

## SYNTHESIS AND PROPERTIES OF ORGANO-FLY ASH/POLYANILINE WITH CORE/SHELL STRUCTURE BASED ON EMULSION POLYMERIZATION\*

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**Abstract** Organo-fly ash (OFA) was prepared with pretreated fly ash (FA) and hexadecyltrimethyl ammonium bromide (HDTMAB), and the composites composed of OFA and polyaniline were obtained by emulsion polymerization at different OFA weight ratios (2.0 wt%, 5.0 wt%, 10.0 wt%, 15.0 wt% and 20.0 wt%) in the presence of dodecylbenzenesulfonic acid as dopant and emulsifier. A polymerization procedure was supposed. The electrical conductivities of the composites were tested by the four-probe technique. The chemical structure and crystallinity of the composites were confirmed by FT-IR and X-ray diffraction, respectively. Morphologies of FA, OFA and the composites were observed by SEM. The element analysis was performed by energy dispersive spectrometry. The thermal stability of the composites was analyzed by TGA. The results showed that the electrical conductivity of the composites decreased with increasing the feed weight ratio of OFA, and the lowest value was 0.62 S/cm. HDTMAB and PAN were just adsorbed on the surface of FA and OFA, respectively according to the physical adsorption without destroying the crystalline structure of FA or OFA. The surface became smoother after organification of FA by using HDTMAB, and its content on FA surfaces was about 26.9 wt%. The core/shell structure of the composite was observed by SEM analysis. The composites showed a higher thermal stability than pure PAN by introduction of OFA into this polymerization system, the heat stability of PAN was increased by decreasing 31.8 wt% of weight loss after introducing 20 wt% of OFA.

**Keywords:** Fly ash; Polyaniline; Hexadecyltrimethyl ammonium bromide; Core/shell; Emulsion polymerization.

### INTRODUCTION

With the discovery of intrinsically conducting polymers (ICPs) in 1977, an attractive subject of research was initiated because of the interesting properties and numerous application possibilities of ICPs. It was expected that ICPs would find their potential applications in multidisciplinary areas<sup>[1–4]</sup>. Polyaniline (PAN) was found to be the most promising candidate because of its ease of synthesis, low cost monomer, tunable properties and better stability compared to other ICPs. However, the weak heat resistance, poor mechanical properties and low processability of PAN have hindered its industrial applications. Introducing inorganic powder, such as graphene<sup>[5]</sup>, MMT, nano-CaCO<sub>3</sub> or nano-Mg(OH)<sub>2</sub>, into PAN can increase firing resistance, heat resistance and mechanical strength as usual.

Since wide scale coal firing for power generation began in the 1920s, many millions of tons of ash and by-products have been generated<sup>[6]</sup>. The disposal of the large amount of fly ash has become a serious environmental problem. FA with negative charge consists of quartz as crystalline phases and some quantity of glassy phase. A

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portion of inorganic constituents was comprised of spheroidal and spherical particles, and their agglomerates<sup>[7–9]</sup>. The processing and applications of FA include, but not limited to, addition to cement and concrete products, structural filler and cover material, roadway and pavement utilization, soil, water and environmental improvement. Usually inorganic powder appears hydrophilic while polymer shows lipophilic. Compatibility of them should be modified in order to obtain the uniform properties of composites. Organo-fly ash (OFA) which has reported as filler in oil and biodegradation composites<sup>[10, 11]</sup> can be obtained by chemical modification or physical adsorption<sup>[11, 12, 13]</sup>.

First, OFA was prepared by using hexadecyltrimethyl ammonium bromide (HDTMAB) as positive surfactant in this article. Then, the composites of polyaniline with different feed weight ratios of OFA were obtained by emulsion polymerization. The conductivity, chemical structure, electrical structure, microstructure and heat resistance of the composites were characterized systematically. This composite is supposed to be used as electromagnetic interference shielding materials and electrorheological fluid.

## EXPERIMENTAL

### Materials

Fly ash with  $d_{\text{mean}}$  as 10.14  $\mu\text{m}$  (Han Cheng Second Power Plant, the composition is shown in Table 1) was saved in drier after being calcined for 1 h at 820°C for decarbonization. Aniline (An, A.R., Xi'an Chemical Reagent Factory, China) was freshly distilled and kept in the darkness before use. HDTMAB was an analytical grade reagent received from Tianjin Chemical Co., Tianjin, China and used without further purification. Dodecylbenzenesulfonic acid (DBSA, C.P., Shanghai Sanyou Reagent Factory, China) and ammonium persulphate (APS, it is a dangerous cargo, Class 5.1) were used without purification. Acetone as well as other reagent was used as received without further purification, which were obtained from Tianjin Reagent Factory of China.

**Table 1.** The composition of FA (wt%)

| Composition | O      | Na <sub>2</sub> O              | MgO             | SiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | Al <sub>2</sub> O <sub>3</sub> |
|-------------|--------|--------------------------------|-----------------|------------------|-------------------------------|--------------------------------|
| Content     | 91.5   | 0.224                          | 0.515           | 46.38            | 0.0910                        | 26.86                          |
| Composition | Cl     | CaO                            | SO <sub>3</sub> | K <sub>2</sub> O | TiO <sub>2</sub>              | Cr <sub>2</sub> O <sub>3</sub> |
| Content     | 0.015  | 4.073                          | 0.141           | 1.76             | 1.00                          | 0.017                          |
| Composition | MnO    | Fe <sub>2</sub> O <sub>3</sub> | NiO             | CuO              | ZnO                           | BaO                            |
| Content     | 0.0465 | 5.091                          | 0.006           | 0.0109           | 0.0138                        | 0.18                           |

### Preparation of OFA

The similar process was described as Ref. [14]: 30 g of FA was dipped into 1 L of HDTMAB aqueous solution (0.03 mol/L) and kept stirred for 24 h at room temperature. Then the mixture was filtered and the solid product was washed with distilled water for several times until the residue surfactant was got rid of. OFA was obtained after the resultant was dried under vacuum at 60°C for 12 h.

### Synthesis of the OFA/PAn Composites with Different Feed Weight Ratios of OFA

The composites of OFA/PAn were obtained by adopting a similar procedure as described in the literature<sup>[15]</sup>. In the polymerization procedure, 4 g of DBSA and 4 mL of aniline were dissolved in 200 mL of distilled water under adequately stirring with various weights of OFA dispersed into this emulsion system for 2 h. The medium was kept at room temperature and an aqueous solution containing 9.8 g of APS dissolved in 50 mL of distilled water was added into the above mixture over 1 h. The total polymerization time was 5 h, and the reaction was terminated by pouring the emulsion into acetone. The precipitate as a fresh green powder was centrifuged, washed five times with acetone and dried under vacuum at 60°C for 12 h. The different feed weight ratios of OFA in this polymerization was 2.0 wt%, 5.0 wt%, 10.0 wt%, 15.0 wt% and 20.0 wt%, respectively.

The similar procedure was performed to prepare DBSA doped PAn (PAn-DBSA) as above only without introducing OFA into this system.

### Characterization

The composites were pressed in a manual hydraulic process in vacuum at 40 MPa into a pellet with 13 mm diameter and about 1.2 mm thickness. Pellet conductivity was measured using a four-probe device (SDY-4 Resistivity Measure Instrument, Suzhou Telecommunication Instrument Plant) at room temperature. The reproducibility of the result was checked by measuring the resistance three times for each pellet.

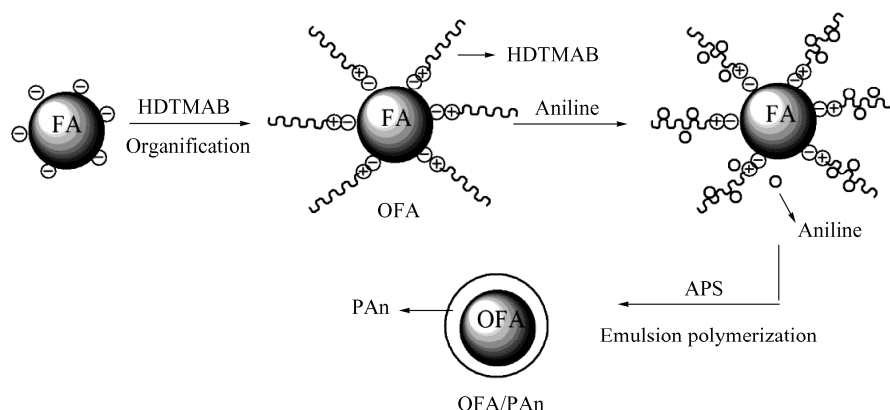
The chemical structure of FA, OFA, pure PAn and the OFA/PAn composites with best conductivity was confirmed by recording infrared spectra using NEXUS 670 (Nicolet) in the range of 400–4000  $\text{cm}^{-1}$  with the resolution of 4  $\text{cm}^{-1}$ . The KBr pellet technique was adopted to prepare the sample for recording the IR spectra. For X-ray diffraction analysis (XRD), a Guinier focusing camera using a germanium monochromator in a D/MAX2200 (Rigaku Corporation, Japan) crystallographic unit with  $\text{Cu K}\alpha$  ( $\lambda = 0.15406 \text{ nm}$ ) radiation mode, was used (40 kV, 40 mA) for recording data in the range of  $2\theta = 5^\circ\text{--}80^\circ$  at a scan rate of 8 ( $^\circ$ )/min with 0.02 $^\circ$  step.

The surface morphologies of FA, OFA, pure PAn and the OFA/PAn composites were observed and composition of the resultants were measured by using scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) combined technique (Quanta-200, FEI Company, U.S.A), which was operated at 20 kV. The weight loss temperatures of samples were determined with a METTLER-TOLEDO TGA/DSC1 at heating rate of 10 K/min from room temperature to 800 $^\circ\text{C}$  under  $\text{N}_2$  atmosphere.

## RESULTS AND DISCUSSION

### Polymerization Procedure of OFA/PAn

In this paper, the reaction conditions of preparing OFA and OFA/PAn were not discussed because the similar optimal way were chosen to synthesize the products according to the work of Shashwat *et al.*<sup>[14]</sup> and Feng *et al.*<sup>[15]</sup>. During this polymerization,  $\text{NH}_4^+$  of HDTMAB was adsorbed onto the surface of FA with negative charge<sup>[14, 16]</sup> due to electrostatic interaction, and then HDTMAB modified FA (named OFA) was formed. The general purpose of the organification of FA with HDTMAB is to introduce the organic chains onto the surface of FA so that its surface can be more hydrophobic and OFA may have more affinity for aniline. Then PAn was formed when APS was added into the emulsion system, and at the same time the OFA/PAn composite with OFA as core and PAn as shell was obtained. Different content of OFA has the same synthesis procedure, which can be described as Scheme 1.



**Scheme 1** Synthesis procedure of OFA/PAn

### Electrical Conductivity

Figure 1 indicates that the OFA/PAn composites exhibit the regular electrical conductivity, ranging from 1.01  $\text{S cm}^{-1}$  (pure PAn) to 0.62  $\text{S cm}^{-1}$  with increasing the feed weight ratio of OFA in this system. OFA was not conductive and only PAn contributed to the observed conductivity. In this work, the conductivity of OFA/PAn

composites were higher than that of SiO<sub>2</sub>/PAn (26 wt% of SiO<sub>2</sub>,  $\sigma = 2.6 \times 10^{-6} \text{ S cm}^{-1}$ ) mentioned in Ref. [17] because the magnetic properties of OFA could probably enhance the conductivity of the composites, as reported before<sup>[18, 19, 20]</sup>. Thus the conductivity of OFA/PAn decreases unconspicuously that is different from PAn composites with other insulators without obvious magnetic property.

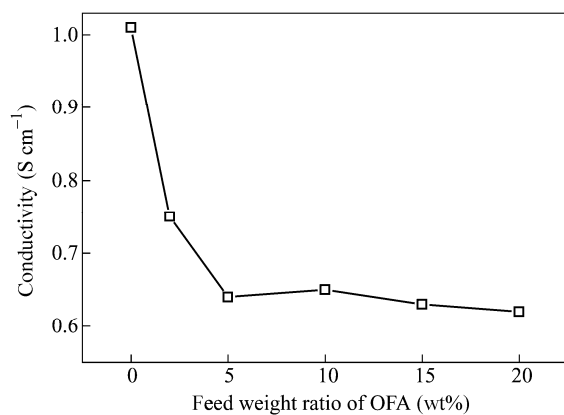


**Fig. 1** The electrical conductivity of OFA/PAn composites with different feed weight ratios of OFA

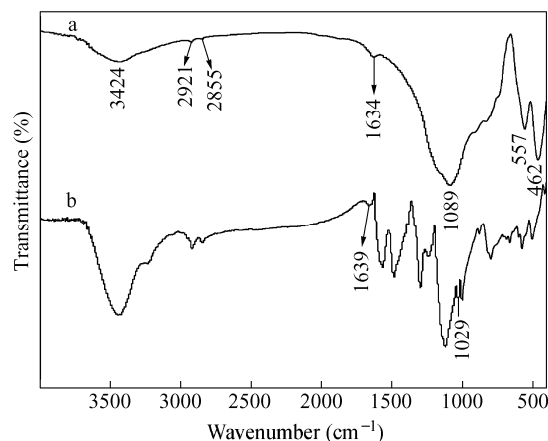


**Fig. 2** FT-IR spectra of OFA (a) and OFA/PAn (b) (The feed weight ratio of OFA is 20 wt%.)

### Spectroscopy

The FT-IR spectrum of OFA (Fig. 2a) shows a strong band at 1069 cm<sup>-1</sup> which can be attributed to Si—O stretching characteristic of quartz<sup>[14]</sup>. The relatively high intensity of the bands at 557 cm<sup>-1</sup> and 462 cm<sup>-1</sup> is due to Fe—O stretching and the presence of calcium silicate, respectively<sup>[14,20]</sup>. The wide absorption band at 3424 cm<sup>-1</sup> indicates the presence of kaolinite and —OH stretching. The band at 1634 cm<sup>-1</sup> can be assigned to the crystal water of OFA. The bands at 2921 and 2855 cm<sup>-1</sup> are ascribed to  $\nu_{\text{as}}$  C—H and  $\nu_{\text{s}}$  C—H of the hexadecyl in HDTMAB. The results suggested that the organic groups were functionalized successfully onto the surfaces of FA particles. Compared with the spectrum of FA (it was not shown.), there was no new band appeared in that of OFA, which demonstrated that there was no any chemical reaction between FA and HDTMAB, as shown in Scheme 1.

The characteristic peaks of OFA/PAn (Fig. 2b) appeared at 3445, 2920, 2843, 1565, 1487, 1297, 1242, 1120 and 797 cm<sup>-1</sup> in turn. It had the similar absorption bands as those of PAn-DBSA<sup>[21]</sup>. The peaks appeared at 1639 and 1029 cm<sup>-1</sup>, which can be assigned to the crystal water of OFA and typical absorption of silicate, respectively, suggested that the composites of OFA/PAn can be formed by emulsion polymerization applied in this work. It's clear from spectra in Fig. 2, there was no new chemical bond formed between OFA and PAn, which was identical with the polymerization procedure described in Scheme 1.

The crystalline structure of FA, OFA and OFA/PAn (the feed weight ratio of OFA is 20 wt%) was illustrated by XRD as shown in Fig. 3. Typical diffraction peaks of FA appeared at 16.62°, 21.03°, 26.38°, 33.43°, 35.37°, 39.4°, 41.1°, 42.7°, 49.7°, 54.1° and 57.68° which could be attributed similarly as those of FA mentioned in Ref. [20]. After organification with HDTMAB, these peaks were not shifted a bit as shown in Fig. 3. According to the results of FT-IR and XRD, it can be concluded that HDTMAB is just adsorbed on the surface of FA by electrostatic interaction without destroying the crystalline structure of FA. The diffraction pattern of OFA/PAn showed both characteristic absorption of FA and PAn-DBSA. The typical peaks at  $2\theta = 20^\circ$  and  $25^\circ$  arose due to the orderliness of PAn<sup>[21]</sup>. Compared with pure OFA, the absorption peaks of OFA in the composites were also not shifted, which may imply that OFA did not affect the crystalline structure of PAn-DBSA. This phenomenon demonstrated the preparing process of OFA/PAn was consistent with Scheme 1.

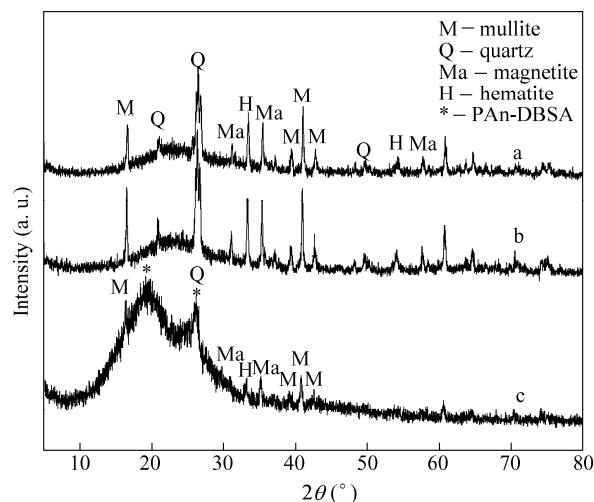


Fig. 3 XRD spectra of FA (a), OFA (b) and OFA/PAn (c) (The feed weight ratio of OFA is 20 wt%).

### Morphology Observation and Elemental Analysis

The morphologies of the powder samples of FA (a), OFA (b) and OFA/PAn (c) are shown in Fig. 4. From Fig. 4(a), it can be seen that FA was a typical sphere and some small granules attached on it. An agglomerate among themselves was also observed due to strong polarity of the hydroxyl groups on FA surfaces<sup>[22]</sup>. After organification with HDTMAB, the surface texture of FA changed obviously and became smoother as shown in Fig. 4(b). The phenomenon is similar as that described in Ref. [10]. Specifically, OFA had a well dispersed nature than that of FA. Figures 4(c), 4(d) showed the morphologies of OFA/PAn composites with two different feed weight ratios of OFA. Compared with the image of OFA, the surfaces of OFA/PAn all appeared rough obviously due to PAn formed on it. It seemed that the more content of OFA, the less PAn appeared on its surface. It's assumed that OFA enjoyed PAn averagely less if more OFA was introduced into the reaction system at the same content of An. In a word, it can be illustrated that the core/shell structure of PAn coated OFA is obtained successfully by the emulsion polymerization method applied in this work.

In order to illustrate the different matter appeared on their surfaces of FA and OFA, points A and B on the surfaces were chosen arbitrarily for analysis by EDS. The results are shown in Table 2. It was found they had the same elements except the intensity of carbon element was different. Comparing A and B of FA, there was 10.76 wt% of carbon element appeared at B, it maybe derived from other non-metallic mine embodied carbonate. After organification of FA, the content of carbon was improved whether in the site of A or B. It was illustrated that HDTMAB was successfully adsorbed on FA and the adsorption content of it was about 26.9 wt% according to the elemental analysis results of FA and OFA.

Table 2. Results of EDS

| Sample |   | Element content (wt%) |       |       |       |      |
|--------|---|-----------------------|-------|-------|-------|------|
|        |   | C                     | O     | Al    | Si    | K    |
| FA     | A | –                     | 52.82 | 16.22 | 27.5  | 1.41 |
|        | B | 10.76                 | 47.65 | 14.27 | 24.66 | 1.26 |
| OFA    | A | 18.08                 | 43.31 | 13.37 | 22.37 | 2.32 |
|        | B | 26.34                 | 42.78 | 11.55 | 16.77 | 1.63 |

### Thermal Stability Analysis

Figure 5 shows the thermogram curves of PAn-DBSA and OFA/PAn composites with different feed weight ratios of OFA. The decomposition of them showed a two-stage pattern. From 200°C to 370°C, an obvious weight loss appeared due to the loss of dopant DBSA and surfactant HDTMAB. Above 370°C, the different material showed different thermal decomposition action. From 370°C to 650°C, there was an about 36.02 wt%

weight loss appeared for PAn-DBSA according to the decomposition of PAn backbone, while the weight loss of that of 2 wt% OFA/PAn and 20 wt% OFA/PAn was similar as 24.17 wt% from 370°C to 600°C, 24.57 wt% to 650°C. From this result, it can be concluded that the weight loss of PAn was decreased by 31.8% especially in the second stage. It was also shown that the residual weight of OFA/PAn composites was much higher than that of pure PAn. In the case of 20 wt% OFA/PAn, the residual weight was 49.07 wt%, and that of PAn-DBSA was only 37.82 wt%. It was proved that the thermal stability of PAn can be enhanced by introduction of OFA into the polymerization system and that could be attributed to the retardation effect of FA as barriers for the degradation of PAn<sup>[23–25]</sup>.

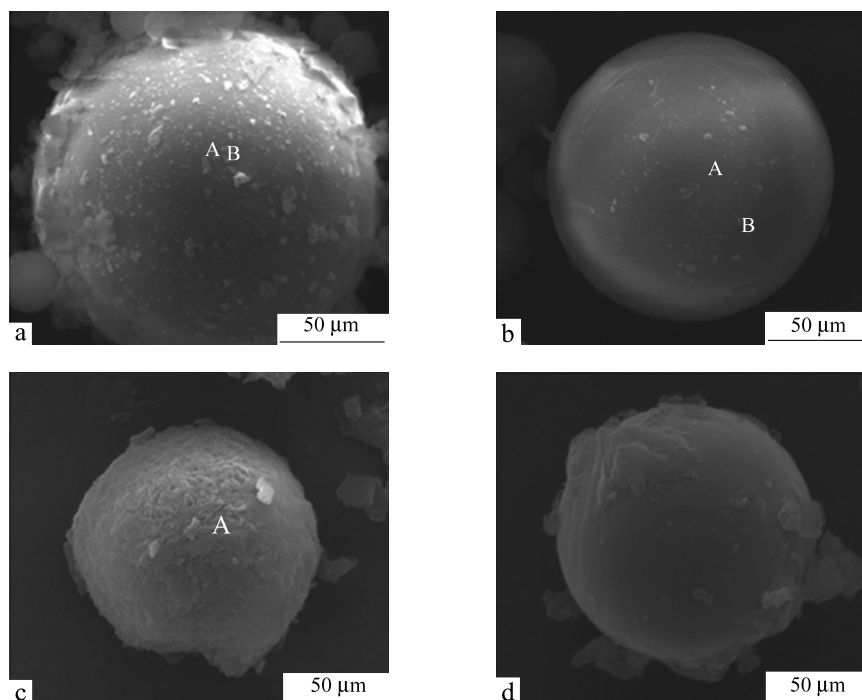


**Fig. 4** SEM images of FA (a), OFA (b) and OFA/PAn (c)–(d) (The feed weight ratio of OFA is 2 wt% and 20 wt%, respectively.)

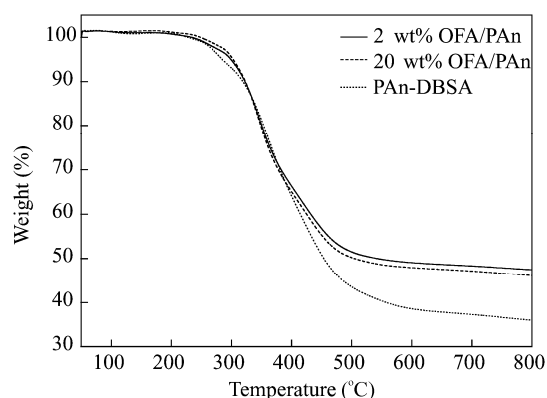


**Fig. 5** TGA curves of PAn-DBSA and OFA/PAn (The feed weight ratio of OFA is 2 wt% and 20 wt%, respectively.)

## CONCLUSIONS

The composites consisting of hydrophobic silicate OFA and conductive PAn-DBSA were synthesized successfully *via* emulsion polymerization method in this work. The conductivities of the OFA/PAn composites with different feed weight ratios of OFA were measured and it was found that the conductivity decreased with increasing feed weight ratio of OFA. The chemical structure and crystallinity of OFA and 20 wt% OFA/PAn composite were confirmed by FTIR and XRD, respectively. Both of them confirmed HDTMAB and PAn-DBSA were just adsorbed on the surface of FA and OFA, respectively, without forming any new chemical bond. The microstructure of OFA appeared smoother than that of FA and the OFA/PAn composites and showed the characteristics of core/shell structure, OFA looked as core and PAn as shell. From EDS analysis, it can be calculated that the adsorption of HDTMAB on FA surfaces was about 26.9 wt%. The introduction of OFA into PAn-DBSA could enhance the thermal stability obviously as demonstrated by TGA.

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