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High Efficiency Photocatalytic Activity of Type-II SnO/Sn₃O₄ Heterostructures via Interfacial Charge Transfer

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Abstract

Flower-like hollow microspheres were synthesized on a large scale using a one-step hydrothermal route. The as-prepared products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and UV-vis diffuse reflectance spectroscopy. The results showed that the shells of the hollow microspheres were composed of numerous type-II SnO/Sn₃O₄ heterostructures. A 500°C annealing treatment changed the type-II SnO/Sn₃O₄ heterostructures into type-I SnO₂/Sn₃O₄ heterostructures; at 700°C, the products were pure SnO₂ semiconductors. A photocatalytic degradation test showed that the highest efficiency degradation of rhodamine B (RhB) was obtained using type-II SnO/Sn₃O₄ heterostructure semiconductors with a degradation rate constant of $2.3 \times 10^{-3}$ min⁻¹. This highly efficient activity was induced by enhanced charge separation in type-II SnO/Sn₃O₄ heterostructure semiconductors.

Keywords: SnO/Sn₃O₄, SnO₂/Sn₃O₄, heterostructures, photocatalytic degradation

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I. Introduction

In recent years, univalent tin oxides, such as SnO$_2$ and SnO, have attracted considerable interest as research subjects because of their wide ranging applications to lithium-ion batteries$^{1,2}$, sensitized solar cells$^{3,4}$, chemical and biological sensors$^{5,6}$ and photocatalysts$^{7,8}$, $^{9,10}$. In addition to univalent tin oxides, heterovalent tin oxides (e.g., Sn$_3$O$_4$, Sn$_2$O$_3$, and Sn$_5$O$_6$) with a variety of coordination structures have been a popular subject in both theoretical calculations and experimental studies on regulating the Sn(II)/Sn(IV) ratio$^{11,12}$. Moreover, heterovalent tin structures have been reported to influence the physical properties of tin oxides. Park et al. found that heterovalent tin oxide exhibits more sensitivity for CH$_2$Cl$_2$ detection than either SnO or SnO$_2$ univalent oxides$^{13}$. Theoretical calculations have confirmed that Sn$_3$O$_4$ has absorption bands that enable its use as a visible-light-driven photocatalyst for environmental remediation$^{14}$.

A univalent tin oxide-based composite, which includes SnO$_2$ and SnO, is a wide band gap semiconductor (SnO$_2$: $\approx$3.5eV, RT, SnO: $\approx$2.7eV, RT) and exhibits good activity and stability under irradiation in both acidic and basic media. However, there have been few reports on the direct use of pure tin oxide-based materials as photocatalysts, and it is well-known that SnO$_2$ exhibits low photocatalytic activity even under UV irradiation because of its large band gap$^{15,16}$. Currently, there are primarily two popular strategies that have been pursued in the literature to improve the photocatalytic activity of SnO$_2$. One strategy is to design various geometries and morphologies for tin oxide-based photocatalysis, because catalytic activity depends on the structural parameters of SnO$_2$ such as geometry, morphology, etc., and many complex nanostructures with novel geometry and morphology have been abundantly documented$^{17}$. Among the aforementioned nanostructures, hollow structures of tin oxide-based architectures have also been extensively investigated for their large catalytically active surface area, high organic pollutant adsorption and the excellent incident light scattering within the structures$^{18}$. Although considerable progress has been made in the synthesis of hollow spheres$^{19,20}$, it is still a major challenge to develop a facile route for the preparation of tin oxide hollow nanostructures with the desired optical properties, especially a one-step synthesis of a hollow structure. However, this strategy does not fundamentally solve
the problem of the fast recombination of photogenerated electron-hole pairs that hinder the industrial application of photocatalytic techniques. Thus, minimizing the recombination of photogenerated electron-hole pairs before they participate in redox processes is critical for enhancing photocatalytic efficiency. A novel development has been the synthesis of tin oxide-based photocatalysts using lower band gap semiconductors to form heterostructures (e.g., SnO$_2$/TiO$_2$\textsuperscript{21, 22}, SnO$_2$/ZnO\textsuperscript{23, 24}, SnO$_2$/SnS$_2$\textsuperscript{25}, and SnO$_2$/Cd\textsuperscript{26}, SnO$_2$–CdSe\textsuperscript{27}). Among these heterostructures, type-II heterostructures are ideal for photocatalytic reactions in which both rapid charge separation and low radiative recombination efficiency are required. The improved photocatalytic activity of the hetero-junctions has also attributed to a large extent to the enhanced separation of photo-induced electrons and holes via interfacial charge transfer. Photo-catalytic activity can be enhanced by the type-II heterostructures that are formed using two types of semiconductors; however, the fabrication of these structures is complex because two steps are usually required. The close correlation between shape and morphology and the use of heterogeneous photocatalysts makes the facile fabrication of desirable hollow nanoarchitectures of tin oxides heterostructures a strongly desirable goal. Heterovalent tin oxides (e.g., Sn$_3$O$_4$, Sn$_2$O$_3$, and Sn$_5$O$_6$) exhibit a narrower band gap than that of univalent tin oxides\textsuperscript{28,29} and are thus candidates for producing heterostructures of type-II univalent tin oxides. To the best of our knowledge, this study is the first time that photocatalytic activity has been reported for heterostructures of a homologous series of tin oxides. Herein, we report a simple one-step hydrothermal route to fabricate SnO/Sn$_3$O$_4$ and SnO$_2$/Sn$_3$O$_4$ hetero-junctions for use as photocatalysts. Heterostructures of homologous tin oxides exhibit excellent photocatalytic performance. Notably, the annealing temperature can be simply tuned to easily control the density of the heterostructures and the band structure of tin oxides, thereby improving the optical properties of these materials. The heterostructures of tin oxides exhibit a much higher efficiency than pure SnO$_2$ for the degradation of rhodamine B (RhB). Moreover, this simple one-step hydrothermal route offers a wide range of practical applications and is a good strategy for employing heterovalent tin oxide to fabricate a homologous series of tin oxides for use as photocatalysts.
II. Experimental Section

The aforementioned heterostructure microspheres with hollow structures were prepared by a facile one step hydrothermal approach using sodium hydroxide, urea, and tin dichloride dehydrate (SnCl₂•2H₂O) as precursors. In a typical synthesis, 60 ml of absolute ethanol and 140 ml of deionized water were mixed in a 250 ml beaker and stirred to ensure complete mixing. Then, 0.48 mM sodium hydroxide, 0.264 mM urea, and 0.04 mM tin dichloride dehydrate were dissolved in the mixture and agitated for approximately 1 h. The resulting mixture was transferred into a 200-ml sealed autoclave and heated in oven at 180 °C for 18 h. The product was then centrifuged several times alternately in deionized water and ethanol, and the residual was dried for 10 h at 60 °C in a vacuum stove. The final product was finally annealed at 300, 400, 500, 600 and 700 °C for 2 h under atmosphere.

The morphologies of the obtained products were characterized using a field-emission scanning electron microscope (FESEM, s-4800II, Hitachi, 15kV). High resolution transmission electron microscopy (HRTEM) images and selective area electron diffraction (SAED) patterns were captured using a Tecnai G2 F30 S-Twin microscope at an accelerating voltage of 300 kV. Crystallographic data were obtained using power X-ray diffraction (Bruker, D8 Advance, Cu kα radiation, λ=1.5406 Å). The phase composition of the as-prepared product was analyzed using an Axis Ultra X-ray photoelectron spectroscope (XPS, Kratos Analytical Ltd., UK) that was equipped with a standard monochromatic Al-kα source (hv=1486.6 eV). The binding energy data were calibrated with respect to the C1s signal of the ambient hydrocarbons (C-H and C-C) at 284.8 eV. The absorption measurements were performed using a UV-vis-NIR spectrophotometer (UV-vis, Cary-5000, Varian) with an integrating sphere.

Photocatalytic experiments were conducted on the as-prepared samples to decompose or remove rhodamine B (RhB) aqueous solutions using the following procedure: 5 mg of the as-prepared samples were suspended in 25 ml of an aqueous solution of 1×10⁻⁵ mol/L RhB. Prior to irradiation, the suspensions were sonicated for 10 min and then magnetically stirred in the dark for 30 min to attain desorption-adsorption equilibrium. The solution was then exposed to UV irradiation from a mercury lamp (300 W) at room temperature. Five-milliliter
samples were collected every 30 min, centrifuged to remove the residual photocatalyst, and the upper clear liquid was analyzed by recording the maximum absorption band (554 nm for RhB) using a Shimadzu UV-3600 spectrophotometer. Also, 5 mg of commercial TiO$_2$ (P25) was used in the control experiment. Additionally, the recycle experiments were performed for five consecutive cycles with irradiation time of 150 min under UV irradiation to test the durability and irradiation time was kept.

III. Results and Discussion

Figure 1 XRD patterns of tin oxide-based powders before and after annealing at 300, 400, 500, 600, and 700 °C for 2 h in air; insets show expanded powder XRD patterns of samples before and after annealing at 500, 600, and 700 °C: inset (a) shows an enlarged spectrum, where peaks marked by (●) correspond to Sn$_3$O$_4$ (JCPDS 16-0737); inset (b) shows an enlarged spectrum, where peaks marked by (♣) correspond to other Sn$_3$O$_4$ phases (JCPDS 20-1293).

The XRD patterns of the as-prepared samples and the tin oxide-based powders formed at varying oxidation temperatures of 300, 400, 500, 600, and 700 °C are shown in figure 1. The as-prepared tin oxide-based powders that were annealed at temperatures of 300 and 400 °C exhibited two sharp diffraction peaks corresponding to the reflections of a tetragonal SnO phase (JCPDS 06-0395). A weak SnO peak was also observed at 29.989° (corresponding to
the (101) plane), indicating the simultaneous existence of the tetragonal SnO phase. Note that
extra peaks from minor phases could also be identified. The inset in figure 1a is an enlarged
spectrum over the 22° to 35° range. In addition to the SnO peaks, six characteristic peaks
could be identified (which are marked by (●)) as (101), (120), (111), (210), (121), and
(210) reflections from Sn3O4 (JCPDS 16-0737). Following annealing above 400 °C, the
XRD spectra of samples changed dramatically. The peaks corresponding to SnO completely
disappeared at 500 °C, and new dominant peaks appeared that were indexed to the tetragonal
SnO2 phase (JCPDS 41-1445), indicating the oxidation of SnO to SnO2. The phase
transformation process is discussed later (see experimental details in †ESI, S1). Furthermore,
the intensities of the SnO2 diffraction peaks increased with the annealing temperature. At 500
and 600 °C, two typical Sn3O4 peaks were simultaneously present. In the inset of figure 1(b),
the peaks marked by a (♣) were indexed to the (001), (100), (101), (111), (020), (021),
and (112) reflections of Sn3O4 (JCPDS 20-1293). When the annealing temperature reached
700 °C, the products were transformed into pure rutile-structured SnO2, which was confirmed
by fitting the SnO2 peaks (JCPDS 41-445), as shown in the inset of figure 1 (d). Therefore, a
phase transition from SnO to SnO2 occurred along with the formation of an intermediate
oxidation state of Sn3O4. The existence of Sn3O4 was confirmed by performing Raman
spectroscopy to clarify the crystalline compositions and structures of the aforementioned
samples (see experimental details in †ESI, S2).

Figure 2 XPS spectra of Sn 3d for tin oxide-based powders before and after annealing at 500 and 700 °C
for 2 h in air
To gain insight into the evolution of the tin oxide during the annealing process, X-ray photoelectron spectra (XPS) was performed to investigate the changes in the Sn-related states under different annealing temperatures (see figure 2). The Sn 3d spectrum exhibited spin-orbit doublet peaks at \( \approx 486 \) eV (Sn\(^{2+}\) 3d\(^{5/2}\)) and \( \approx 495 \) eV (Sn\(^{2+}\) 3d\(^{3/2}\)). After annealing above 500 °C, the main peaks shifted to higher binding energies, which matched the binding energies of Sn\(^{4+}\) (at 486.7 eV and 495.4 eV for 3d\(^{5/2}\) and 3d\(^{3/2}\), respectively) well, and the Sn\(^{4+}\) content increased and gradually dominated the material composition. The binding energies of the Sn-related states obtained in this experiment were consistent with the XRD results.

Figure 3 SEM images of tin oxide-based microspheres (a) before and after annealing at (b) 300, (c) 500, and (d) 700 °C for 2 h in air; inset in (a) is a TEM image of the as-synthesized tin oxide microspheres.

The product morphologies were studied by SEM. Figure 3 shows typical SEM images of the collected tin oxide microspheres before and after annealing treatments at different temperatures. Three-dimensional (3D) microspheres assembled into sheet-like subunits with diameters ranging from 3 to 5 \( \mu m \). TEM measurements were performed to characterize the sample structures further and are shown in the inset of figure 3 (a). The obvious contrast between the dark edges and the pale centers confirms that these microspheres were hollow. It has been reported that this hollow structure can improve light harvesting through multiple light reflections and scattering effects that can be used for applications in the photo-decomposition of organic compounds. Furthermore, the morphology of the hollow
microsphere structures was faithfully preserved during the calcination process. Therefore, hollow microspheres can be synthesized on a large scale, where the shells of the microspheres are covered with numerous nanoflakes.

Figure 4 HRTEM images and SAED patterns of as-synthesized tin oxide-based heterostructures; lattice-resolved HRTEM images were taken from the edge of the microspheres obtained (a) before and (b) after annealing at 500 °C for 2 h in air; insets show corresponding SAED patterns.

To obtain detailed information about the microstructure of the as-synthesized tin oxide-based microspheres, HRTEM observations and selected-area electron diffraction (SAED) analysis were carried out: the results are shown in figure 4. The SAED patterns in the insets of figure 4 show two different types of crystal phases in the samples: both phases of the heterostructures were crystalline. Meanwhile, the HRTEM images of the region that are marked by a white line confirmed the presence of crystalline SnO/\(\text{Sn}_3\text{O}_4\) and \(\text{SnO}_2/\text{Sn}_3\text{O}_4\) crystal lattices in the interfacial region, as shown in figure 4. The HRTEM images also clearly revealed the in situ formation of heterostructures within the interface, which would have facilitated interfacial electron transfer and accordingly increased the photocatalytic activity. The aforementioned analysis confirmed that SnO/\(\text{Sn}_3\text{O}_4\) and \(\text{SnO}_2/\text{Sn}_3\text{O}_4\) composites with heterostructures formed in our prepared samples. Note that the SnO content in the SnO/\(\text{Sn}_3\text{O}_4\)
semiconductors disappeared as the annealing temperature increased until finally, only SnO$_2$ was observed at 700 °C; thus, the annealing temperature could be tuned to adjust the tin oxides constituents to produce the required optical properties.

Typical UV-vis spectroscopy measurements were used to further confirm the formation of the heterostructures. In the literature$^{30, 31}$, SnO$_2$ has been reported to be a direct band gap material, and SnO and Sn$_3$O$_4$ have been reported to be indirect band gap materials: the optical band gap energy ($E_g$) of these materials can be calculated using the equation given below$^{32}$,

$$\alpha h \nu = C (h \nu - E_g)^n,$$

where $n$ is equal to 1/2 and 2 for direct allowed transitions and indirect transitions, respectively.

![Figure 5](image)

**Figure 5** Plots of $(\alpha h \nu)^{n/2}$ vs. photon energy ($h \nu$) for (a) as-prepared tin oxide-based heterostructures and heterostructures formed at oxidation temperatures of (c) 500 and (e) 700 °C; (b), (d) and (f) are the corresponding schematic diagrams of the energy band structures of tin oxide-based heterostructures.

The spectra of the SnO/Sn$_3$O$_4$ and SnO$_2$/Sn$_3$O$_4$ heterostructures are plotted in figure 5 (a and c): two slopes can be clearly observed that indicate the formation of heterostructures. The $E_g$ values of SnO and Sn$_3$O$_4$ in the SnO/Sn$_3$O$_4$ heterostructures were evaluated as 2.47 and 2.19 eV, respectively. Upon heating to 500 °C, the $E_g$ values for SnO$_2$ and Sn$_3$O$_4$ in the SnO$_2$ /Sn$_3$O$_4$ heterostructures were evaluated as 3.41 and 2.19 eV, respectively. Meanwhile, further increasing the annealing temperature to 700 °C yielded only one slope in figure 5(e).
and the $E_g$ was estimated at 3.61 eV, which was in agreement with the reported value for SnO$_2$ (3.5-3.7 eV). The valence band edge positions of the tin oxide-based heterostructures were estimated using electronegativity concepts. The valence band potentials of a semiconductor at the point of zero charge can be calculated using the following empirical equation\textsuperscript{33, 34, 35}:

$$E_{vB} = X - E^e + 0.5E_g$$  \hspace{1cm} (1),

where $E_{vB}$ is the $VB$ edge potential, and $X$ is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms. The $X$ values for SnO, SnO$_2$ and Sn$_3$O$_4$ are 5.68, 6.24 and 5.91 eV, respectively. The energy of the free electrons on the hydrogen scale is denoted by $E^e$ ($\approx$4.5 eV), $E_g$ is the band gap energy of the semiconductor, and $E_{CB}$ can be determined from $E_{CB} = E_{vB} - E_g$. Figure 5 (b, d, and f) shows the schematic diagrams of the energy band structures of the tin oxide-based heterostructures. Sn$_3$O$_4$ exhibited a narrower band gap than the band energy alignment of SnO and SnO$_2$, and the valence and conduction band alignments for Sn$_3$O$_4$ were staggered relative to those of SnO and SnO$_2$; therefore SnO/Sn$_3$O$_4$ was a type-II heterostructure. In SnO$_2$/Sn$_3$O$_4$, the band gap Sn$_3$O$_4$ was embedded in that of SnO$_2$; thus, SnO$_2$/Sn$_3$O$_4$ was a type-I heterostructure.

**Figure 6** (a) Comparison of photocatalytic degradation of RhB in the presence of tin oxide-based heterostructures; (b) Cycling runs for the photocatalytic degradation of RhB over SnO/Sn$_3$O$_4$ under UV irradiation
The photocatalytic activities of the as-synthesized different heterostructures were evaluated by the degradation of a RhB dye in water under UV light irradiation, as shown in figure 6(a). Figure 6(a) shows the absorption spectra of the RhB solution in the presence of tin oxide-based semiconductors. Figure 6(a) shows that the tin oxide-based heterostructures SnO/Sn₃O₄ and SnO₂/Sn₃O₄ exhibited a better catalytic degradation than SnO₂, whereas the SnO/Sn₃O₄ heterostructure semiconductors performed the most efficient degradation of RhB. The poor performance of SnO₂ semiconductors could be attributed to the low negative conduction potential of SnO₂, because the conduction band bottom potential of SnO₂ is near that of O₂/O²⁻ (−0.046 eV vs. SHE), indicating that SnO₂ readily undergoes photocorrosion in aqueous media containing oxygen and that the over potential is too small to reduce O₂ with photoexcited electrons; therefore, photocatalytic degradation using SnO₂ was not effective.

For practical photocatalytic applications, the recycling of photocatalyst is very important. In the durability tests, SnO/Sn₃O₄ was repeatedly used for the RhB photodegradation reaction 5 times (Figure 6 (b)). The experimental results indicated that no apparent deactivation of photocatalyst is seen after 5 cycles as compared to the fresh catalyst.

Catalytic degradations of dye have been reported in the literature. For SnO/Sn₃O₄ with a type-II heterostructure, electrons could be excited from the valence bands to the conduction bands of SnO semiconductors by UV irradiation because of the band offset: the generated electrons on the conduction band of SnO were directly injected into the conduction band of Sn₃O₄, whereas the holes remained on the valence band (as shown in Fig. 5b). Thus, more electrons accumulated in the conduction band of the SnO, resulting in more holes in the valence band of SnO, i.e., interfacial charge separation occurred. The electrons that were eventually localized in the conduction band of Sn₃O₄ reduced O₂ to form superoxide ions *O₂⁻, and the holes located in the valence band of SnO reacted with the hydroxyl group to produce the hydroxyl radicals (*OH) that degraded RhB in the photoreaction. The high efficient photodegradation activity of SnO/Sn₃O₄ can be explained as, on the one hand, the morphology of SnO/Sn₃O₄ exhibits a high surface-to-volume ratio, which is benefit to the adsorption of dye RhB molecules, the photodegradation efficiency will improve; on the other hand, the life span of photogenerated electron-hole pair is large enough to migrate and is available for redox reactions at photocatalyst surface, as the recombination rate of the electron
and hole excited from indirect semiconductor SnO is lower than that of the direct semiconductor, which will be favorable for the charge separation. Therefore, the samples SnO/Sn$_3$O$_4$ prepared at room temperature show a high efficient photodegradation activity, as shown in Figure 6.

For the type-I SnO$_2$/Sn$_3$O$_4$ heterostructure, electrons were excited upon light irradiation of both the SnO$_2$ and Sn$_3$O$_4$ semiconductors. Then, unlike in the type-II heterostructures, more electrons and holes recombined while electrons and holes were produced for both the SnO$_2$ and Sn$_3$O$_4$ semiconductors, resulting in a photocorrosion effect as the electrons and holes recombined in the conduction and valence bands of SnO$_2$ and Sn$_3$O$_4$. Sn$_3$O$_4$ is an indirect semiconductor; therefore, the recombination rate of the indirect semiconductor was relatively lower, and some electrons and holes participated in the photocatalytic degradation of RhB before recombination, which explains why the type-I SnO$_2$/Sn$_3$O$_4$ heterostructure had a much higher photocatalytic degradation effect than the SnO$_2$ semiconductor. The degradation efficiency of a photocatalyst can be defined as follows$^{39}$:

$$\text{Degradation(\%) } = (1 - \frac{C}{C_0}) \times 100\% \quad (2),$$

where $C_0$ is the RhB concentration at equilibrium adsorption, and $C$ is the residual concentration of RhB at different illumination intervals. The photodegradation of RhB follows pseudo-first-order kinetics, which can be expressed as follows:

$$\ln(\frac{C}{C_0}) = -kt \quad (3),$$

where $k$ (min$^{-1}$) is the degradation rate constant. Equation (3) was used to calculate the degradation rate constants of $2.3 \times 10^{-3}$ and $3.6 \times 10^{-5}$ min$^{-1}$ for the SnO/Sn$_3$O$_4$ and SnO$_2$/Sn$_3$O$_4$ semiconductors, respectively. Although the degradation rate constant for SnO/Sn$_3$O$_4$ is much smaller than the P25 ($9.2 \times 10^{-2}$). We believe that our report provides a new approach to realize high Efficiency Photocatalytic of heterostructures of type-II univalent tin oxides. Therefore, enhanced photocatalytic degradation of RhB solutions was observed using SnO/Sn$_3$O$_4$ with type-II heterostructures as photocatalysts, as shown in Figure 6. The observed phenomenon was consistent with other reports.$^{40}$ Furthermore, the flower-like
hollow microspheres is still inherited after five consecutive cycles (See Figure S3 in the supporting Information).

IV. Conclusions

In summary, tin oxide semiconductors with a morphology of flower-like hollow microspheres were synthesized using a one-step hydrothermal route and a series of annealing processes. The as-prepared products were characterized by XRD, scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and UV-vis diffuse reflectance spectra. Systematic measurements revealed that the as-prepared flower-like hollow microspheres had a type-II SnO/Sn3O4 heterostructure. After a 500°C annealing treatment, the original SnO/Sn3O4 heterostructure changed into SnO2/Sn3O4 with a type-I heterostructure, and the products were SnO2 at 700°C. The original prepared SnO/Sn3O4 semiconductors with type-II heterostructures performed the highest efficiency degradation of rhodamine B (RhB) with a degradation rate constant of 2.3×10^-3 min^-1. This highly efficient activity was induced by the enhanced charge separation in the SnO/Sn3O4 semiconductors with type-II heterostructure. This typical hollow structure has two advantages for photocatalytic activity: the structure has a high surface-to-volume ratio, which enables multi-reflections of irradiated light within the interior cavities, and the products consist of two phases of homologous tin oxides. We believe that our prepared SnO/Sn3O4 and SnO2/Sn3O4 heterostructures microspheres can be used as visible-light-driven high-performance photocatalysts. Studies on such applications are currently underway.

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