Research Article


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Porous F-WO$_3$/TiO$_2$ (mTiO$_2$) films are prepared on titanium sheet substrates using microarc oxidation (MAO) technique. The X-ray diffraction patterns show that visible-light (Vis) enabling mTiO$_2$ films with a very high content of anatase TiO$_2$ and high loading of WO$_3$ are successfully synthesized at a low applied voltage of 300 V using electrolyte containing NaF and Na$_2$WO$_4$ without subsequent heat treatment. The cross-sectional transmission electron microscopy micrograph reveals that the mTiO$_2$ films feature porous networks connected by many micron pores. The diffused reflection spectrum displays broad absorbance across the UV-Vis regions and a significant red shift in the band gap energy ($\sim$2.23 eV) for the mTiO$_2$ film. Owing to the high specific surface area from the porous microstructure, the mTiO$_2$ film shows a 61% and 50% rate increase in the photocatalytic dye degradation, as compared with the N,C-codoped TiO$_2$ films under UV and Vis irradiation, respectively.

1. Introduction

Titanium dioxide (TiO$_2$), known for being environmentally friendly and chemically stable, is one of the most suitable semiconductors for several environmental applications, including air purification, water disinfection, hazardous waste remediation, and, in recent years, the splitting of water to produce hydrogen [1–3]. Upon irradiation of photons with energies greater than or equal to the band gap energy (3.2 eV for anatase TiO$_2$) of the photocatalyst, the photogenerated electrons and holes can either recombine in the bulk or migrate to the surface to initiate various redox reactions. The photocatalytic (PC) reaction is usually accepted to be a surface-oriented phenomenon, regardless of whether it involves fine particles or films [1]. The surface area reportedly dominates the PC activities of the porous anodized TiO$_2$ oxides [4]. A high specific surface area favors PC efficiency. Hence, films that have a rough surface with a high surface area provide superior PC performance. In recent years, substantial effort has been made to improve the PC activities of TiO$_2$ films [4–10]. Porous TiO$_2$ films with a high surface area, such as porous anodized TiO$_2$ oxides [4], nanotube arrays [5, 6], ordered nanopore arrays [7], nanograinized thin films [8], mesoporous structures [9], and hierarchical micro-/nanoporous structures [10], are of great interest for their potential to improve PC activities. Interestingly, in addition to being mechanically stable, the ordered nanopore TiO$_2$ arrays exhibit superior PC and photoelectrochemical (PEC) activities in the degradation of organic compounds against nanotube counterpart arrays, because of their excellent separation and the transport properties of photogenerated electron-hole pairs. In addition to having a high specific surface area, the ordered nanopore TiO$_2$ arrays have a network-framed structure that increases the carrier transport routes.

The use of TiO$_2$ is limited by its wide band gap (~3.2 eV). Semiconductors with smaller band gaps, such as
CdS (2.4 eV), Fe₂O₃ (2.3 eV), and Cu₂O (2.2 eV), commonly suffer from photocorrosion in electrolyte solution and rapid recombination of the photogenerated carriers [1]. Coupling a semiconductor with a high work function with another semiconductor can greatly enhance the oxidation of holes photogenerated in the semiconductor, by increasing the efficiency of carrier separation. Heterostructured oxides, such as TiO₂/ITO, TiO₂/WO₃, CdS/TiO₂, and TiO₂/SnO₂, have been proposed for providing a potential driving force for separating photogenerated charge carriers [2, 11–14]. Of the coupled semiconductors, ITO is the most popular transparent conductive substrates used in photoanodes and photocatalysis [2, 12], but it is one of the most expensive materials and has a detrimental effect on its PEC activity due to the increase in resistivity of the ITO substrate [15]. Among the various heterostructured oxides, TiO₂/WO₃ has been shown to have applications in photocatalysis [9, 16, 17], biophotocathodes [18], and anticorrosion [19]. The improved PC activity of the TiO₂/WO₃ particles has been attributed to the increased surface acidity and improved charge separation due to the proper coupling of WO₃ species with TiO₂ within the nanoparticles [9, 16, 17, 20]. The adsorption affinity of reactant molecules on the surface of the TiO₂/WO₃ photocatalyst is a more important factor than the surface reaction of the photogenerated carriers in determining PC activity. The increase in the adsorption of MB solution is more likely to be associated with an increase in the surface area of the TiO₂/WO₃ particles. However, the enhancement of PC activity under visible-light (Vis) irradiation is reportedly around one tenth of that measured under ultraviolet (UV) irradiation [21].

Some researchers have shown that the introduction of fluorine (F) atoms into a photocatalytic system effectively increases the Vis PC activity of TiO₂ [22–27]. Wu and Chen presented a high Vis PC efficiency of F-doped TiO₂ particulate thin films assisted by NaF solution. They concluded that the presence of F⁻ ions is critical not only to the formation of particulate TiO₂ films, but also to the formation of Ti³⁺ and oxygen vacancies upon F⁻ ion doping, which results in a superior PC efficiency [23]. Moreover, it has been reported that the photocatalytic activity and the anatase crystallinity of porous TiO₂ films can be enhanced by adding appropriate amount of F⁻ ions into the electrolyte in microarc oxidation (MAO) process [26, 27].

MAO, a plasma-assisted electrochemical process, has been used to fabricate a TiO₂ surface layer by applying a positive voltage to a Ti sheet that is immersed in an electrolyte [26]. In addition to its short process duration and less-sophisticated equipments, the MAO process is reportedly a potentially good approach for preparing porous and network-structured TiO₂ films that adhere robustly to a Ti sheet substrate [26–30]. The main mechanism in MAO involves dielectric breakdown, which causes spark discharge and microarcning. Therefore, porous oxide films form on the anode surface [29]. The porous network is regarded as an open, wormlike structure on the surface of the film, with randomly orientated channels. The approach has several potential applications, mostly involving biocompatibility, such as biomimetic apatite [31], orthopedic implants with antimicrobial coatings [30, 32–34], and wear protection [35]. Recently, some related studies have addressed the degradation of dye [4, 26, 27, 36, 37] or dye-sensitized solar cells (DSSC) [38]. For instance, He et al. recently synthesized WO₃/TiO₂ composite films using pulse-MAO at an applied voltage of 400–460 V and electrolyte consisting of Na₂WO₄, NaOH, and NaF. Most recent, porous WO₃/TiO₂ films were also fabricated by DC-MAO at an applied voltage of 450 V using Na₂WO₄ and Na₃PO₄ solution as electrolyte [36]. The relatively high applied voltage of the above-mentioned processes, however, resulted in a significant increase in the content of TiO₂ rutile phase, which is well known to be photocatalytically inferior to the anatase phase in various applications [4]. This is because that applying high voltages results in not only increasing the content of rutile phase but also decreasing the amount of WO₃ loading or W dopant in the porous TiO₂ film.

One of the advantages of MAO process is the possibility of incorporating anionic and/or cationic ions into the TiO₂ layer on an inexpensive Ti substrate, by controlling the composition and concentration of the electrolyte [28–30]. However, the MAO TiO₂ film is liable to contain some free Ti elements and has large pores and a high pore density. Postalkali or heat treatments have been used to improve the morphological and intrinsic characters of MAO coatings [4, 31, 38].

In this study, porous F-TiO₂/WO₃ (mTiO₂) films with incorporated cationic and anionic ions were formed by an MAO process at a relatively low applied voltage using an electrolyte with a properly chosen composition. The PC properties of the as-anodized films were tested by degrading methylene blue (MB) solution under UV and Vis irradiation.

2. Experimental Procedure

2.1. Sample Preparation. Porous mTiO₂ were formed on Ti substrates (25 × 75 × 1 mm) using an in-house MAO system, in which the Ti sample was applied as an anode and a stainless steel container was used as a cathode. The surfaces of the Ti substrates were polished using silicon carbide paper and ultrasonically cleaned three times for 15 min each time, in 100% acetone, 100% ethanol, and distilled water. In a series of screening experiments, the electrolyte solutions were NaF (2 g/L) with Na₂WO₄ (15 g/L), and the applied voltage was 300 V. For comparison, an undoped TiO₂ film (uTiO₂) and an N,C-codoped TiO₂ (nTiO₂) films both deposited on ITO glass substrates with about the same thickness of 1.8 μm were prepared using DC magnetron sputtering system. Details of the nTiO₂ films, which were prepared at a low doping concentration of N and C (<2%) were presented elsewhere [39].

2.2. Sample Characterization. The crystal structures of the samples were analyzed using a high-resolution X-ray diffractometer (XRD, Rigaku ATX-E) and a Micro-PL/Raman spectroscopy (Jobin-Yvon T64000). The surface topography of each sample was determined using an atomic force microscope (AFM, SPI 3800N, Seiko). Surface morphology and chemical composition of the samples were examined by using a scanning electron microscope (SEM, JEOL...
JSM-6700F) equipped with an energy dispersive X-ray spectrometer (EDS). A transmission electron microscope (TEM, Philips Tecnai 20) was employed for microstructure characterization. TEM cross-sectional specimens of the samples were prepared using a focused ion beam (FEI Quant D 200) at a voltage of 30 kV.

The TiO₂ powders from scraping the porous mTiO₂ film was taken to have a BET (Brunauer-Emmett-Teller) surface area measurement. The diffused reflectance of the films was measured by using a UV-vis-NIR spectrometer (Hitachi U-4100) equipped with an integration sphere. Since the Ti substrates are completely opaque and zero transmittance to the incident light, the absorption and band gap energy (E_g) of the samples were calculated using the formula stated in [36, 37, 40]. Two light sources, UV lamps (λ ∼ 365 nm) and blue-light-emitting diodes (BLED, 420 < λ < 530 nm), were used to provide irradiated light intensities of 2.7 and 12.5 mW/cm², respectively. The PC activity was evaluated using aqueous MB solution as model pollution [15]. Aqueous MB solutions without samples were also illuminated in the same manner to generate a blank value, and such a solution with samples was not irradiated, as an adsorption test.

3. Results and Discussion

3.1. Microstructural Measurements. Figure 1 presents the XRD patterns of as-anodized mTiO₂ sample along with the N,C-codoped TiO₂ (nTiO₂) and pure TiO₂ (uTiO₂) for comparisons. The XRD patterns of mTiO₂ reveal a fully dominant anatase TiO₂ phase. The peak marked by a triangle is associated with Ti, and may derive from the Ti substrate and from not well-anodized TiO₂ oxide, which is the result of random arcing by MAO [35]. Sample mTiO₂ also exhibits an intense diffraction peak at 2θ = 23.67° of crystalline WO₃ peaks of (020) plane, as also detailed in the inset in Figure 1. A broad diffraction peak from 2θ = 33° to 34.5° is assigned to a crystalline WO₃ phase [41]. Comparing with uTiO₂ in the inset of Figure 1, the diffraction (101) plane is shifted slightly toward a lower 2θ value, suggesting possible distortion of the crystal lattice of TiO₂ by the tungsten, fluorine, or/and other dopants. However, a small shift towards higher diffraction angles, due to different ion radii of Ti and W, has been observed in the XRD patterns of the anatase TiO₂ phase as W is doped on titania [37]. Sample mTiO₂ has a slightly broader peak at 2θ = 25.18° than the uTiO₂, indicating the smaller crystallite size of the mTiO₂. These findings imply that the substitution of Ti⁴⁺ ions for W⁴⁺ in the TiO₂ lattice to form a nonstoichiometric WₓTi₁₋ₓO₂ solid solution may have occurred in the mTiO₂ film [9]. In the case considered herein, the loaded WO₃ likely favors the formation of the anatase TiO₂ phase by the MAO process, which can be further studied by acquiring Raman spectra. Thus, the WO₃ phase was loaded with a noticeable content on the TiO₂ matrix. The amounts of O, Ti, and W were found to be 68.27, 25.59, and 6.14 at.%, respectively, whereas the fluorine was too small beyond the detectable limit of the EDS. Noted also that the relative high amount of tungsten oxides of which could be promoted by addition of fluorine in the electrolyte was reportedly attributable to the high photocatalytic ability [27, 37].

Raman spectra in the range of 100–1150 cm⁻¹, shown in Figure 2, reveal further information on the structure of the films. Sample mTiO₂ yields four distinct Raman peaks at 146, 394, 516, and 637 cm⁻¹ with slight broadening, as compared with the other two samples, which are directly attributable to the anatase phase [42]. This result is ascribed to the crystallinity of the anatase phase and is consistent with the XRD patterns. A shift in the high wave number and broad peak of the Raman spectrum at 146 cm⁻¹ implies that the substitution of W ions into the MAO-anodized TiO₂ lattice and less well-crystallized TiO₂ particles probably occurred. The Raman peak at 810 cm⁻¹ which is associated with the
crystallized monoclinic or orthorhombic WO₃ is extremely weak, as shown in the inset of Figure 2, perhaps because of interference with a broad background signal of anatase TiO₂ [21]. A relatively broad band at 970 cm⁻¹ is assigned to a terminal W=O stretching vibration in tungsten trioxide hydrates. Additionally, a shift in the high wave number of the WO₃ Raman spectrum at ~970 cm⁻¹ reveals that WO₃ nanocrystallites had formed along the TiO₂ surface or grain boundaries in a relatively high W concentration [9, 16, 43], which was previously conformed by the EDS measurement.

3.2. XPS Analysis. High-resolution XPS measurements were performed to elucidate the surface chemical composition and the oxidation state for the porous mTiO₂ film. Curve fitting using Gaussian distribution function plotted in Figure 3(a), the XPS spectrum of Ti₂p core level of the mTiO₂ film shows two well-known peaks at binding energy of ~459.0 eV and at ~464.1 eV, corresponding to Ti₂p₃/2 and Ti₂p₁/2, respectively, of Ti⁴⁺ oxidation state of TiO₂. A minor peak at binding energy of ~457.0 eV is also observed, which is assigned to Ti³⁺ of Ti₃O₇ phase and is in accordance with the XRD result presented in Figure 1. Alternatively, the O₁s core level binding energies for sample mTiO₂ were deconvoluted into three distinct components, indicating that there are different kinds of O binding states in the mTiO₂ film, as shown in Figure 3(b). It is well stated that the peak at binding energy of 530.7 eV can be assigned as the crystal lattice oxygen of Ti–O and W–O binding, while the peaks at binding energy of 531.6 and 532.8 eV represent the oxygen in hydroxyl groups (O–H) and in adsorbed water molecules on the film [9, 37]. It is worthy to note that the area under hydroxyl groups (O–H) is estimated to be as large as 26.2%, which is ascribed for enhancing photocatalytic activity [44].

As seen in Figure 3(c), though the peak positions of W⁴f₅/₂ (A) and W⁴f₇/₂ (B) shift to a higher binding energy compared to the reported values, their oxidation state of the incorporated tungsten species is reportedly assigned as W⁶⁺ oxidation state of pure WO₃ [9]. The lower binding energy
shift can also be seen in the W4d peaks of sample mTiO2, as shown in the inset of Figure 3(c). These indicate that sample mTiO2 was loaded with a considerably high amount of WO3 phase. The other two peaks (C and D) are intuitively assigned to other tungsten oxide (i.e., WO2) or some nonstoichiometric tungsten oxides such as W12O39n− and impurities from the precursors used. Nevertheless, some other phases possibly form, since stoichiometric ion exchange between W4+ and Ti4+ may occur [17]. In fact, W4+ can substitute Ti4+ in the lattice of TiO2 due to the similarity in their ion radii; nonstoichiometric solid solution of WxTi1−xO2 forms. Thus, nonstoichiometric solid solution of WxTi1−xO2 can form and leads to produce a tungsten impurity energy level [17]. Some researchers have reported that the W4f peaks of WO3-loaded TiO2 shift to a lower binding energy [43], but others have found a backward shift, as compared to that of pure WO3 [37]. This may be due to different methods and precursors involved in sample preparation. This is being under taken further investigation in our lab. As seen in Figure 3(d), a weak and broad F1s peak at binding energy of ~684.9 eV is observed for sample mTiO2, which is mostly originated from F− ions physically adsorbed on the TiO2 surface [24]. Park and Choi have conclude that the adsorbed F− ions induce enhancement in the production of •OH radicals [44] when the F-containing compounds were used as TiO2 precursors. However, no peak around 687.6 eV is observed which is attributed to the doped F atoms in TiO2 [24, 45].

On the basis of the XPS results stated above, it can be briefly concluded that F− ions is physically adsorbed on the TiO2 surface in a very low concentration and W ions are likely loaded as a pure WO3 phase along with other tungsten oxides and WxTi1−xO2 composite on the mTiO2 film.

3.3. Morphological and Topographical Observations. Porous TiO2 films with improved connectivity are reportedly important for adsorbing organic contaminant ions or initiating various redox reactions [29]. Figure 4(a) presents the morphological SEM image of sample mTiO2, showing a typical porous MAO structure with some submicron pores and colloidal particles on a large cavity. Moreover, Figure 4(d) shows a FIB projected image of the mTiO2, where sponge-like morphology is filled with various micron and submicron pores. These submicron pores were probably formed by the secondary breakdown of the large pores that were produced by the primary breakdown of arcing [29]. The wall of the larger pores includes smaller pores and several pores inside the film of which increases its reactive site surface area. On the other hand, as shown in Figures 4(b) and 4(c), samples nTiO2 and uTiO2 exhibit a typical columnar-like morphologies deposited by a DC magnetron sputtering.
Table 1: Some properties and apparent rate constants of three samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band gap energy, eV</th>
<th>Specific surface area, m²/g</th>
<th>Apparent rate constant, h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>mTiO₂</td>
<td>2.23</td>
<td>1.75</td>
<td>UV 0.53</td>
</tr>
<tr>
<td>nTiO₂</td>
<td>2.93</td>
<td>0.16*</td>
<td>Vis 0.42</td>
</tr>
<tr>
<td>uTiO₂</td>
<td>3.25</td>
<td>0.14*</td>
<td>Vis 0.28</td>
</tr>
</tbody>
</table>

* estimated from the AFM measurement [37].

Figure 5: Cross-sectional TEM micrograph of the mTiO₂ film in which the porous TiO₂ was formed on a 300 nm-thick TiO₂ layer supported by Ti substrate.

3.4. Optical Properties. Figure 6 shows the diffused reflection spectra of sample mTiO₂ film, displaying broad absorbance across the UV-Vis regions. Obviously, sample mTiO₂ has a better optical absorption in the region of 400–700 nm owing to the presence of tungsten oxides and solid solution of WₓTi₁₋ₓO₂ than the N,C-TiO₂ and pure TiO₂ [17]. It is well known that the absorption edge of the samples shift toward the Vis region as WO₃ is loaded on TiO₂ matrix [9, 16–19, 37]. The band gap energies are calculated according to the equation $E_g = \frac{hc}{\lambda}$, where $E_g$ is the band gap energy (eV), $h$ is the Planck’s constant (4.136 × 10⁻¹⁵ eV s), $c$ is the velocity of light (2.99 × 10⁸ m/s), and $\lambda$ is the wavelength (nm) of absorption onset [36, 40]. The band gap energies are 2.23 eV for mTiO₂ and 2.93 eV for nTiO₂ films, whereas that is estimated to be 3.25 eV for the pure TiO₂ [39]. Although some researchers reported that only F-doping did not cause any significant change in the optical absorption of TiO₂ (2.90–2.95 eV [24, 26]), they observed a new absorption band in the visible range of 400–550 nm in addition to a strong fundamental absorption edge (∼387 nm) of TiO₂ [24, 45]. Thus, the shift towards the longer wavelengths markedly originates from the band gap narrowing of TiO₂ by coupling with tungsten oxides [37, 43] and possibly a complex of WₓTi₁₋ₓO₂ [17].

3.5. Photocatalytic Activities. PC activity can be increased by increasing the apparent reaction rate constant and the equilibrium adsorption constant of the catalysts [16]. Figure 7 plots the degraded concentration of the MB solution against the reaction time of three different samples. No significant MB degradation is observed in a blank substrate under UV radiation. As expected, Figure 7 clearly reveals that the adsorption of MB by sample mTiO₂ was stronger than that of samples nTiO₂ and uTiO₂, due to the cationic nature of MB dye [17]. The MB adsorption capacity of TiO₂/WO₃ composites usually increases with the loading technique [15, 39]. Thus, a low specific surface area is expected, rendering a low active area in contact with aqueous solution. The cross-sectional TEM micrograph of the mTiO₂ film in Figure 5 reveals that a pore diameter ranging from 400 to 800 nm was formed on a WO₃/TiO₂ layer with a thickness of about 300 nm. The porous network connected by many micron pores is regarded as an open with randomly orientated channels in the porous film.

The specific roughness factor of nTiO₂ and uTiO₂ films (Figures 4(b) and 4(c)) were previously reported to be about 1.3 and 1.2, which were equal to surface areas of about 0.16 m²/g and 0.14 m²/g, respectively (Table 1) [15, 39]. The mTiO₂ shows a BET surface area of 1.75 m²/g, which is ten times greater more than that of the nTiO₂ and uTiO₂. Thus, extremely rough, network-structured, and well-crystallized TiO₂ films can be obtained by MAO process without any subsequent heat treatment.

Figure 6: Diffused reflection spectra of the mTiO₂ and nTiO₂ films.
As listed in Table 1, under UV irradiation, sample mTiO$_2$ exhibits the highest activity of the three samples tested, showing the highest apparent rate constant of 0.53 h$^{-1}$–61% greater than that, 0.33 h$^{-1}$, of sample nTiO$_2$. Sample mTiO$_2$, broad absorbance observed in the Vis regions, exhibits significant PC activity under BLED irradiation, an apparent rate constant of 0.42 h$^{-1}$–50% greater than that, 0.28 h$^{-1}$, of sample nTiO$_2$, as shown in Figure 8. Sample nTiO$_2$ has an apparent rate constant of 0.36 h$^{-1}$ and 0.06 h$^{-1}$ under UV and Vis irradiation, respectively.

The PC activity of TiO$_2$ depends on several factors, including crystallinity [47], surface area [8], crystal orientation [48], surface hydroxyl density, and phase composition [49, 50]. In general, the photogenerated charge carrier transfer to the film surface would be limited by the interfacial diffusion between crystalline WO$_3$/TiO$_2$ particles, which is faster than volume diffusion. And the sponge-like porous structure of the mTiO$_2$ film can make charge carrier easier to reach the surface than a typical planar nTiO$_2$ sample. The porous mTiO$_2$ film exhibits the highest PC activity among the oxides of interest; surprisingly, only 50%–61% higher in photocatalytic activity obtained from the film with ten times greater in the surface area than others. Qualitatively, the mTiO$_2$ film consists of TiO$_2$ and WO$_3$ crystallites with a higher specific surface area and a lower crystallinity than the nTiO$_2$ and uTiO$_2$ films. The PC activity of mTiO$_2$ is enhanced by its WO$_3$ crystallites and high specific surface area but is reduced by its low crystallinity and some impurities, such as Ti and Na elements. Impurities act as carrier recombination centers in an oxide and always detrimentally affect PC activity. In contrast, high crystallinity is associated with a small fraction of crystal defects that act as recombination sites [7–9], allowing the generated charges to diffuse to the crystallite surface without undergoing recombination [4]. Thus, improvement of crystallinity is a possible way to increase the film photocatalytic ability.

In addition, though WO$_3$ has a conduction band that allows for the transfer of photogenerated electrons from TiO$_2$, its valence band is not positioned properly toward to the coupled TiO$_2$; therefore, effective charge separation cannot be fully obtained in crystalline TiO$_2$/WO$_3$ heterostructures [41]. The formation of WO$_3$ crystallites, randomly distributed along TiO$_2$ nanocrystals, rather than the highly adsorbing WO$_3$ monolayer or amorphous WO$_x$, reduces the adsorption capacity of WO$_3$ [20, 41]. Finally, the amount of tungsten loaded onto TiO$_2$ was not optimized herein, but this factor reportedly is important in determining PC activity [9, 16, 21, 46].

4. Conclusions

In this study, a porous F-TiO$_2$/WO$_3$ film with crystallized anatase TiO$_2$ phase and network-framed structure was successfully obtained by microarc oxidation without subsequent heat treatment. The F-TiO$_2$/WO$_3$ film exhibits high photocatalytic activity in MB degradation under UV and BLED irradiation. The Vis PC efficiency is dominated by the incorporation of tungsten oxides and possibly a complex of W$_x$Ti$_{1-x}$O$_2$. The specific surface area of the film
is one of the most important parameters in determining the efficiency of the PC process, because a higher specific surface area favors the adsorption of more MB molecules on its active sites. Thus, the elucidated MAO process is one of the most cost-effective methods for producing films in practical photocatalytic applications.

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References


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