Photocatalytic Activity of TiO₂-containing Al-Mesoporous Silica Thin Films

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Abstract: The photocatalytic activity of TiO₂ coated on Al-modified folded mesoporous silica thin films (Al-MSF), TiO₂/Al-MSF and Ti-, Al-MSF, has been investigated by monitoring the decomposition of methylene blue (MB). The TiO₂/Al-MSF and Ti-, Al-MSF were prepared on substrates by two independent procedures, i.e., ion-exchange and sol-gel. The Ti-, Al-MSF was found to exhibit higher reactivity than TiO₂/Al-MSF, while both films showed higher performance than conventional powdered TiO₂. A detailed analysis of the origin of the photocatalytic reactivity for these TiO₂ coated Al-modified mesoporous silica thin films toward the decomposition of MB is presented here.

Key words: aluminum modified folded mesoporous silica thin films (Al-MSF), titanium dioxide, photocatalytic decomposition, methylene blue (MB)

1 Introduction

Since the pioneering work of the Honda-Fujishima effect in 1972, many investigations into TiO₂ photocatalysis for the decomposition of water into hydrogen and oxygen have been carried out (1,2). The elimination of harmful and toxic substances in our environment is an urgent issue and in order to address such concerns, photocatalysts involving titanium oxide have been shown to be the most promising since it possesses a large surface area, leading to more efficient, greater reactivity (3-6). Presently, commercially available TiO₂ powders, P25 and Degussa, are fine particles of *ca.* 30 nm in average diameter, however, they do not possess a sufficiently large surface area (*ca.* 50 m² g⁻¹) necessary for the complete depletion of harmful compounds within a reasonably short period on a large scale.

Thus, catalyst-supporting materials incorporating

TiO₂ which have a large surface area and, at the same time, large mesoporous cavities, have the potential to be effectively applied for the complete depletion of such dangerous hormonal compounds as estradiol chemicals (7,8). Along these lines, the present study deals with the hybridization of TiO₂ with folded mesoporous silica, especially Al-modified folded mesoporous silica, for the adsorption of polar substances dissolved in water. The photocatalytic activity of these functionalized mesoporous silica has been examined by monitoring the decomposition of methylene blue (MB).

2 Experimental

2.1 Chemicals

Tetraethyl orthosilicate (TEOS, WAKO Pure & Chemicals), aluminum tri(*sec*-butoxide) (ATSB), octadecyltrimethylammonium chloride (C18TAC,

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Tokyo Kasei Corp.), titanium (IV) ammonium oxalate n-hydrate (TAO, Kishida Chemicals), titanium tetraisopropoxide (TIPT, WAKO Pure & Chemicals), and methylene blue (MB, Tokyo Kasei Corp) were used without further purification.

2·2 Apparatus

Powder X-ray diffraction analysis (XRD) was carried out with a Rigaku RINT-2100 XRD apparatus operating at 40 mA and 40 kV, and equipped with a Rigaku CN2173C3 goniometer set at 1.54 Å with Ni-filtered $\text{CuK}\alpha$ radiation and a Rigaku PTC-20A temperature controller. The XRD patterns were measured in the $2\theta/\theta$ mode within a 2θ range of $1.5^\circ - 30^\circ$ and a scan rate of 1 deg/min. The obtained data were collected five times and then averaged. The UV-Vis and IR absorption spectra were investigated by V-550 and FT/IR-300E spectrophotometers, respectively. Scanning Electron Microscopic (SEM) images were taken by a JEOL scanning electron microscope (JSM 5600). Transmission electron micrographs (TEM) of the samples were taken on a Hitachi H-7000 transmission electron microscope with an accelerating voltage of 100 kV. The composite nano-order surface images were measured with atomic force microscope (AFM), i.e., table-type probe microscope (Nanopics 2100) by SEIKO Instruments. Simi-quantitative elemental analysis was carried out with a JEOL energy dispersed X-ray spectroscope (JED-2200) at energy of 0–20 keV with an acceleration voltage of 20 kV. The photocatalytic decomposition of MB was investigated under UV light illumination (< 380 nm) by a 300 W Xenon lamp equipped with a color glass filter U340 (HOYA Corp.).

2·3 Preparation of Al-modified Mesoporous Silica Thin Films (Al-MSF)

The Al-modified folded mesoporous silica thin films (Al-MSF) were synthesized by procedures previously reported by Ogawa *et al.* (9). Aluminum tri(*sec*-butoxide) or ATSB was added to a mixed solution of TEOS, ethanol, H_2O , conc. HCl and C18TAC in a molar ratio of 1:4:1.2:0.006:1, respectively, under conditions of pH = 2 while the Al contents were adjusted to 0, 1, 2, 3 mol% (i.e. Al/Si = 0, 0.01, 0.02 and 0.03). This precursor solution was cast on a substrate (5 cm $\times$ 5 cm, typically quartz was used as a substrate, except in case of IR measurement silicon wafer was used) with a spin coater at the humidity of 60% and the resulting sub-

strate glass was heated at 500°C for 5 hrs to form a transparent film.

2·4 Support of Titania on Al-MSF

These composites were synthesized by the following two procedures:

2·4·1 An ion-exchange method

The present TiO_2 -supported Al-MSF hybrids were prepared by an ion-exchange method previously reported for the preparation of TiO_2 -supported zeolites (10). The silica thin films were cast on a quartz substrate and immersed for 48 hrs in 10 ml of a 1×10^{-3} M aqueous solution of $(\text{NH}_4)_2 [\text{TiO}(\text{C}_2\text{O}_4)_2] \cdot n\text{H}_2\text{O}$ (TAO). After washing with water, the substrate was dried at 70°C for 12 hrs and heated further at 500°C for 5 hrs in air. The obtained TiO_2 -supported Al-MSF thin films are referred to as $\text{TiO}_2/\text{Al-MSF}$.

2·4·2 The sol-gel method

A mixture of TEOS, ethanol, water, and HCl in a molar ratio of 1:4:1.2:0.006 was stirred for 10 min at 50°C. ATSB was added to this solution to obtain solutions with Al contents of 0, 1, 2, 3 mol%. Then TAO was added to each of these solutions to obtain solutions with Ti content of 0.1, 0.5, 1, 2, 5 mol% (i.e. Ti/Si = 0.001, 0.005, 0.01, 0.02 and 0.05). The mixed solutions were then stirred for 10 min at 50°C. Next, C18TAC and HCl (pH = 2) were added and the resulting solutions were each spin-coated on a quartz substrate (5 cm $\times$ 5 cm). After heating at 500°C for 5 hrs, Ti-, Al-modified folded mesoporous silica thin films of various Al and Ti contents were obtained and are collectively referred to here as Ti-, Al-MSF.

2·5 Titania Thin Films without Al-MSF

Titania thin films without Al-MSF were also prepared by a sol-gel method (11). At 0°C, 2.332 mL ethanol, 0.128 mL water and 0.081 mL of conc. HCl were slowly added to a mixture of 2.8 g TIPT and 2.332 mL ethanol. The resulting mixture was stirred for 8 hrs at room temperature. A quartz substrate was repeatedly immersed into this precursor solution. After immersion treatment of 6 cycles, the TiO_2 transparent films were obtained.

2·6 Adsorption of Methylene Blue (MB)

MB was adsorbed on Al-MSF, $\text{TiO}_2/\text{Al-MSF}$ and Ti-, Al-MSF by immersion of the functionalized mesoporous silica coated substrates into an aqueous $1.0 \times$

10^{-3} and 5.0×10^{-3} M MB solution under dark conditions at room temperature for 48 hrs.

3 Results and Discussion

3.1 Characterization of the Al-modified Mesoporous Silica Thin Films (Al-MSF)

The Al-modified mesoporous silica thin film (Al-MSF) cast on a quartz substrate exhibited a sharp peak at $2\theta = 2.2\text{--}2.5^\circ$ which corresponded to the diffraction peak of the (1 0 0) plane of a hexagonal mesoporous silica structure, as shown in **Fig. 1** (9, 12). With an increase in the Al content, the peak (1 0 0) broadened due to a decrease in the crystallinity, just as reported by Ogawa *et al.* (9), confirming previous reports on the solid solubilization of Al atoms into “Al-FSM-16” by Kitayama *et al.* (13) and “Al-MCM-41” by Eimer *et al.* (14). The UV-Vis spectrum showed that this film possesses more than 95–100% transmittance between 350–800 nm as shown in **Fig. 2**. Analysis of the AFM images of the film showed a thickness of 500–600 nm with a roughness in surface texture of *ca.* 100 nm as shown in **Fig. 3**. Moreover, Al-MSF showed a high dispersion of Al atoms for Al content of 1 mol%, as observed by the good coincidence between the molar ratios of ATSB/TEOS used and that of Al/Si of the film measured by EDX analysis, as shown in **Table 1**. However, the degree of Al dispersion may be lower with an

Fig. 1 XRD Profiles of the Al-MSF with Varying Al Contents (a. 0; b. 1; c. 2; d. 3 mol%).

Fig. 2 UV-Vis Spectrum Expressing the Transmittance of the Al-MSF Film with Al Content of 2 mol%.

Fig. 3 AFM Image of the Al-MSF (a) from the Top, and (b) Thickness Profile at the Edge.

Table 1 Content of Al and Si in the Al-MSF Measured by EDX.

Element	mol %	mol %	mol %
	Al (1)*	Al (2)*	Al (3)*
Al	0.72	1.05	1.60
Si	60.45	62.68	63.12
Al (mol %)	1.2	1.7	2.5

* The figures in parenthesis denote the added amounts of Al atom (mol%).

increase in the Al content of Al-MSF. The tape test was performed to check the adhesion strength of the Al-MSF onto the substrate. The Al-MSF thin film was not observed to be peeled off from the substrate, and thus concluded that the Al-MSF film possesses a good affinity toward the substrate. This could be also confirmed by the fact that Al-MSF film did not detached from the substrate during the immersion process.

3.2 Characterization of TiO₂/Al-MSF

The TiO₂/Al-MSF were prepared by the ion exchange at the anionic sites on the Al-MSF surface using (NH₄)₂[TiO(C₂O₄)₂]·nH₂O, i.e., TAO, and subsequent calcination at 500 °C. **Figure 4** shows the XRD patterns of this TiO₂/Al-MSF film. By comparing between the diffraction peaks of **Fig. 1** and **4**, the *d*₁₀₀ values with and without TAO treatment showed the diameter of the

Fig. 4 XRD Profiles of the TiO₂/Al-MSF with Varying Al Contents (a. 0; b. 1; c. 2; d. 3 mol%).

mesoporous cavity of TiO₂/Al-MSF to be *ca.* 0.1 nm smaller than that of Al-MSF. That is, the inner surface of the TiO₂/Al-MSF cavity was covered by nano sized TiO₂. As shown in **Fig. 5**, the end absorption of the titania coated mesoporous silica thin film, TiO₂/Al-MSF, was shifted to < 300 nm from 380 nm of bulk TiO₂ (anatase). This fact shows that the TiO₂ thin films on the surface of Al-MSF are assumed to be highly and homogeneously dispersed and minimized up to nano-order thickness. This hypsochromic shift of the end absorption of the band gap of the semiconductors are well-known as “quantum size effect”, which has sometimes observed in cases of the TiO₂ supported on zeolites (15-18). Moreover, TiO₂ modification of Al-MSF was confirmed by the stretching vibrations of Ti-O observed at 1087 cm⁻¹ and Ti = O at 975 cm⁻¹, as shown in **Fig. 6** (10,19).

EDX investigations revealed the presence of Ti atoms in the TiO₂/Al-MSF, as summarized in **Table 2**. Ti content (mol%) of the film tends to be saturated by increasing the used Al content of Al-MSF, suggesting that TiO²⁺ was not quantitatively adsorbed to the anionic sites on the mesoporous inner surfaces. This is explainable by the suppression of the smooth introduction of the TiO²⁺ by a static repulsion nearby the ion exchange sites on the mesoporous surface. Now it could be concluded that the ion exchange method is fairly useful in supporting the limited amounts of TiO₂ nano-particles on the surface of Al-MSF.

Fig. 5 UV-Vis Absorption Spectra of Al-MSF (a) and of the TiO₂/Al-MSF with Varying Al Contents (b. 0; c. 1; d. 2; e. 3 mol%).

Fig. 6 FT-IR Spectra of Al-MSF (a) and of the TiO₂/Al-MSF with Varying Al Contents (b, 0; c, 1; d, 2; e, 3 mol%).

3.3 Characterization of Ti-, Al-MSF

The Ti-, Al-MSF were prepared by the co-addition of both ATSB and TAO into the sol-gel MSF precursor solution. The XRD patterns of the Ti-, Al-MSF with Ti contents of 0.1–2 mol% exhibited (1 0 0) diffraction peaks at $2\theta = 2.3$ – 2.4° , which are characteristic of an hexagonal structure, as shown in **Fig. 7(a)** and (b). An increase in the Al or Ti atoms led to a broadening of the diffraction peaks which may be due to a decrease in the crystallinity. However, Ti-, Al-MSF with Ti contents of 5 mol% showed a broadening of the cavity, indicating the distortion of the crystalline mesoporous materials. These facts are comparable with the transmission electron micrographs, as shown in **Fig. 8**, which shows the existence of the slightly distorted hexagonal structure of the porous materials.

The UV-Vis spectra of the Ti-, Al-MSF prepared under conditions of: (a) Al content constant at 1 mol%

with a Ti content of 0.1–5 mol%; and (b) a Ti content constant at 2 mol% with an Al content of 0–3 mol%, are shown in **Fig. 9**. Upon introducing Ti atoms into Al-MSF, the absorption centered at 245 nm increased in intensity and, at the same time, the end absorption also shifted to longer wavelengths of around 300 nm, as can be seen in **Fig. 9(a)** (17,20,21). Even with a constant Ti content of 2 mol%, as shown in **Fig. 9(b)**, the UV absorption tended to shift towards longer wavelengths (22,23). However, the absorption intensity at 245 nm

Fig. 7 XRD Profiles of Ti-, Al-MSF Prepared under Conditions of Ti Content of (a) 0.1 mol%, (b) 0.5 mol%, (c) 1 mol%, (d) 2 mol%, (e) 5 mol% with Varying Al Contents (a, 0; b, 1; c, 2; d, 3 mol%).

Table 2 Elemental Analysis of the TiO₂/Al-MSF Measured by EDX.

Element	mol %			
	Al (0)*	Al (1)*	Al (2)*	Al (3)*
Al	-	0.56	0.80	1.01
Si	41.03	42.26	40.78	38.61
Ti	0.43	0.55	0.44	0.50
Al (mol %)	-	1.3	2.0	2.6
Ti (mol %)	1.0	1.3	1.1	1.3

*The figures in parenthesis denote the amount of Al added (mol%).

Fig. 8 Transmission Electron Micrographs of the Ti-, Al-MSF with Ti of 2.0 mol% and Al of 1.0 mol%.

Fig. 9 UV-Vis Absorption Spectra of the Ti-, Al-MSF Prepared under Conditions of (a) Al Content of 1 mol% and Varying Ti Contents (a. 0.1; b. 0.5; c. 1; d. 2; e. 5 mol%) and (b) Ti Content of 2 mol% and Varying Al Contents (a. 0; b. 1; c. 2; d. 3 mol%).

Fig. 10 SEM Images of the Surface of the Ti-, Al-MSF with Varying Ti Contents (a. 0.1; b. 0.5; c. 1; d. 2; e. 5 mol%).

remained almost constant since the amount of Ti added is not so large and, thus, the end absorption was located shorter than 300 nm, implying the high dispersion of the Ti atoms within Ti-, Al-MSF.

The surface appearance of the Ti-, Al-MSF films on the quartz substrate was investigated by SEM imaging analysis and found to be variable by the change of Ti contents, as shown in **Fig. 10**. The images show that for Ti-, Al-MSF with Ti content of less than 2 mol%, a flat surface could be retained, however, with contents higher than 2 mol%, the excess Ti components were

deposited as microcrystals outside the mesoporous silica, leading to a rougher texture.

Elemental analysis of the Ti-, Al-MSF by EDX measurements are summarized in **Table 3**. The Ti contents of the synthesized Al-MSF were observed to correspond with the Ti contents of the starting reagents used. This indicates the homogeneous and high dispersion of the Ti atoms into the films with Ti content less than 2 mol%. On the other hand, contents of the coexisting Al contents in the films tend to deviate from the ratios of the reagents used. Investigations to quantitatively intro-

Table 3 Elemental Analysis of the Ti-, Al-MSF Measured by EDX.

Element	mol %		mol %		mol %	
	Ti (0.1) Al (3)*	Ti (0.5) Al (3)*	Ti (1) Al (3)*	Ti (2) Al (3)*	Ti (5) Al (3)*	
Al	0.68	0.61	0.61	0.36	0.38	
Si	26.38	37.55	42.12	25.12	27.78	
Ti	0.02	0.38	0.55	0.48	1.56	
Al (mol %)	2.6	1.6	1.4	1.4	1.4	
Ti (mol %)	0.1	1.0	1.3	1.9	5.6	

*The figures in parenthesis denote the amount of Al added (mol%).

duce both Al and Ti are now underway.

3.4 Adsorption of Methylene Blue (MB) into the TiO₂/Al-MSF and Ti-, Al-MSF

The adsorption capacity of the TiO₂/Al-MSF and Ti-, Al-MSF were determined by investigating the time necessary in attaining an adsorption equilibrium. The intensity of the MB absorption maxima were plotted against the immersion period (hr), as shown in **Fig. 11**, using the Ti-, Al-MSF with Ti = 0.5 mol% and Al = 0–3 mol% as a representative example.

An adsorption equilibrium could be obtained within 7 hrs, as shown in **Fig. 11**. For the other thin films with varying Al and Ti contents, similar adsorption equilibrium was observed within immersion period of *ca.* 10 hrs.

Fig. 11 The Plots of the Absorption Maximum Intensity for MB at 600 nm against the Immersion time (hr) of the Ti-, Al-MSF (with Ti Content of 0.5 mol% and Al Contents of 0–3 mol%)-coated Substrate in Aqueous MB Solution.

3.5 Isothermal Profiles for MB Adsorption

Measurements of the adsorption isothermal profiles were carried out after immersion of the TiO₂/Al-MSF, Ti-, Al-MSF and untreated TiO₂ thin films in 1.0×10^{-4} – 5.0×10^{-3} M aq. solution for 48 hrs, as shown in **Fig. 12**.

The Ti-, Al-MSF thin films with Al contents of 0 and 1 mol% were found to have better MB adsorption ability than the films with contents of 2 and 3 mol%. This may be because, interestingly, the amount of Al atoms on the surface decreased with an increase in the amount of Al incorporated. An increase in the Ti content was seen to improve the adsorption ability, indicating an increase in the hydrophilicity of the well dispersed Ti atoms containing surface of the mesoporous silica as the one of the crucial factors controlling the MB adsorption. It could be concluded that Ti-, Al-MSF with Al = 1 mol% and Ti = 2 mol% showed the best adsorption for MB. In comparison, **Fig. 12(c)** shows the adsorption profile of TiO₂/Al-MSF prepared by ion exchange in which the adsorption of the MB increases with the increase in Al content. However still the adsorption was much less efficient compared with Ti-, Al-MSF. This is because in case of TiO₂/Al-MSF, the ion-exchange sites are buried by TiO₂ in the first place so that they cannot fully function as the active anionic sites for the adsorption of MB. On the other hand, for Ti-, Al-MSF, since Ti atoms are co-included within the silica network, the anionic sites formed by Al introduction retained their function as adsorptive sites. Simplified depictions of the mesoporous networks for (a) TiO₂/Al-MSF and (b) Ti-, Al-MSF are shown in **Scheme 1**. Finally, even in case of TiO₂/Al-MSF, they still have the 10 times higher MB adsorption ability compared to TiO₂ film prepared by sol-gel, as shown in

Fig. 12 Isothermal Profiles for MB Adsorption in (a) Ti-, Al-MSF with Ti of 0.1 mol%, (b) Ti-, Al-MSF with Al of 1.0 mol%, (c) $\text{TiO}_2/\text{Al-MSF}$, and (d) the Untreated TiO_2 Thin Films.

Scheme 1 Simplified Depictions for the Mesoporous Networks of (a) $\text{TiO}_2/\text{Al-MSF}$ and (b) Ti-, Al-MSF .

Fig. 12(d).

It could be concluded that the present Ti-, Al-MSF possess an adsorption ability that is *ca.* 40 times more efficient than conventional TiO₂ thin films, as can be seen by the results shown in Fig. 12 and the comparative graph in Fig. 13.

3·6 Photodecomposition of MB Adsorbed on the Ti-, Al-MSF and TiO₂/Al-MSF

MB was easily decolorized by visible light irradiation in aqueous solution, as shown in Fig. 14. Once introduced into mesoporous silica cavities, however, MB is quite stable under light irradiation, which was shown in the same figure (Fig. 14). This fact indicates that the MB adsorbed on the Al-MSF is very durable and would not easily decompose compared to free MB in water.

The photoactivity of the TiO₂/Al-MSF prepared by ion exchange was investigated by monitoring the amount of MB decomposed. Fig. 15 shows the photodecomposition of the MB adsorbed on the TiO₂/Al-MSF. Although the Ti content did not increase with an increase in the Al content, as shown in Table 2, the decomposition of MB was accelerated, presumably because the MB is adsorbed on TiO₂/Al-MSF with a higher adsorptivity with an increase of Al content. This observation indicates that the ion-exchange sites will be used catalytically and adsorbed unreacted MB repeatedly.

Fig. 16(a) shows that the photocatalytic decomposition of MB adsorbed on Ti-, Al-MSF, was accelerated with an increase in the Ti content, and the most efficient

Fig. 14 Comparison of the Decomposition of MB between MB Adsorbed on Al-MSF and MB in Water.

decomposition was observed with Ti content of 2 mol%. On the other hand, as shown in Fig. 16(b), Ti-, Al-MSF thin films with Al content of 1 mol% appeared to have the best decomposition of the MB of the films with various Al content. These results are well correlated with the fact that the maximum adsorption of the MB was observed with Ti content of 2% and Al content of 1%. That is, it is concluded that higher the MB adsorption, the higher the decomposition of the MB.

Control experiments of the photocatalytic decomposition of MB were carried out using conventional, unmodified TiO₂ thin films as a reference standard and the results are shown in Fig. 17.

3·7 Comparative Study of the Ti-, Al-MSF and TiO₂/Al-MSF

The results of the photodecomposition of MB

Fig. 13 Comparison of the MB Adsorption Amounts for Ti-, Al-MSF, TiO₂/MSF (A) and the Unmodified TiO₂ (B) Thin Films.

Fig. 15 Photocatalytic Decomposition of the MB Adsorbed on TiO₂/Al-MSF with Al = 0, 1, 2, 3 mol%.

Fig. 16 Photocatalytic Decomposition of MB Adsorbed on Ti-, Al-MSF (a) Al = 1 mol% and Ti = 0.1, 0.5, 1, 2, and 5 mol%; (b) Ti = 0.1 mol% and Al = 0, 1, 2, 3 mol%.

Fig. 17 Photocatalytic Decomposition of MB Adsorbed on Unmodified TiO_2 Thin Films.

Fig. 18 Comparison of the Photoactivity for the Decomposition of MB Adsorbed on Ti-, Al-MSF, $\text{TiO}_2/\text{Al-MSF}$ (A) and the Unmodified TiO_2 (B) Thin Films.

adsorbed on the Ti-, Al-MSF and $\text{TiO}_2/\text{Al-MSF}$ thin films were analyzed by a comparative study with unmodified TiO_2 thin films and the results are depicted graphically in Fig. 18.

The amount of decomposition for the MB adsorbed on Ti-, Al-MSF, $\text{TiO}_2/\text{Al-MSF}$ and the untreated TiO_2 thin films was measured by irradiation with a Xenon lamp for 480 min. Among these films, the Ti-, Al-MSF exhibited the most efficient photocatalytic reactivity, indicating that the larger Ti atom content for Ti-, Al-MSF than for $\text{TiO}_2/\text{Al-MSF}$ can be considered the one determining factor in the reactivity. Additionally, Ti-, Al-MSF exhibited photocatalytic activity of about 10 times that of the unmodified TiO_2 , as shown in Fig. 18, expressing that the amount of adsorbed MB is another determining factor.

4 Conclusion

The photocatalytic efficiency for the decomposition of methylene blue (MB) was evaluated using TiO_2 loaded Al-modified mesoporous silica prepared by two independent procedures, i.e., $\text{TiO}_2/\text{Al-MSF}$ by an ion-exchange and Ti-, Al-MSF by a sol-gel method. The Ti-, Al-MSF composite films showed higher efficiency than the $\text{TiO}_2/\text{Al-MSF}$ films while both films exhibited far higher performance than the unmodified powdered TiO_2 .

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