

In-situ investigations of the photoluminescence properties of $\text{SiO}_2/\text{TiO}_2$ binary and Boron- $\text{SiO}_2/\text{TiO}_2$ ternary oxides prepared by the sol-gel method and their photocatalytic reactivity for the oxidative decomposition of trichloroethylene

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ABSTRACT. Photoluminescence behavior of TiO_2 , $\text{SiO}_2/\text{TiO}_2$ binary and Boron- $\text{SiO}_2/\text{TiO}_2$ ternary oxides prepared by the sol-gel method was investigated. The differences in their photocatalytic reactivities of TiO_2 -based photocatalysts were interpreted in terms of the relationship of the difference in their photoluminescence characteristics. The addition of SiO_2 into TiO_2 matrix induced new photoluminescence sites, which were due to anchored titanium oxide species (i.e., the formation of $\text{Ti}-\text{O}-\text{Si}$ bonds) located on the surface. The photoluminescence was found to be very sensitive to the presence of oxygen. These new photoluminescence completely disappeared by the addition of boron into $\text{SiO}_2/\text{TiO}_2$ binary oxide, since the emitting sites having a $\text{Ti}-\text{O}-\text{Si}$ bond were destroyed and the new sites having $\text{B}-\text{O}-\text{Ti}$ or $\text{Si}-\text{O}-\text{B}$ bonds were constructed on the surface, being in agreement with the results obtained by FT-IR measurements. For all TiO_2 -based photocatalysts, a significant quenching of photoluminescence was observed by the addition of oxygen. It was found that the photocatalytic reactivity of TiO_2 -based photocatalysts for the decomposition of trichloroethylene was clearly associated with their relative quenching efficiencies of photoluminescence; photocatalyst showing high quenching efficiency exhibited a high photocatalytic reactivity.

1. INTRODUCTION

TiO_2 nano-particles are the best candidate as a photocatalyst having high thermal stability and high activity for the decomposition of various toxic organic materials in aqueous solutions [1-6]. The enhancement of photoreactivity of TiO_2 photocatalysts has been a big objective in the research field of photocatalysis. The following factors can be considered to play vital roles in controlling the photocatalytic reactivity of TiO_2 ; particle size, crystal phase, temperature of heat treatment, surface area, surface-bounded species, pH of solution, and the kinds of additives [2, 4, 7-11]. In recent years, the second metal oxide such as SiO_2 , AlO_3 , ZrO_2 , and WO_3 are frequently used as additives to modify the surface or bulk properties of TiO_2 photocatalysts [12-16]. Photocatalytic reactions proceed on the surface of TiO_2 catalysts, therefore, it is important to know the detailed morphology of the surface active sites which interact with photogenerated electrons and/or holes as well as the reactant molecules.

The measurement of photoluminescence of the photocatalysts is one of the most important and useful

ways to elucidate the surface properties related to adsorption, catalysis, and photocatalysis [17]. For example, the photoluminescence spectrum of TiO_2 nano-particles is efficiently quenched by the addition of oxygen onto the surface through an increase in the extent of the band bending of TiO_2 photocatalyst due to the adsorption of O_2^- species [18-22]. Thus, it is possible to monitor the changes in the reactivity of the photocatalyst in various atmosphere by measuring the photoluminescence properties of the photocatalysts.

In this work, three kinds of TiO_2 -based photocatalysts (TiO_2 , $\text{SiO}_2/\text{TiO}_2$, Boron- $\text{SiO}_2/\text{TiO}_2$) were prepared by the sol-gel method and their characteristics of photoluminescence properties were investigated to elucidate the factors which control the photoactivity of these photocatalysts.

2. EXPERIMENTAL

The conventional sol-gel technique was used to prepare TiO_2 -based photocatalyst. Titanium ethoxide (TEOT, Aldrich, ~ 20% Ti in excess ethanol) and Tetraethylorthosilicate (TEOS, Aldrich, 98%) were used as TiO_2 and SiO_2 precursor, respectively. Boric acid (Aldrich, 99.99%) was used as the precursor of boron. Pure TiO_2

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Table 1. Physicochemical properties of as-prepared TiO₂ based oxides.

| Catalyst | Calcination temperature (K) | Crystal phase | D _c ^{c)} (nm) | BET (m ² /g) |
|--|-----------------------------|---------------|-----------------------------------|-------------------------|
| TiO ₂ | 773 | Anatase | 23.1 | 45.9 |
| SiO ₂ /TiO ₂ ^{a)} | 1073 | Anatase | 14.1 | 189.9 |
| Boron-SiO ₂ /TiO ₂ ^{b)} | 1173 | Anatase | 14.5 | 33.5 |

a) Ti/Si = 2.3 (30 at.% of Si),

b) Ti/B = 19(5% of Boron) and Ti/Si = 2.3,

c) crystallite size calculated by the Scherrer equation at $2\theta = 23.3^\circ$.

particles were prepared in an excess water solution ($\text{H}_2\text{O}/\text{M}^+ = 150$ mole %, where M^+ indicates the total mole of alkoxide used) containing HCl ($\text{H}^+/\text{M}^+ = 0.2$) and ethyl alcohol ($\text{Et-OH}/\text{M}^+ = 1$). For SiO₂/TiO₂ binary oxide, TEOS was hydrolyzed in the first step with the pre-mixed water solution because the hydrolysis rate of TEOS was much slower than that of TEOT. The hydrolyzed precursor solution was mixed for 24 hrs at room temperature and for 5 hrs at 348–353 K to remove the added and produced alcohol. Finally, the sol solution was dried in a dry oven at 373 K for 12 hrs and then the obtained xerogel was calcined at 773 to 973 K. For Boron-SiO₂/TiO₂ ternary oxide, boric acid was added to the silica/titania sol solution which was prepared by hydrolyzing both TiO₂ and SiO₂ precursors in the same ways as the preparation of SiO₂/TiO₂ binary oxide. The percentage of silicon and boron with respect to titanium atom in SiO₂/TiO₂ binary or Boron-SiO₂/TiO₂ ternary oxides was fixed to be 30 atm. % and 5%, respectively.

The major crystal phase of all TiO₂-based photocatalysts was determined from the X-ray diffraction patterns obtained by using a Rigaku D/MAX-III(3 kW) diffractometer. Surface areas of the prepared Ti-based particles were determined by nitrogen physisorption data at 77 K using a Micromeritics ASAP 2400. FT-IR spectra of the catalysts were obtained by a Bomem MB-100 spectrometer. UV/visible spectra were measured by an UV/visible spectrophotometer (UV-250 1PC, Shimadzu).

Semi-circulation batch reactor of annular shape was used to test the photoreactivity of these TiO₂-based photocatalysts for the decomposition of trichloroethylene (TCE). The photocatalyst used and the initial concentration of TCE were fixed to be 1 g/l and 37 ppm, respectively. The reaction solution suspending photocatalyst particles and solving reactant molecules was irradiated by ultraviolet light (15 W, black light). The change in the TCE concentration was monitored by Cl⁻ electrode (Orion, model 96-17B) as a function of reaction time.

The photoluminescence spectra of these photocatalysts were measured at 77 K using a Shimadzu RF-5000 spectrofluorophotometer. A quartz cell with a window and furnace section connected to a vacuum system (10^{-6} Torr) was used for the in situ measurements of the photoluminescence spectra before and

after various thermal pretreatments. Prior to spectroscopic measurements, each photocatalyst sample (TiO₂, SiO₂/TiO₂, and 5% Boron-SiO₂/TiO₂) was evacuated at 573 K for 3 hrs then calcined at 473 K with oxygen of 200 Torr for 2 hrs followed by the evacuation at the same temperature.

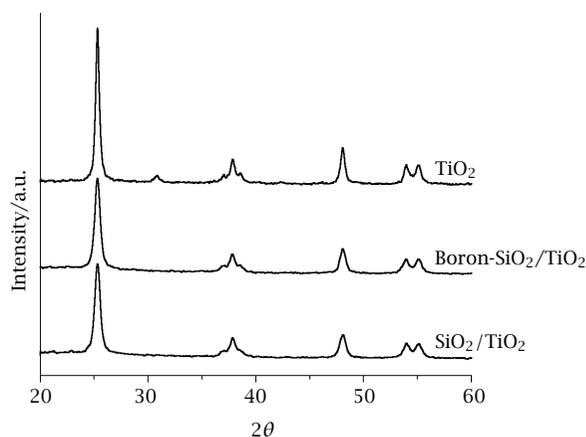


Figure 1. XRD patterns of TiO₂ (calcined at 773 K), SiO₂/TiO₂ (calcined at 1073 K), and Boron-SiO₂/TiO₂ (calcined at 1173 K) powder prepared by the sol-gel method.

3. RESULTS AND DISCUSSION

The photocatalytic reactivity of these binary and ternary oxide photocatalysts is strongly dependent on the crystal phase of the moiety of TiO₂. Figure 1 shows the XRD patterns of the TiO₂-based photocatalysts prepared by the sol-gel method. All samples exhibit a pure anatase phase even after the calcination of SiO₂/TiO₂ binary and Boron-SiO₂/TiO₂ at 1073 and 1173 K, respectively. The physicochemical properties of these TiO₂-based photocatalysts are summarized in Table 1. It should be noted that the crystallite sizes of TiO₂ which were calculated by the Scherrer equation at $2\theta = 23.3^\circ$ increase in the order of SiO₂/TiO₂ (14.1 nm) < Boron-SiO₂/TiO₂ (14.5 nm) < TiO₂ (23.1 nm).

For the SiO₂/TiO₂ and Boron-SiO₂/TiO₂ catalysts, SiO₂ moiety is embedded into the TiO₂ moiety to form SiO₂/TiO₂ binary oxide and may exist as a segregated amorphous phase of SiO₂ which prevents TiO₂ moiety to form large crystals. In such cases, it is expected

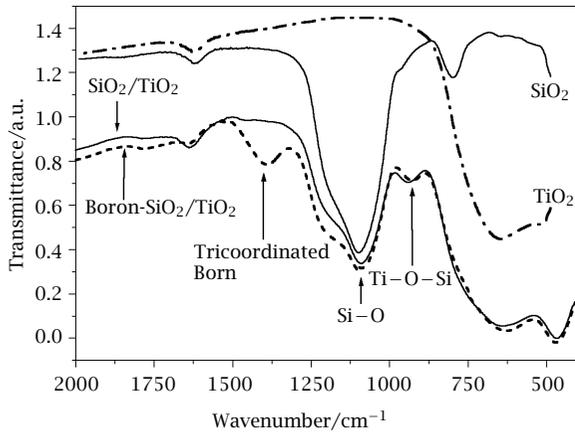


Figure 2. FT-IR spectra of TiO₂, SiO₂, SiO₂/TiO₂, and Boron-SiO₂/TiO₂.

that the Ti-O-Si bonds are formed in some part of the SiO₂/TiO₂ matrix. Figure 2 shows the FT-IR spectra of TiO₂, SiO₂/TiO₂, and Boron-SiO₂/TiO₂ catalysts as well as SiO₂ as a reference. The peak observed at around 1095 cm⁻¹ corresponds to the asymmetric vibration of a Si-O-Si bond [27, 28]. The peak at around 940 cm⁻¹ attributed to the linkage of the Ti-O-Si bond are observed with both SiO₂/TiO₂ binary and Boron-SiO₂/TiO₂ ternary oxides, indicating that the Ti-O-Si bonds are formed by mixing SiO₂ with TiO₂ to form binary oxides [27]. An intrinsic peak at 1393 cm⁻¹ can be seen only with Boron-SiO₂/TiO₂ ternary oxide. This characteristic peak can be associated with the formation of tri-coordinated boron in the SiO₂/TiO₂ binary oxide frameworks [29, 30]. These results clearly suggest that Si-O-Ti bonds are successfully produced by mixing TiO₂ phase and amorphous SiO₂ phase, it resulting in the prevention of the formation of large TiO₂ crystals, while boron exists in a tri-coordinated state in the SiO₂/TiO₂ binary oxides.

Figure 3 shows the UV/Vis reflectance spectra of TiO₂, SiO₂/TiO₂, Boron-SiO₂/TiO₂ catalysts. TiO₂ exhibits a typical absorption band due to the bandgap transition of TiO₂ having an anatase phase ($\lambda < 390$ nm), while the absorption spectra of SiO₂/TiO₂ binary and Boron-SiO₂/TiO₂ ternary oxides were found to shift toward shorter wavelength regions. Since the absorption bands were found to shift toward shorter wavelength regions with a decrease in the TiO₂ crystal size of the catalysts (TiO₂(23.1 nm) > Boron-SiO₂/TiO₂ (14.5 nm) > SiO₂/TiO₂(14.1 nm)), such a spectral shift toward shorter wavelength can be attributed to the size quantization effect due to the presence of TiO₂ particles of particularly small size of TiO₂ moiety in the SiO₂/TiO₂ binary oxide.

As shown in Figure 4, TiO₂-based photocatalysts shows the photoluminescence spectra at around 450-550 nm upon the excitation when excited with light

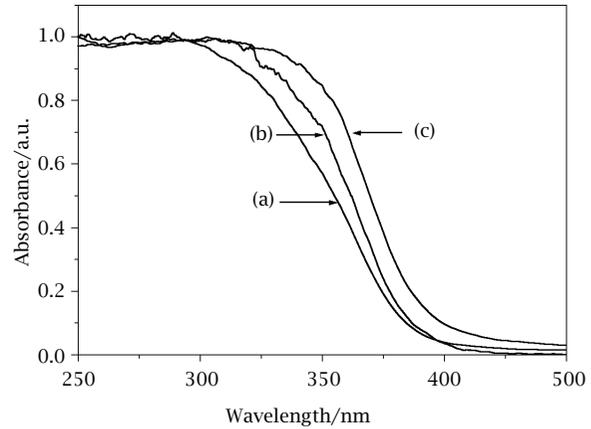


Figure 3. UV/Vis reflectance spectra of SiO₂/TiO₂ (a), Boron-SiO₂/TiO₂ (b) and TiO₂ (c).

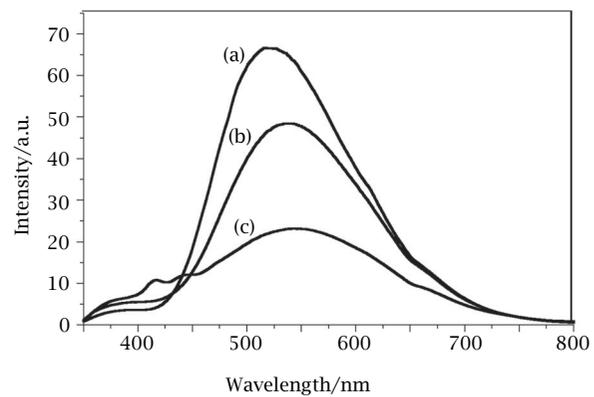


Figure 4. Photoluminescence spectra of TiO₂ (a), Boron-SiO₂/TiO₂ (b) and SiO₂/TiO₂ (c) measured at 77K under a vacuum condition.

having energies larger than the bandgap energy of the catalyst. These observed photoluminescence spectra can be attributed to the radiative decay processes from the photoformed electron and hole pair states at the specific surface sites. The difference in the photoluminescence yields of these catalysts can be ascribed to the differences in numbers of the surface sites responsible for the photoluminescence or the different efficiency in the rates of the thermal deactivation process of the photoformed electron and hole pair states. It is notable that the SiO₂/TiO₂ binary oxide calcined at 1073 K shows a new photoluminescence peak at around 400-480 nm. This peak, however, could not be observed with the Boron-SiO₂/TiO₂ ternary oxide or pure TiO₂ powder. In general, the photoluminescence peak with bulk TiO₂ is observed at around 450-550 nm [20, 23]. The peak at around 400-480 nm is not due to bulk TiO₂ but highly dispersed TiO₂ moiety anchored onto the SiO₂ surfaces or into zeolite framework [24-26].

Photocatalysis is a surface phenomenon initiated by the irradiation of UV light of higher energy than the bandgap of the photocatalyst used. It can be seen that the surface properties involving the nature of active sites and its numbers play a key role in determining the photocatalytic reactivity of the catalysts. It is, therefore, important to characterize the surface active sites and their reactivity for various photocatalysts prepared by different preparation methods. The quenching of the photoluminescence of the catalyst can be related to the changes in the surface properties which result from the interaction between the surface and the electron acceptor molecules. In the present work, therefore, the relative reactivity of photocatalysts toward oxygen molecule was estimated by the quenching degree of the photoluminescence by the addition of O_2 .

For all TiO_2 -based photocatalysts, the addition of 20 Torr of O_2 led to a considerable quenching of the photoluminescence. As shown in Figure 5, in the presence of 20 Torr of O_2 , the intensity of the photoluminescence decreased to 89% of its original intensity for SiO_2/TiO_2 , 37% for TiO_2 and 26% for Boron- SiO_2/TiO_2 , respectively. It has been reported that the addition of O_2 at 298 K onto TiO_2 photocatalyst leads to the formation of O_2^- anion radicals stabilized on Ti^{4+} sites. The formation of such negatively charged adducts (O_2^-) results in an increase in the surface band bending of the TiO_2 , leading to a quenching of the photoluminescence through a suppression of the efficiency of the radiative recombination of the photoformed electrons and holes at the surface [20]. The photoluminescence can be easily quenched by the addition of O_2 in the case of TiO_2 -based catalysts with high photocatalytic reactivity since an efficient formation of surface O_2^- anion radicals which play a important role in oxidation reaction can be expected. In line with these arguments, the reactivity of the photocatalysts toward oxygen was found to increase in the order of SiO_2/TiO_2 , TiO_2 and Boron- SiO_2/TiO_2 . It is notable that the peak at around 400–480 nm, attributed to the photoluminescence from TiO_2 moiety having Ti–O–Si bonds is quenched completely by the addition of oxygen. These results clearly show that the peak at around 400–480 nm is attributed to the photoluminescence from the TiO_2 moiety having Ti–O–Si bonds and these TiO_2 moieties play an important role as the active sites leading to the formation of O_2^- anion radicals. On the other hand, with the Boron- SiO_2/TiO_2 ternary oxides, the photoluminescence peak at around 400–480 nm could not be observed. These results showed a good agreement with that the TiO_2 moieties having Ti–O–Si bonds are not formed on the Boron- SiO_2/TiO_2 oxides but the TiO_2 moieties having Ti–O–B or Si–O–B bonds are formed at the surface. However, the FT-IR peak which could be observed at around 940 cm^{-1} , as shown in Figure 2, suggest that the Ti–O–Si bonds still remain in the bulk of the Boron- SiO_2/TiO_2 matrix.

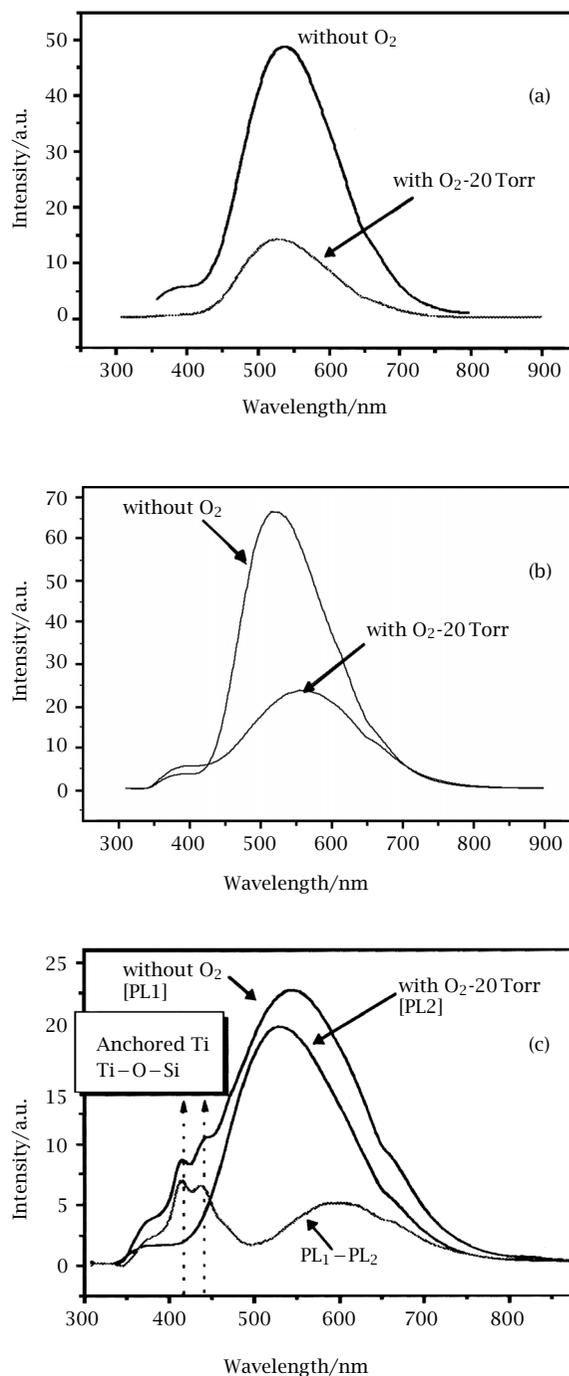


Figure 5. Photoluminescence spectra of Boron- SiO_2/TiO_2 (a), TiO_2 (b) and SiO_2/TiO_2 (c) and measured at 77K with and without O_2 . Added O_2 : 20 Torr.

It has been reported that O_2^- as well as OH radicals formed on the TiO_2 surface under UV irradiation act as important oxidants in the photodegradation of organic compounds in aqueous solution. As mentioned above, the quenching of the photoluminescence in the presence of O_2 are closely related to the formation of the

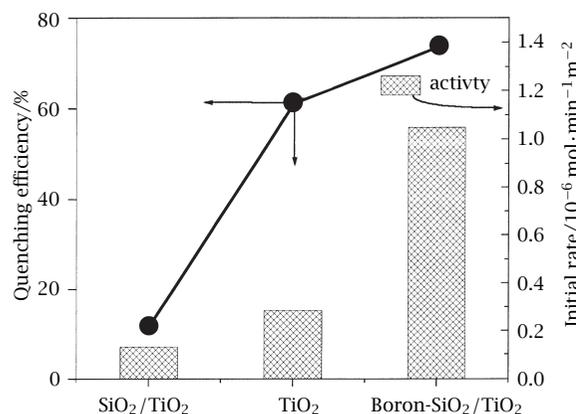


Figure 6. Relationship between the quenching efficiency and the intrinsic photoactivity (TCE decomposition) of TiO₂, SiO₂/TiO₂, and Boron-SiO₂/TiO₂.

O₂⁻ anion radicals on the TiO₂ surface. Figure 6 shows the relationship between the quenching efficiency of photoluminescence and the photocatalytic reactivity of TiO₂-based photocatalysts for the decomposition of TCE. The quenching efficiency (QE) is defined as follows:

$$QE(\%) = 100 * (PL_{\text{vacuum}} - PL_{O_2}) / PL_{\text{vacuum}},$$

PL_{vacuum} : Intensity of photoluminescence under vacuum,

PL_{O₂} : Intensity of photoluminescence in the presence of 20 Torr of O₂.

It is clear that there is a close relationship between quenching efficiency and photocatalytic activity, i.e., the higher the quenching efficiency, the higher is the photocatalytic activity. Here, the effect of the crystal structure on the photocatalytic activity can be excluded since all of the prepared TiO₂-based photocatalysts have an anatase phase structure. Therefore, it can be considered that O₂⁻ anion radicals are efficiently formed on the TiO₂-based photocatalyst which exhibits the high quenching efficiency, leading to the high decomposition rate of TCE through the efficient reaction of O₂⁻ anion radicals with TCE. Thus, it is demonstrated that the photoluminescence investigations of the photocatalysts can be applied to estimate the activity of the photocatalysts for the various oxidative reactions, especially by monitoring the quenching efficiency of the photoluminescence in the presence of gaseous oxygen [17].

4. CONCLUSIONS

Three kinds of different photocatalysts such as TiO₂, SiO₂/TiO₂ binary and Boron-SiO₂/TiO₂ ternary oxides were prepared by the sol-gel method. The photoluminescence properties of these TiO₂-based photocatalysts

were investigated and applied to interpret the difference in the photocatalytic reactivity of these three types of catalysts for the decomposition of TCE.

For all prepared TiO₂-based photocatalysts, a considerable quenching of photoluminescence was observed in the presence of oxygen, which leads to an efficient electron scavenging to form O₂⁻ anion radicals on the surfaces. It was found that the photocatalytic reactivity of TiO₂-based photocatalysts for the decomposition of trichloroethylene is related to their relative quenching efficiency of photoluminescence, i.e., photocatalyst showing larger quenching efficiency in photoluminescence exhibit higher photocatalytic reactivity.

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