Surface Disorder Engineering of Flake-Like Bi_2WO_6 Crystals for Enhanced Photocatalytic Activity

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The NaBH_4 reduction method has been used to engineer the surface of flake-like Bi_2WO_6 (BWO) crystals with the aim of creating disordered surface structure and enhancing the photocatalytic activity. The disorder-engineered BWO samples were investigated by means of x-ray powder diffraction, field-emission scanning electron microscopy, field-emission transmission electron microscopy, x-ray photoelectron spectroscopy, ultraviolet–visible diffuse reflectance spectroscopy, photoluminescence, electrochemical impedance spectroscopy and photocurrent response. Simulated sunlight, UV light and visible light were separately used as the light source to evaluate the photocatalytic activity of the samples toward the degradation of rhodamine B in aqueous solution. It is demonstrated that 0.03 M-BWO treated at 0.03 M NaBH_4 solution exhibits the highest photocatalytic activity, ca. 2.4 times higher than pristine BWO under simulated sunlight irradiation. The significant increase in the photocatalytic activity is observed at UV irradiation, which can be explained by the fact that the disordered surface states (formed in the forbidden gap of BWO) can act as electron acceptors to facilitate the separation of photogenerated electron/hole pairs. A slightly enhanced photocatalytic activity is observed under visible light irradiation, which is attributed to the enhanced visible light absorption induced by the disordered surface states. In addition, it is found that the treatment with high NaBH_4 concentrations is detrimental to the photocatalytic activity due to the creation of bulk defects in BWO crystals.

Key words: Flake-like Bi_2WO_6 crystals, engineered disorder, photocatalytic activity, photocatalytic mechanism

INTRODUCTION

The rapid development of chemical industries simultaneously causes serious environmental pollution. In particular, a huge amount of wastewater containing more than one million tons of organic dyes is produced worldwide annually from textile, paper, leather, paint, cosmetic and oil manufacturers. To cope with the environmental pollution,

semiconductor-based photocatalysis has recently aroused a tremendous interest because of its capability of using sunlight as the power source to decompose organic dyes into harmless inorganic molecules.^{1–5} The photocatalysis process is highly associated with the generation and separation of electron/hole (e^-/h^+) pairs under irradiation of sunlight. Nevertheless, most of the famous semiconductor photocatalysts (e.g. TiO_2 , ZnO , SrTiO_3 , CaTiO_3 , Bi_2WO_6 , $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ^{6–11}) possess a large bandgap $E_g > 3.0$ eV and can only absorb ultraviolet (UV) light occupying only 4% of the incoming solar energy. Furthermore, the photogenerated

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electrons and holes in these semiconductor photocatalysts are easily recombined in pairs, thus limiting their photocatalytic activity. To widen the light-responsive region and facilitate the photogenerated electron/hole pair separation is one of the key points in the design of excellent photocatalysts. The most common strategies to achieve this aim include doping with impurity elements, construction of heterojunction composites, assembly with carbon materials, decoration with noble metals and surface disorder engineering.^{12–22}

Recently, Bi_2WO_6 (BWO) has been extensively studied as a promising photocatalyst on the degradation of organic pollutants and O_2 evolution from water splitting.^{23–30} The pronounced photocatalytic performance of BWO could be attributed to its special layered crystal structure of perovskite-like units (WO_4)^{2–} sandwiched between (Bi_2O_2)²⁺ layers and unique band structure with valence band (VB) consisting of O 2p + Bi 6s hybrid orbitals.³¹ Nevertheless, the utilization ratio of sunlight needs to be improved since BWO can only be excited by the light with $\lambda < 420$ nm, and the photogenerated electron/hole pair separation needs to be facilitated. Various strategies have been therefore deployed to enhance the overall photocatalytic performance of BWO under sunlight irradiation.^{32–41} Moreover, recently Lv et al.⁴² introduced surface oxygen vacancies into BWO via a controllable hydrogen reduction method and found that the photoresponse wavelength range was extended, and the photocatalytic activity was increased. Li et al.⁴³ reported the creation of oxygen vacancies on flower-like BWO through an etching process using NaBH_4 as reducing agent and demonstrated that the resultant samples exhibited enhanced performance of photoelectrochemical water splitting. However, the flower-like BWO does not have a monocrystalline structure. It is expected that the surface reconstruction of a special photocatalytically-active facet offers a great potential to achieve an excellent photocatalyst. In this work, we reported surface disorder engineering of flake-like BWO crystals with highly exposed (001) facets via a NaBH_4 reduction method. The photocatalytic activity of the disorder-engineered BWO samples was evaluated by degrading rhodamine B (RhB) under irradiation of simulated sunlight, UV light and visible light, and was found to be much higher than that of pristine BWO.

EXPERIMENTAL

Flake-like BWO crystals used in this study were prepared via a hydrothermal route. In a typical synthesis process, 0.9702 g (0.002 mol) of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.3298 g (0.001 mol) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 20 mL acetic acid solution (2.5 mol L^{-1}) and 20 mL deionized water with the help of magnetic stirring, respectively. The Na_2WO_4 solution was dropped slowly into the

$\text{Bi}(\text{NO}_3)_3$ solution under magnetic stirring. After another 60 min of stirring, the mixture was adjusted to a pH 7 with the addition of a certain amount of NaOH, and then filled up to 70 mL by adding deionized water. The obtained mixture was transferred and sealed in a 100 mL Teflon-lined stainless steel autoclave. The autoclave was placed into a thermostatic oven and heated at 200°C for 24 h. The precipitated crystals were collected after the completion of the reaction, washed three times with deionized water and two times with absolute ethanol, and dried at 60°C for 12 h. The final product was obtained as flake-like BWO crystals. The surface treatment process of BWO crystals was as follows: 0.1 g of the as-prepared BWO was loaded into 20 mL of NaBH_4 solution with different concentrations [0.01 mol L^{-1} , 0.03 mol L^{-1} , 0.05 mol L^{-1} and 0.1 mol L^{-1} (M)]. After reaction for 40 min in an ice bath under magnetic stirring, the product was collected, washed with deionized water and absolute ethanol, and dried at 60°C for 6 h. The samples treated at 0.01 M, 0.03 M, 0.05 M and 0.1 M NaBH_4 solution were designated as 0.01 M-BWO, 0.03 M-BWO, 0.05 M-BWO and 0.1 M-BWO, respectively.

Simulated sunlight, UV ($\lambda = 254$ nm) and visible light ($\lambda > 450$ nm) were separately used as the light source to evaluate the photocatalytic activity of the samples by degrading 5 mg L^{-1} RhB aqueous solution. Then 0.1 g of the photocatalyst and 100 mL of RhB solution were loaded in the photoreactor, and magnetically stirred in the dark for 30 min. Then, the mixture was subjected to photocatalysis. At reaction intervals of 60 min, 2.5 mL of the reaction solution was sampled from the photoreactor and centrifuged at 4000 rpm for 10 min to remove the photocatalyst. The residual concentration of RhB was determined by measuring the absorbance of the reaction solution at $\lambda = 554$ nm on a ultraviolet–visible (UV–Vis) spectrophotometer. The degradation percentage of RhB is given as: $D\% = (C_0 - C_t)/C_0 \times 100\%$, where C_0 = initial RhB concentration and C_t = residual RhB concentration after reaction for t min.

The morphology and microstructure characterization of the samples was carried out by using field-emission scanning electron microscopy (SEM) and field-emission transmission electron microscopy (TEM). X-ray powder diffraction (XRD) with Cu $K\alpha$ radiation (wavelength: 0.15406 nm) was employed to determine the crystal structure of the samples. N_2 adsorption–desorption technique was used to analyze the Brunauer–Emmett–Teller (BET) surface area of the samples. UV–Vis diffuse reflectance spectroscopy (DRS) was applied to characterize the optical absorption and bandgap of the samples. X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical states of the elements in the samples. The photoluminescence (PL) spectra of the samples were measured on a

fluorescence spectrophotometer (excitation wavelength: 315 nm).

The photocurrent response and electrochemical impedance spectroscopy (EIS) measurements of the samples were performed on a CST 350 electrochemical workstation. A standard three-electrode configuration was used during the photoelectrochemical test, where a standard calomel electrode (SCE) served as the reference electrode and a platinum foil electrode acted as the counter electrode. The working electrode was prepared according to the procedure described in the literature.⁴⁴ Then 25 mg of the photocatalyst, 1.25 mg of carbon black and 1.25 mg polyvinylidene fluoride (PVDF) were uniformly mixed into 1 mL 1-methyl-2-pyrrolidone (NMP) that acted as the dispersant. The paste mixture was homogeneously pasted onto fluorine-doped tin oxide (FTO) glass substrate (effective area: $1 \times 1 \text{ cm}^2$). After drying at 60°C for 5 h, the final working electrode was obtained. A 0.1 M Na₂SO₄ aqueous solution was used as the electrolyte. Simulated sunlight was used as the light source.

RESULTS AND DISCUSSION

Figure 1a, b, c, d, and e shows the apparent colors of BWO samples before and after treatment with NaBH₄ solution of different concentrations. It is seen that pristine BWO appears cream white in color. With increasing the NaBH₄ concentration, the color of the NaBH₄-treated BWO samples gradually becomes deeper, and is changed into a blackish color for the 0.1 M-BWO sample treated by 0.1 M NaBH₄ solution. This color change is ascribed to the creation of a disordered surface layer on BWO. The disordered surface layer gradually becomes thicker with increasing the NaBH₄ concentration, and thus more surface states corresponding to the disordered surface layer are introduced in the forbidden gap of BWO. The increased surface states result in the enhanced visible-light absorption of the NaBH₄-treated BWO samples due to the electron excitation from the VB to the surface states, and as a result, the color of the samples becomes deeper black.

The photocatalytic activity of the samples was evaluated by the degradation of RhB in aqueous solution under simulated sunlight irradiation ($C_{\text{RhB}} = 5 \text{ mg L}^{-1}$, $C_{\text{photocatalyst}} = 1 \text{ g L}^{-1}$), as shown in Fig. 2a. After 180 min of photocatalysis, the

degradation percentage of RhB reaches 58.4%, 75.3%, 87.9%, 72.6% and 47.5% photocatalyzed by BWO, 0.01 M-BWO, 0.03 M-BWO, 0.05 M-BWO and 0.1 M-BWO, respectively. The highest photocatalytic activity is observed for 0.03 M-BWO. It is obvious that the surface treatment by NaBH₄ solution with an appropriate concentration can significantly enhance the photocatalytic activity of BWO. In addition, the adsorption percentage of RhB onto the samples is obtained to be 4.9–12.5%, exhibiting an increasing trend with increasing the NaBH₄ solution. The increased dye adsorption is due to the created surface defects and increased BET surface area of NaBH₄-treated BWO samples. To further quantitatively compare the photocatalytic activity between the samples, the kinetic plots of the dye degradation are derived, as shown in Fig. 2b. The good linear variation of $\ln(C_t/C_0)$ with irradiation time t suggests that the dye degradation process conforms well to the first-order kinetic equation $\ln(C_t/C_0) = -k_{\text{app}}t$.⁴⁵ From the slope of the regression lines, the apparent first-order reaction rate constant k_{app} is obtained as 0.00466 min^{-1} , 0.00769 min^{-1} , 0.01125 min^{-1} , 0.00719 min^{-1} and 0.00359 min^{-1} for BWO, 0.01 M-BWO, 0.03 M-BWO, 0.05 M-BWO and 0.1 M-BWO, respectively. The optimal sample 0.03 M-BWO exhibits a photocatalytic activity ca. 2.4 times higher than that of pristine BWO. Using UV light ($\lambda = 254 \text{ nm}$) or visible light ($\lambda > 450 \text{ nm}$) as the light source, the photocatalytic performance of BWO and 0.03 M-BWO toward the RhB degradation was further comparatively investigated, as shown in Fig. 2c. It is observed that pristine BWO is photocatalytically active under UV irradiation, but shows a minor or negligible photocatalytic activity under visible light irradiation. This is due to the fact that BWO has a wide bandgap ($\sim 3.0 \text{ eV}$). In contrast, 0.03 M-BWO displays enhanced photocatalytic activity under both UV and visible light irradiation.

The recycling photocatalytic experiment was carried out to investigate the reusability of 0.03 M-BWO for the degradation of RhB under simulated sunlight irradiation. The photocatalyst was collected after the completion of the first photocatalysis cycle, and recovered by washing with deionized water and then drying at 60°C for 5 h. The recovered 0.03 M-BWO was loaded into fresh RhB solution for the next photocatalytic experiment under

Fig. 1. (a)–(e) Apparent colors of BWO samples before and after treatment with NaBH₄ solution of different concentrations.

Fig. 2. (a) Time-dependent photocatalytic degradation of RhB over all the samples under simulated sunlight irradiation. (b) Kinetic plots of the dye degradation under simulated sunlight irradiation for all the samples. (c) Photocatalytic degradation of RhB over BWO and 0.03 M-BWO under irradiation of UV ($\lambda = 254$ nm) and visible light ($\lambda > 450$ nm). (d) Photocatalytic degradation of RhB over 0.03 M-BWO repeatedly used for four times under simulated sunlight irradiation.

the same conditions. Figure 2d shows the photocatalytic degradation of RhB over 0.03 M-BWO repeatedly used for four times. The degradation percentage of RhB reaches 82.0% (reaction for 120 min) at the fourth cycle of the photocatalysis, and 87.9% at the first photocatalytic cycle. The slight loss of the photocatalytic efficiency implies that 0.03 M-BWO manifests an excellent photocatalytic stability toward the dye degradation.

Further comparative investigation was performed on pristine BWO and 0.03 M-BWO. Figure 3a shows the SEM image of pristine BWO, revealing that BWO crystallizes in the form of flake-like crystals with average thickness of ca. 90 nm. The flake-like morphology of BWO was further confirmed by the TEM image, as shown in Fig. 3b. The high resolution TEM (HRTEM) image shown in Fig. 3c demonstrates that the flake-like BWO crystal appears to be monocrystalline and has perfect crystal lattice fringes with no internal defects. The lattice fringes with a d-spacing of 0.385 nm

correspond to the (220) facet of the orthorhombic structure of BWO. Figure 3d shows the selected area electron diffraction (SAED) pattern of BWO, which can be indexed according to the [001] zone axis of BWO orthorhombic structure.⁴⁶ The regular and periodical arrangement of diffraction spots further confirms a single-crystalline nature of the flake-like BWO crystal. The HRTEM and SAED results suggest that the flake-like BWO crystals are highly exposed by (001) facets. The energy-dispersive x-ray spectroscopy (EDS) spectrum of BWO was measured to determine its chemical composition, as shown in Fig. 3e. Besides the Bi, W and O elements, Cu and C signals are also observed in the EDS spectrum, which could arise from the microgrid used for supporting the sample in the TEM experiment. The atomic ratio of Bi/W obtained from the EDS spectrum is in good agreement with that in BWO phase. However, the derived O content is much lower than the stoichiometric O content in

Fig. 3. SEM image (a), TEM image (b), HRTEM image (c), SAED pattern (d) and EDS spectrum (e) of pristine BWO.

Fig. 4. HRTEM image (a) and EDS spectrum (b) of 0.03 M-BWO.

BWO phase, which is due to the non-sensitivity of EDS to light elements.⁴⁷

Figure 4a shows the HRTEM image of 0.03 M-BWO, revealing that an amorphous layer with thickness of ca. 2 nm is created on the surface of the BWO crystal by 0.03 M NaBH_4 solution treatment. However, the basic orthorhombic lattice structure of BWO is not destroyed since the lattice

fringes with a d-spacing of 0.385 nm, which correspond to the BWO (220) crystal plane, are still clearly visible in the HRTEM image. The EDS spectrum obtained from 0.03 M-BWO (Fig. 4b) is very similar to that of pristine BWO, indicating that the NaBH_4 treatment does not cause loss of Bi or W in the BWO crystals. The variation of O content is difficult to be determined due to the limitation of

EDS. A possible reason for the formation of disordered surface structure after treatment with NaBH_4 solution is that NaBH_4 could act with oxygen species and thus make the rearrangement of surface atoms. The formation of Bi metal can be excluded by the XRD and Bi 4f XPS analyses.

Figure 5a shows the XRD patterns of BWO and 0.03 M-BWO, along with the standard XRD line pattern of orthorhombic BWO (PDF#73-2020). It is clear that the diffraction peaks of 0.03 M-BWO are identical to those of pristine BWO, both of which can be perfectly indexed in terms of the BWO orthorhombic phase. This indicates that the dominant crystal structure of BWO undergoes no destruction after NaBH_4 treatment though a disordered surface layer is created on BWO. Figure 5b shows the N_2 adsorption–desorption isotherms of BWO and 0.03 M-BWO, both of which belong to type II according to the IUPAC classification.⁴⁸ No obvious hysteresis loop is observed in the isotherms,

implying the absence of mesopores in both samples. The inset in Fig. 5b shows the pore size distribution curves derived from the adsorption branch of the isotherms using the Barrett–Joyner–Halenda (BJH) method. The extremely small value of dV/dD implies negligible micropores or mesopores in BWO and 0.03 M-BWO. The BET surface area of BWO and 0.03 M-BWO is obtained as $1.5661 \pm 0.0606 \text{ m}^2 \text{ g}^{-1}$ and $2.2307 \pm 0.1155 \text{ m}^2 \text{ g}^{-1}$, respectively. Figure 5c shows the UV–Vis DRS spectra and the corresponding first-derivative curves (inset) of BWO and 0.03 M-BWO. Compared to pristine BWO, 0.03 M-BWO shows a slight increase in the visible light absorption. The bandgap energy (E_g) of the samples can be derived from the peak on the first-derivative curves,⁴⁹ indicating that both samples have a similar E_g of 2.97 eV.

The chemical states of the elements in BWO and 0.03 M-BWO were investigated by XPS. Figure 6a–c display the Bi 4f, W 4f and O 1s XPS spectra,

Fig. 5. (a) XRD patterns of BWO and 0.03 M-BWO, along with the standard XRD line pattern of orthorhombic BWO (PDF#73-2020). (b) N_2 adsorption–desorption isotherms and pore size distribution curves (inset) of BWO and 0.03 M-BWO. (c) UV–Vis DRS spectra and the corresponding first-derivative curves (inset) of BWO and 0.03 M-BWO.

Fig. 6. Bi 4f (a), W 4f (b) and O 1s (c) XPS spectra of pristine BWO and 0.03 M-BWO.

respectively. For pristine BWO, the Bi 4f XPS spectrum presents two peaks at 158.9 (Bi 4f_{7/2}) and 164.2 eV (Bi 4f_{5/2}), and the W 4f XPS spectrum displays two peaks at 35.0 (W 4f_{7/2}) and 37.2 eV (W 4f_{5/2}). For 0.03 M-BWO, the Bi 4f and W 4f binding energies exhibit a slight increase compared to those of pristine BWO, which could be ascribed to the creation of a disordered surface layer on BWO. For both samples, no additional peaks are observed on the Bi 4f and W 4f XPS spectra, implying that bismuth and tungsten species behave as Bi³⁺ and W⁶⁺ oxidation states without the existence of other oxidation states.^{50–53} On the O 1s XPS spectra of BWO and 0.03 M-BWO, the peak at 529.9 (or 530.2) eV is ascribed to the crystal lattice oxygen and the peak at 531.3 (or 531.7) eV is attributed to the surface adsorbed oxygen.^{37,53} The surface adsorbed oxygen is generally associated with oxygen vacancies.¹⁹ It is seen that the formation of a disordered surface layer on BWO by NaBH₄ treatment results in no obvious increase in oxygen vacancies, though it leads to a slight increase in the O 1s binding energy.

Transient photocurrent response, EIS and PL spectroscopy are very useful to investigate the separation behavior of photogenerated electron/hole pairs in BWO and 0.03 M-BWO.⁵⁴ As seen from the transient photocurrent responses measured for several on/off cycles of simulated sunlight illumination (Fig. 7a), 0.03 M-BWO exhibits an obviously enhanced photocurrent density when compared with pristine BWO. The Nyquist plots of the EIS spectra illustrated in Fig. 7b demonstrate that 0.03 M-BWO has a relatively smaller charge-transfer resistance. The PL spectra of BWO and 0.03 M-BWO are shown in Fig. 7c, revealing that the latter has a PL emission peak (ca. 580 nm) obviously weaker than that for the former. It is concluded from these properties that NaBH₄-treated BWO manifests more efficient separation of photogenerated electron/hole pairs than pristine BWO.

Based on the aforementioned experimental results, we propose a possible mechanism to elucidate the enhanced photocatalytic activity of NaBH₄-treated BWO, as schematically illustrated Fig. 8. When BWO is treated by NaBH₄ solution with an appropriate concentration, a disordered layer (or amorphous layer) is created on the surface of flake-like BWO crystals. Simultaneously surface states corresponding to the disordered surface layer are introduced in the forbidden gap of BWO. The created surface states are generally shallow ones and can act as electron acceptors to trap photogenerated electrons.^{19,55} Under irradiation of UV light, VB electrons are excited to the conduction band (CB) or surface states of BWO. The photogenerated electrons in the CB tend to be trapped by the surface states, thus leading to a decreased recombination of the photogenerated electron/hole pairs. As a result, more photogenerated holes are able to participate in the photocatalytic reactions. This is the dominant reason that NaBH₄-treated BWO samples exhibit enhanced UV photocatalytic activity when compared with pristine BWO. Further, the increased BET surface area of NaBH₄-treated BWO samples can provide more active sites, which is also beneficial to improve the photocatalytic performance. On the other hand, under irradiation of visible light ($\lambda > 450$ nm), the VB electrons cannot be excited to the CB of BWO due to its large bandgap of 2.97 eV. Consequently pristine BWO exhibits a minor or negligible photocatalytic activity under visible light irradiation. Whereas for NaBH₄-treated BWO samples, the visible light irradiation could induce the electron excitation from the VB to the surface defect states, thus resulting in a slightly enhanced visible-light photocatalytic activity. It is noted that, however, when NaBH₄ concentration is increased to a high value (0.05 M), the treated samples exhibit a decrease in the photocatalytic performance. A possible reason for this phenomenon is that bulk defects could be created in BWO crystals, which could act as

Fig. 7. Transient photocurrent response (a), Nyquist plots of the EIS spectra (b) and PL spectra (c) of BWO and 0.03 M-BWO.

Fig. 8. Schematic illustration of the photocatalytic mechanism of the surface disorder-engineered BWO.

charge carrier recombination centers to facilitate the photogenerated electron/hole pair recombination.^{56,57} According to previously reported results, the CB and VB potentials of BWO are + 0.20 V and + 3.17 V versus normal hydrogen electrode (NHE), respectively.³⁷ From a thermodynamic point of view, the photogenerated holes can react with OH^- or H_2O to produce $\cdot\text{OH}$ since the VB potential of BWO is more positive than the redox potentials of $\text{H}_2\text{O}/\cdot\text{OH}$ (+ 2.38 V versus NHE) and $\text{OH}^-/\cdot\text{OH}$ (+ 1.99 V versus NHE).^{58,59} However, no $\cdot\text{OH}$ radicals are detected by PL technique as described in the literature,⁶⁰ implying a minor role of $\cdot\text{OH}$ in the dye degradation. On the other hand, the CB potential is not sufficiently more negative than the redox potential of O_2/O_2^- (- 0.33 V versus NHE),⁵⁷ indicating that the photogenerated electrons cannot thermodynamically react with O_2 to produce $\cdot\text{O}_2^-$. It is conjectured that the photogenerated holes are the dominant reactive species directly causing the dye degradation.

CONCLUSIONS

Surface-disorder-engineered flake-like BWO crystals were achieved via a NaBH₄ reduction method. Simultaneously, disordered surface states are introduced in the forbidden gap of BWO, which can act as electron acceptors to facilitate the separation of photogenerated electrons and holes. As a result, the disorder-engineered BWO samples, particularly the sample 0.03 M-BWO treated by a 0.03 M NaBH₄ solution, manifest a significantly enhanced photocatalytic activity toward the degradation of RhB under UV irradiation. Moreover, the disorder-engineered BWO samples also display a slightly enhanced photocatalytic activity under visible light irradiation, which can be explained as the result of enhanced visible light absorption due to the electron excitation from the VB to the disordered surface states. However, the creation of bulk defects in BWO crystals at high NaBH₄ concentrations is detrimental to the photocatalytic activity.

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