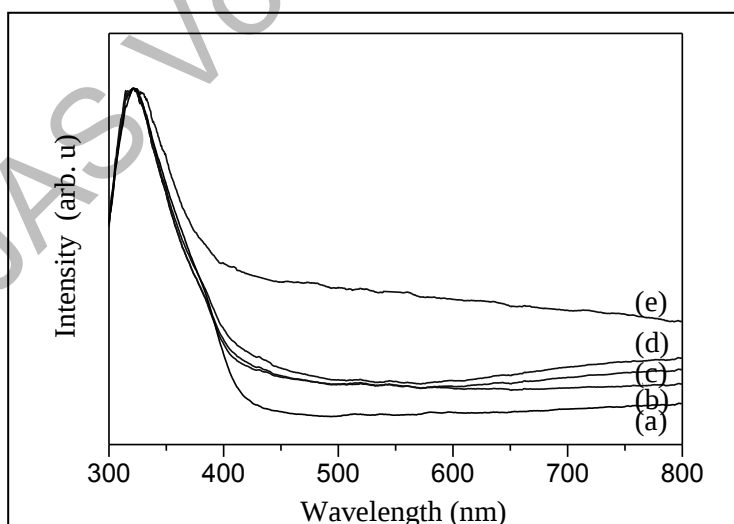


Figure 3. Normalized reflectance UV-Visible spectra of (a) P25 TiO₂, (b) 0.1 mol% Cu/P25 TiO₂, (c) 0.5 mol% Cu/P25 TiO₂, (d) 1 mol% Cu/P25 TiO₂, and (e) 5 mol% Cu/P25 TiO₂ samples

In order to study the interaction between the P25 TiO₂ and the copper oxide, the emission spectra of the samples were measured at the excitation of P25 TiO₂, which was at 218 nm. Figure 4 shows the emission spectra of P25 TiO₂ and the Cu/P25 TiO₂ samples. It was obvious that the emission intensity of P25 TiO₂ was reduced with the addition of copper oxide. The emission intensity was further reduced with the further increase of the copper oxide loading. This result clearly showed that there were interactions between P25 TiO₂ and the added copper oxide. Since emission intensity can be corresponded to the electron-hole recombination, the decreased emission intensity can be assigned to the suppression of electron-hole recombination.

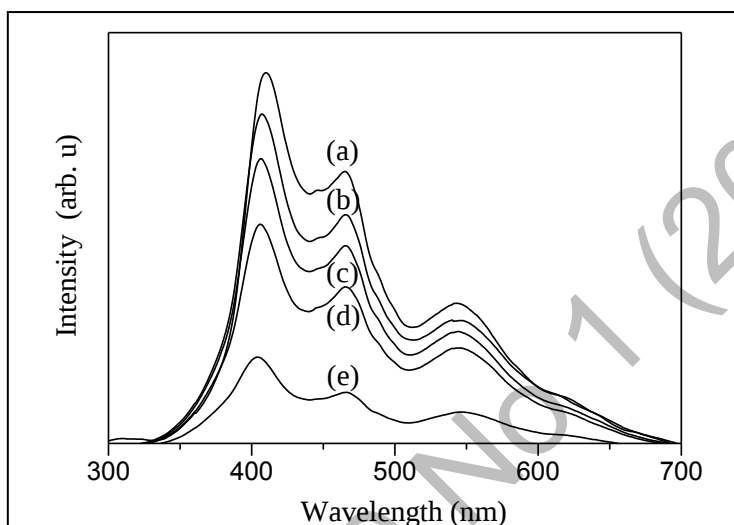


Figure 4. Emission spectra of (a) P25 TiO₂, (b) 0.1 mol% Cu/P25 TiO₂, (c) 0.5 mol% Cu/P25 TiO₂, (d) 1 mol% Cu/P25 TiO₂, and (e) 5 mol% Cu/P25 TiO₂ samples, monitored at excitation wavelength of 218 nm

As discussed previously, copper ions might alter the band gap energy of P25 TiO₂. Therefore, copper oxide might act as the co-catalyst to trap electron, thus enhancing the charge separation in the P25 TiO₂ that would lead to the enhanced activity. However, if the amount of copper oxide was too high, it would reduce the electrons in the conduction band of the P25 TiO₂ that might reduce the efficiency. Moreover, the large amount of copper oxide might also block the active sites of the P25 TiO₂ and reduce the photocatalytic activity. In other words, there would be an optimum amount of copper oxide that would give the optimum activity, which would be explained in the following part.

Photocatalytic activities of Cu/P25 TiO₂ samples

Figure 5 shows the photocatalytic removal of 2,4-D on the P25 TiO₂ and Cu/P25 TiO₂. It can be clearly shown that after 1 hour reaction, the photocatalytic activity of TiO₂ increased from 48.3 to 59.4 % with the increase of copper oxide loading up to 0.5 mol%. Unfortunately, the higher loading amount of copper oxide resulted in the lower photocatalytic activity. When the loading amount was 5 mol%, the activity decreased to 25.8 %. This result clearly suggested that the small amount of copper oxide, which was 0.5 mol%, was the optimum amount in this study to give the highest activity for the Cu/P25 TiO₂. The higher photocatalytic activity would be originated from the lower electron-hole recombination. On the other hand, the high loading amount of copper oxide might reduce the electrons in the conduction band of P25 TiO₂ or might block the active surface of P25 TiO₂, thus reduced the photocatalytic activity. Therefore, the optimum amount of copper oxide that would result in the optimum activity would be related to the optimum electron-hole separation, without reducing electrons in the conduction band of P25 TiO₂ and/or blocking active sites of the TiO₂. Similar results have been reported elsewhere [19 – 21]. The high amount of copper oxide may give masking effect on the P25 TiO₂, which prevented the UV light source to reach the active sites of TiO₂.

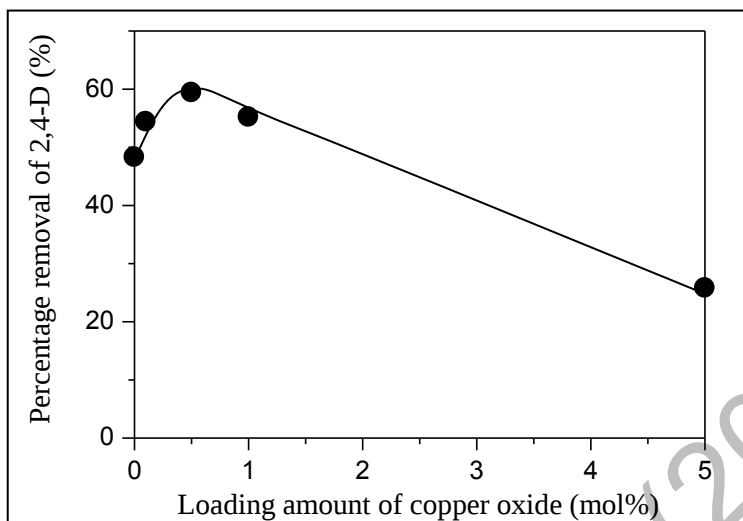


Figure 5. Photocatalytic removal of 2,4-D herbicide on the P25 TiO₂ and Cu/P25 TiO₂ samples.

Conclusion

The Cu/P25 TiO₂ samples were prepared successfully by an impregnation method. The addition of copper oxide did not much affect the crystallite size and the crystal phase of the P25 TiO₂. On the other hand, the addition of copper oxide increased the visible light absorption and slightly altered the band edge absorption of P25 TiO₂. Copper oxide also reduced the emission intensity, suggesting that optimum amount of copper oxide might act as good co-catalyst to trap electrons, thus suppress the electron-hole recombination. The 0.5 mol% was found to be the optimum amount of copper oxide that enhance the activity of P25 TiO₂ for the photocatalytic removal of 2,4-D herbicide.

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