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Microfluidic chip-based analytical system for rapid screening of photocatalysts

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ABSTRACT

A simple and efficient microfluidic chip-based analytical system for rapid screening of photocatalysts was developed. The catalyst screening system consisted of a microchip with multiple channels for parallel reactions, a UV light source, and a CCD camera-based photometric detection system for monitoring the photocatalytic reaction. A novel microfluidic introduction method for loading particle samples into chip microchannels was established using dry sample powders and wedge-structure channel design. With this method, multiple different photocatalyst samples could be quickly introduced into the microchip with good reproducibility without the need of additional pumps or valves. We applied the present system in the rapid screening of doping TiO_2 photocatalysts in terms of their activity for methylene blue (MB) degradation under UV light irradiation. Ten parallel photocatalyst screening reactions were achieved within 15 min in the multi-channel chip. We also examined nine element doped TiO_2 materials to investigate the doping effects of different elements on TiO_2. Compared with conventional systems, the photocatalyst consumption (0.1 mg) in the present system was significantly reduced at least 100 times. High reaction rate in chip microreactors was obtained with an increase of two orders of magnitude over bulk reactors. The miniaturization of the photocatalytic reaction on the microchip significantly improves the reaction rates, reduces the sample and reagent consumptions, and increases the throughput of screening for multiple catalyst samples in parallel. The present work provides a novel application for microfluidic chip-based analytical systems, as well as a rapid, highly-efficient and low-consumption method for screening of photocatalysts.

1. Introduction

The discovery of highly active photocatalysts is of vital importance in many applications such as environmental protection and the generation/distribution of sustainable energy. At the same time, photocatalyst development is one of the most laborious and know-how intensive fields. In order to expedite this process, combinatorial methods based on automated synthesis and screening have been successfully implanted [1–3]. Nakayama et al. developed a combinatorial method to accelerate the discovery of new thin-film photocatalysts. High throughput evaluation of photocatalytic activity was realized by using a two-dimensional pH imaging technique [1]. A modified scanning electrochemical microscopy (SECM) technique has also been applied to evaluate the photo-induced currents. Lee et al. recently reported a rapid screening of photocatalysts using a modified SECM technique. They prepared an array of photocatalysts containing spots of different compositions. The scanning tip of the SECM was replaced by a fiber optic connected to a Xenon lamp and was rapidly scanned over the array. In this arrangement, the photocatalytic performance of the spots was evaluated by measuring the photocurrent at the substrate of the array [2]. Zhang's group reported a cataluminescence-based array imaging method for high-throughput screening of active catalysts for CO oxidation [3].

Recently, much attention has been paid to performing chemical reactions in microfluidic chips utilizing the features unique to microspace such as short molecular diffusion distance, fast mixing, and large surface-to-volume ratio. In some studies, the microfluidic technique was used to improve mass transfer, photon transfer, reaction surface cleaning and long-term stability in photocatalytic reactions, and thus obtained higher reaction rates compared with bulk systems [4–8]. Moreover, unlike traditional bench-top chemistry in which the throughput level of screening is difficult to be increased due to the limitations in system scale and

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laborious operations, multiple channels can be easily fabricated in microchip-based systems to achieve parallel reactions to increase screening throughput. Currently, in most of microfluidic chip systems for screening of heterogeneous catalysts, microreaction systems with catalytic coatings on microchannels are mainly used [9–16,24,25,27]. Since special catalyst preparation methods are usually required to produce the catalytic coatings in microsystems, they may exhibit different structural, morphological and, thus, catalytic properties in comparison with conventionally prepared catalysts [17,18].

In the present work, we proposed a different strategy from the above-mentioned systems for performing microfluidic heterogeneous catalyst screening by directly using particle catalysts produced by conventional methods instead of catalyst coatings in microchannels, to improve the consistency with currently-used routine screening systems. To achieve such a goal, a novel microfluidic introduction method for solid particle samples was established to load different particle catalysts into chip channels. On the basis of this method, we developed a simple and efficient microchip-based analytical system for rapid screening of photocatalysts. The system is capable of performing parallel screening in channel arrays with low sample consumption of 0.1 mg. We applied it in the rapid screening of photocatalysts in terms of their activity for methylene blue (MB) degradation under UV light irradiation.

2. Experimental section

2.1. System setup

The catalyst screening system (Fig. 1a) consisted of a microchip with multiple channels for parallel reactions, a UV light source, and a CCD camera (DCM130, Touptek Photonics, Hangzhou, China) for monitoring the photocatalytic reaction. The microchip (Fig. 1b) with a wedge structure in each channel was fabricated using a standard photolithographic and wet etching technique as described previously [19] (Fig. S1). The substrate with a shallow channel (15 μm depth, 500 μm width, and 600 μm length) and the substrate with a deep channel (100 μm depth, 225 μm width) were aligned under a stereomicroscope and then bonded together using room temperature prebonding and high-temperature (560 °C) bonding techniques [20].

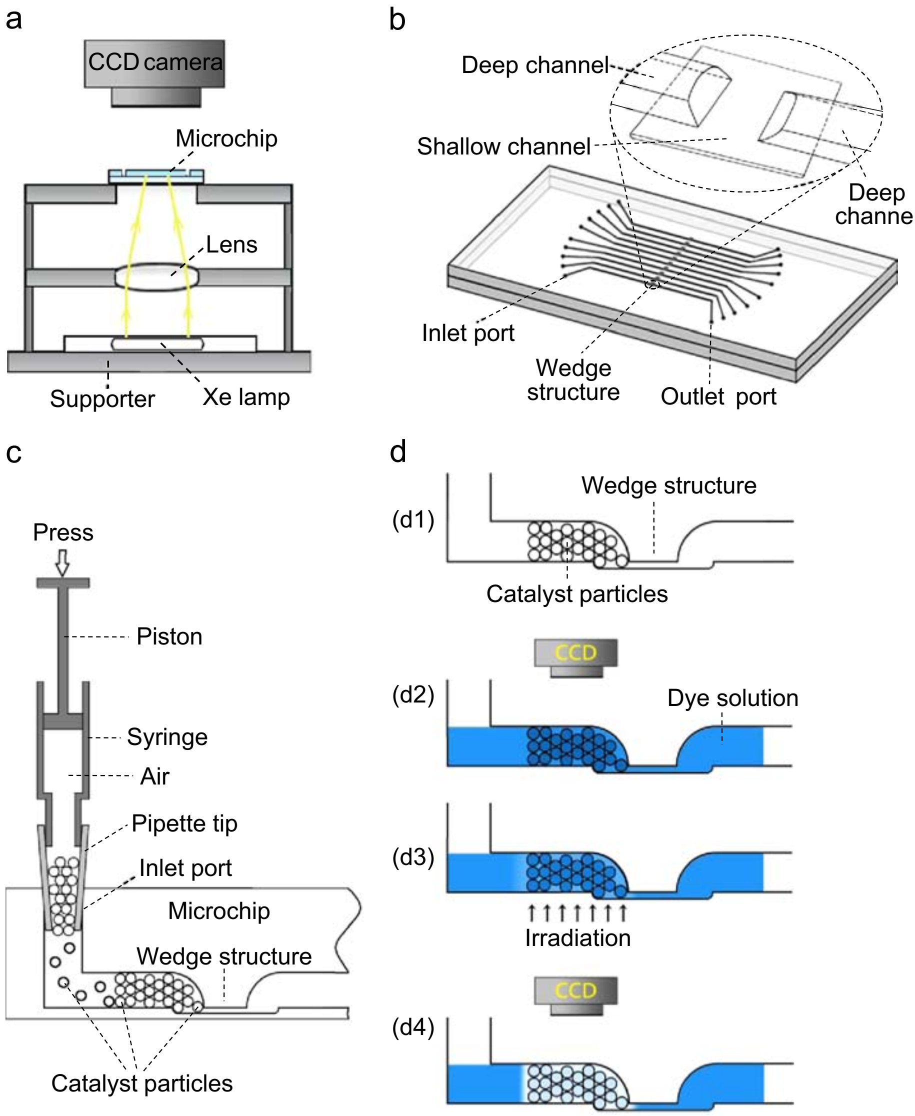

Fig. 1. (a) Setup of the microchip-based photocatalyst screening system. (b) Schematic diagram of the multi-channel array chip with a wedge structure in each channel. (c) Schematic diagram of the catalyst loading operation. (d) Illustration of the catalyst screening procedure. (d1) Loading catalyst particles in the microchannel to form the column; (d2) introducing MB solution into the channel and recording the initial channel image by the CCD camera; (d3) MB degradation under irradiation of UV light; and (d4) recording the channel image after definite reaction time. (not to scale)

A 120-W Xe lamp was used as the light source. The beam passed through a plano-convex lens (GCL-010810, Daheng Co., Beijing, China), and was focused on the chip channels with an irradiation region of 15 × 15 mm^2. The captured CCD images were analyzed by ImageJ software, and the two maximum gray values are defined as 255 units (white) and 0 unit (black). The detailed photometric detection method has been previously reported [21].

2.2. *Synthesis of mesoporous catalysts*

Mesoporous M-TiO$_2$ catalysts (M=F, Si, K, Mn, Co, Ni, Cu, Mo and Au) are prepared by the acetic acid, hydrochloric acid, and ethanol (AcHE) synthesis method [22]. In a typical synthesis of 1.0% F-TiO$_2$, 10 mmol of Ti(OBu)$_4$, 40 mmol HOAc, 12 mmol HCl (or HNO$_3$), 0.033 mmol of CF$_3$COOH, and 1.6 g of F127 (EO$_{96}$PO$_{70}$EO$_{96}$, MW=12,000 g mol^{-1}) are dissolved in 30 mL ethanol. The mixture is stirred vigorously for 1 h and transferred into a Petri dish (diameter 125 mm). The ethanol is evaporated at 40 °C for 12 h with a relative humidity of ~40% to form a membrane. The membrane is aged in a 65 °C oven for 24 h, and then calcined at 350 °C in air for 6 h (ramp rate 2 °C/min) to obtain a mesoporous membrane. The membrane is ground into fine powder before use for the catalytic reaction.

2.3. *Procedures*

Mesoporous M-TiO$_2$ catalysts (M=F, Si, K, Mn, Co, Ni, Cu, Mo and Au) were first prepared. In order to avoid the blockage of the channels, each catalyst was ground and then sieved using two sieves of 400 mesh and 700 mesh, corresponding to sieve pore size of 38 and 20 μm, respectively. The catalyst particles with sizes ranging from 20 μm to 38 μm were used in the following screening experiments. The dry sample catalyst powder was manually introduced into the chip channel using a 20 mL syringe connected with a pipette tip (Fig. 1c). The pipette tip was first filled with ca. 1 mg catalyst powder, and then was inserted into the inlet port of the chip channel. The catalyst powder was blown by air in the syringe into the channel by pressing the piston of the syringe. The introduced catalyst particles were blocked at the wedge structure of the channel, forming a column with the length range of 5.5–6.0 mm (Fig. 1d1).

In the photocatalytic reaction, MB was used as the dye since it is one of the most commonly-used model dyes for testing TiO$_2$ photocatalyst, and could be detected by the photometric detection system. A MB solution (10^{-2} mol L^{-1}) was continuously introduced into the channel using another syringe (Fig. 1d2). The photocatalytic reaction was started and carried out by irradiating the columns with the UV light for a definite time (Fig. 1d3), with an irradiating region of 5.5 × 7.0 mm^2 (length × width) (Fig. 2). After removing the UV light, the images of the channels were recorded by the CCD camera (Fig. 1d4), the gray values of the chip channels in the detection region (4.0 × 6.5 mm^2, length × width) were measured using the software ImageJ.

In the comparison experiments, a conventional reaction system (XPA, Xujiang Machine Factory, Nanjing, China) with a bulk container of 15 mL was used to perform the catalytic reaction with the same ratio of MB/TiO$_2$ as in microchip system. Before reaction, 1 g of catalyst powder and 7 mL of the MB solution (10^{-2} mol L^{-1}) were added into the container. The MB photodegradation was carried out under the side-irradiation of a 300 W high-pressure Hg lamp. The absorption spectra of the photodegraded solutions in the container were analyzed after 5 min, 10 min, and 15 min of exposure. The degradation process was monitored by measuring the absorbance change of MB solution at 664 nm.

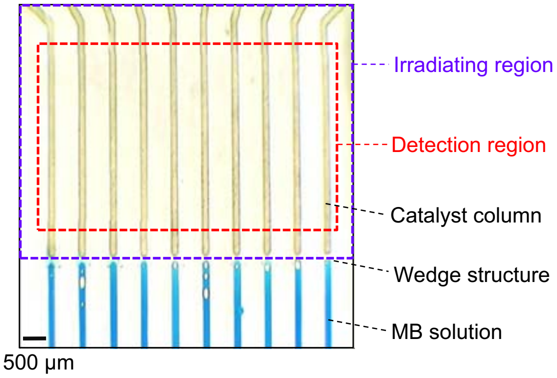

Fig. 2. Image of the chip channels loaded with mesoporous TiO$_2$ and MB in each channel after a 15-min irradiation of UV light. The irradiating region (5.5 × 7.0 mm^2) and detection region (4.0 × 6.5 mm^2) are indicated by dashed line frames.

3. Results and discussion

3.1. *Dry sample loading method for particulate catalysts*

The first challenge of the present work is how to load particle catalyst into the microchannels. Differing from reported film [11–14,23–25] or supported spot samples [10,26–28], widely used particulate TiO$_2$-based samples were investigated in our study. In general, the particulate catalysts have less mass-diffusion limitation as compared to film samples. However, in the loading process for catalyst particle suspension, the microchannels were easily blocked by the particles, particularly under relatively high loading flow rates, which resulted in an incomplete or ununiform sample loading. This would significantly deteriorate the system reproducibility and the reliability for catalyst screening.

In this work, a wedge-microstructured channel design and a dry sample loading method were used to address this issue. In the present system, the loading operations for catalyst and dye solution were conducted separately. The dry sample catalyst powder instead of suspension used in other chip-based systems [29] was directly introduced into the chip channel using a 20 mL syringe connected with a pipette tip (see Fig. 1c) without the need of additional pumps or valves. The dry catalyst powder in the pipette tip was blown by air into the channel smoothly, and the introduced catalyst particles were blocked at the wedge structure of the channel to form a catalyst column. During this process, no obvious channel blockage was observed in the other regions of the channel. The use of the dry sample loading method significantly simplified the system setup and operation, and ensured a good reproducibility for solid sample loading (see Fig. 3), which is essential for a multi-channel screening system.

Benefiting from miniaturizing photocatalytic reactions in microchannels, 10 microchannels could be simultaneously irradiated by the UV light beam. This not only significantly increases the screening throughput of the present system, but also enables it to achieve screening for multiple catalyst samples in parallel. To ensure the consistency of catalyst capacities in different channels used for screening, we used a restrictive detection region with a length shorter than those of the irradiating region as well as catalyst columns (Fig. 2). In the detection region, 10 catalyst columns have the same length (i.e. same capacity) parts to be measured, which ensure the reliability in screening of different photocatalysts (see section "*Testing for system reproducibility*"). The other reason for using shorter detection region is to eliminate the effect of MB diffusion from out of the irradiating region (Fig. 2).

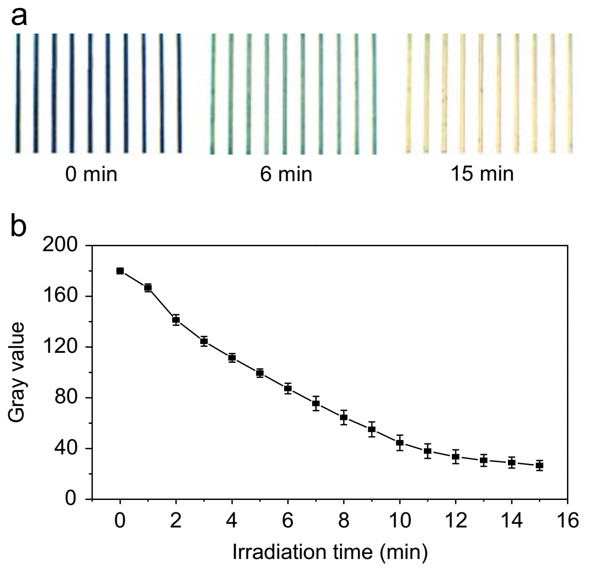

Fig. 3. Reproducibility experiment of the chip system. (a) Typical images of the 10 channels at reaction times of 0, 6, and 15 min. (b) Curve of average gray value of 10 channels vs. irradiation time during the photocatalytic reaction process. The error bars are the standard deviation obtained from the data of 10 channels. Catalyst, mesoporous TiO_2; and dye, 10^{-2} mol L^{-1} methylene blue.

3.2. *Testing for system reproducibility*

We tested the reproducibility of the present system with the 10-channel array using the same photocatalyst of mesoporous TiO_2 (Fig. 3). Fig. 3b shows typical recordings of gray values of 10 channels in the detection region during the 15-min catalytic reaction. The gray value decreased with the irradiation time, showing the degradation of MB with the catalyst mesoporous TiO_2. Consistent results were obtained among the 10 channels with reproducibilities of the gray values in 1.8–16.3% (relative standard deviation, $n=10$), which ensured the reliability of the present system in screening for multiple samples.

3.3. *Rapid screening of doping TiO_2 photocatalysts*

The present system was applied in rapid screening of doping TiO_2 photocatalysts in MB photodegradation. In order to investigate the doping effects of different elements on TiO_2, We examined nine element doped TiO_2 materials. The results are shown in Fig. 4. The K^+ doped catalyst does not show evident change in the catalytic activity. It is apparent that the Co^{3+}, Mn^{2+}, Ni^{2+}, Mo^{6+} and Cu^{2+} doped TiO_2 materials have decreases in catalytic activities compared with the undoped TiO_2. However, doping TiO_2 with F^-, Si^{4+} and Au^0 obviously enhances the catalytic activities. The F-doped TiO_2 catalyst shows the highest catalytic performance in the MB photodegradation.

3.4. *Effect of F-doped TiO_2 with different doping concentrations*

We further studied the doping effect of F-doped TiO_2 catalyst using TiO_2 materials with different F-doping concentrations of 0.1%, 0.5%, 1.0%, 2.0% and 5.0% (molar percentage concentration). As shown in Fig. 5, almost all of the F-doped TiO_2 catalysts show higher catalytic activity than undoped TiO_2. In this case, F^- shows strong positive co-doping effect on the catalytic activity of TiO_2. When F-doping concentration is 1.0%, the catalyst shows higher activity than others.

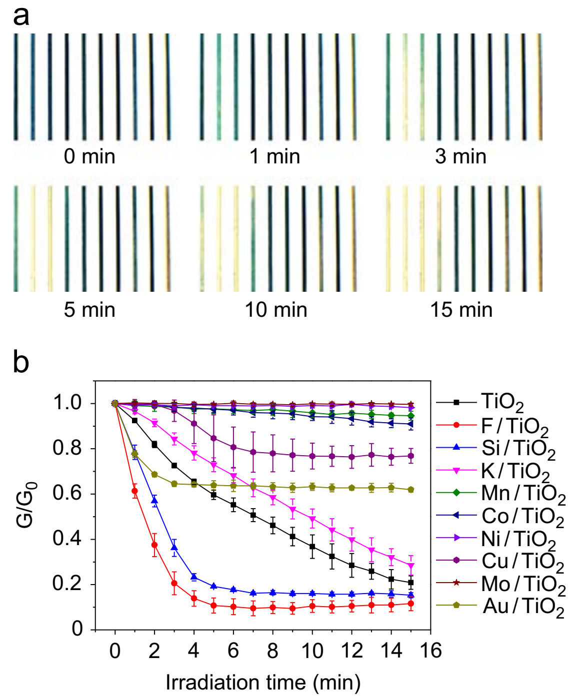

Fig. 4. (a) Typical channel images during the photocatalytic reactions with different element-doped TiO_2. (b) Curves of channel gray value vs. irradiation time during the photocatalytic reactions using different element-doped TiO_2, including undoped, 1.0% F^-, 1.0% Si^{4+}, 1.0% K^+, 1.0% Mn^{2+}, 1.0% Co^{3+}, 1.0% Ni^{2+}, 1.0% Cu^{2+}, 1.0% Mo^{6+}, and 1.0% Au^0 (molar percentage concentration). Dye, 10^{-2} mol L^{-1} methylene blue.

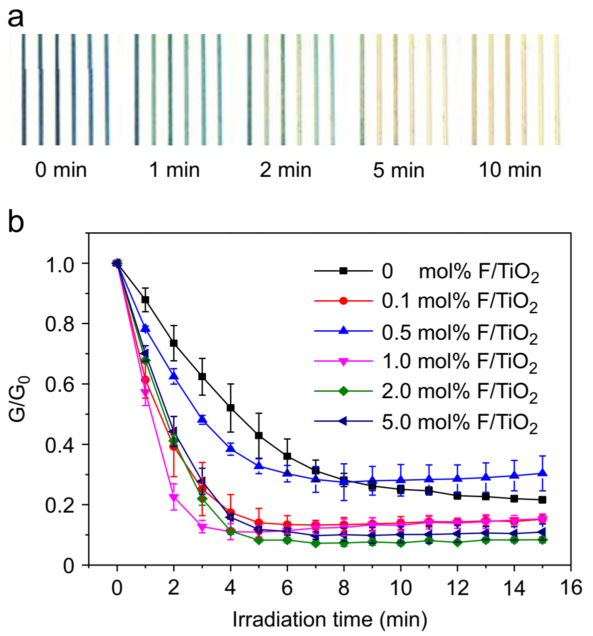

Fig. 5. (a) Typical channel images during the photocatalytic reactions using F-doped TiO_2 with different doping concentrations. (b) Curves of channel gray value vs. irradiation time during the photocatalytic reactions using F-doped TiO_2 with different doping concentrations, including undoped, 0.1%, 0.5%, 1.0%, 2.0% and 5.0% (molar percentage concentration). Dye, 10^{-2} mol L^{-1} methylene blue.

3.5. *Comparison experiment with conventional reaction system*

Using the 1.0% F-doped TiO_2 catalyst and dye MB, we made a comparison experiment between the present system and a conventional reaction system with a bulk container of 15 mL and catalyst consumptions in the gram scale. With 1 min irradiation, 99% of MB in the catalyst column of the microchip was degraded. We also calculated the average reaction rate constant k for MB photodegradation, given that the degradation is a pseudo-first order reaction (Fig. S2 and S3). The k value of 1.0% F-doped TiO_2 in the microchip is $1.5 \pm 0.1\ \text{min}^{-1}$ ($n=3$), which is ca. 520 times of that with the conventional system ($k=(2.9 \pm 0.4) \times 10^{-3}\ \text{min}^{-1}$, $n=3$). We measured illuminances of the light sources in the two systems using an illuminometer. The illuminance for microchip system was 22,500 fc (1 fc=10.76 lx) that is 4–5 times as high as that for conventional photocatalytic reaction system (4850 fc). Giving that the rate constant for microchip system is 520 times higher than that for conventional reaction system, a rough two-order-of-magnitude increase of the reaction rate is achieved in the microchip system. This demonstrates that performing photocatalytic reaction on the microfluidic chip indeed brings in remarkable improvement of reaction rate. This remarkable improvement of reaction rate can be attributed to the scale effects of microchip-based photocatalytic reactors including short molecular diffusion distances, high mass transfer rates, and large surface-to-volume ratios, which could significantly enhance the photon transfer and mass transfer efficiencies of the photocatalytic reaction [30,31].

4. Conclusion

In the present work, we achieved rapid screening of photocatalysts with a microfluidic chip-based system for the first time. High reaction efficiencies more than two orders of magnitude over conventional systems were obtained with the on-chip catalyst columns. The miniaturization of the photocatalytic reaction on a microchip not only significantly improved the reaction rates and thus increased the screening throughput, but also reduced the sample and reagent consumptions to extremely low level. In addition, benefiting from the reactor miniaturization, the screening throughput could be further increased using the multi-channel array chip. These characteristics are likely to meet the increasing demands on high efficiency and large-scale screening.

So far, to load solid particle samples into microchips is still a challenge work. In this work, we presented a simple and effective method to achieve such an operation without channel blockage. This method could also be used in other heterogeneous reaction systems, and has potential applications in studies of combinatorial chemistry, reaction dynamics, and rapid chemical and biological screening.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.08.012.

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