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RESEARCH ARTICLE

Electrochemical analysis of dye adsorption on aligned carbon nanofiber arrays coated with TiO_2 nanoneedles for dye-sensitized solar cell

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Abstract An electrochemical method has been developed to analyze dye absorption on the aligned carbon nanofiber arrays coated with TiO_2 nanoneedles for dye-sensitized solar cell. The unique nanostructure with the roughness factor of 90.6 provides a large effective surface area for dye adsorption. The experimental results showed that the dye molecules cover 39.7% of the TiO_2 surface area which influences the performance of dye-sensitized solar cell. The electrochemical method provides the information of the coverage of dye molecules which is a key issue to optimize solar cell performance.

Keywords electrochemical analysis, aligned carbon nanofibers, dye adsorption, solar cell

1 Introduction

Dye adsorption plays a key role in the performance of dye-sensitized solar cells, in which photoanodes constructed from a three-dimensional mesoporous network of TiO_2 nanoparticles (NPs) [1], vertically aligned TiO_2 nanotubes (NTs) [2,3], ZnO nanowires (NWs) [4,5], ZnO NTs [6], and Si NWs [7,8] and vertically aligned carbon nanofibers coated with a thin nanoneedle-textured anatase TiO_2 film [9,10]. Generally, the photoanodes were immersed in the dye solution to attach the dye on the photoanodes surface, which consisted of chemisorbed and physisorbed dyes. The high surface area of photoanodes can provide large dye adsorption. However too much physisorbed dyes may compete with the chemisorbed dyes for incident photons and limit the performance of the solar cell [11]. In order to improve the efficiency of dye-sensitized solar cells, it is important to determine the coverage of the dye on the photoanode surface. Various methods have been developed to detect the dye adsorption on the surface of photoanodes. Neale et al. measured the amount of adsorbed dye on the TiO_2 surface by optical absorption of the desorbed dye, which can be taken by immersed TiO_2 anode into 1 mM KOH solution for at least 20 min. Furthermore, they found that, even at low dye loading, sufficient amount of dye molecules were present to absorb a significant fraction of the incident light [12]. Hirose et al. demonstrated the infrared absorption spectroscopy with a multiple-internal-reflection geometry can be used to investigate the dye adsorption on TiO_2 surface with different adsorption [11]. We have previously fabricated dye-sensitized solar cells based on the architecture of vertically aligned carbon nanofiber (VACNF) nanobrushs coated with a nanoneedle-textured anatase TiO_2 film [10]. This architecture combines the highly conductive VACNF core as the electron collector and the nanostructured TiO_2 shell as the charge separation barrier. The nanostructured TiO_2 coating also provides a large surface area for dye adsorption toward high-efficiency development of dye-sensitized solar cells (DSSCs). How to determine the coverage of the dye is a key issue to optimize our solar cells.

Here we report that the electrochemical analysis is applied to detect dye adsorption on aligned carbon nanofiber arrays coated with TiO_2 nanoneedle for dye-sensitized solar cell. Electrochemical methods can provide information about activities rather than total amount of chemical species [13].

2 Experiment

2.1 Preparation of DSSC photoanodes

VACNF arrays were grown on the Si substrates coating with 100 nm Cr at about 800°C with a DC-biased plasma

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enhanced chemical vapor deposition (PECVD) system (AIXTRON) following previously published procedures [14–17] using a 22 nm thick Ni catalyst film and a mixture of C_2H_2 and NH_3 as the gas precursors. Then a TiO_2 layer was deposited on the VACNF via a metal-organic chemical vapor deposition strategy using titanium isopropoxide vapor under 150 mTorr at 550°C for 60 min. The DSSC Photoanodes were prepared by immersing the TiO_2-coated VACNF array in 0.2 mM ethanol solution of cis-bis(isothiocyanoto) bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium (II) bis-tetrabutylammonium dye (N719, Solaronix) for 12 h and were thoroughly rinsed with ethanol before being testing in the acetonitrile solution. The structure of the VACNF samples and TiO_2 nanoneedles coating was routinely examined with scanning electron microscopy (Hitachi VP-SEM S-3400N and Leo 1550 FESEM) and transmission electron microscopy (FEI CM100).

2.2 Electrochemical measurements

All electrochemical experiments are performed using a CHI 400 A potentiostat (CH Instruments, Electrochemical Analyzer) in a three electrode configuration using a platinum coil as a counter electrode, a Ag/AgCl (sat’d KCl) reference electrode, and one of the three types of working electrodes including a glassy carbon electrode, VACNF arrays coated with TiO_2 nanoneedles, dye adsorption on the surface of TiO_2-coated VACNF arrays. Cyclic voltammetry (CV) measurements were performed with 0.1 M $LiClO_4$ in acetonitrile solution.

3 Results and discussion

To evaluate the electrochemical properties of dye N719 in the acetonitrile solution with 0.1 M $LiClO_4$, we first choose a glassy carbon electrode as a working electrode to measure the CV behavior. Figure 1 shows the structure of N719 dye molecular and the CV measurement in the 0.1 mM dye and 0.1 M $LiClO_4$ in acetonitrile solution. The peak at around 0.61 eV is due to the oxidation of dye molecular.

Furthermore the effective surface area can be calculated from the back ground charging-discharging current according to

$$\Delta i = 2A \times C \times \mathrm{d}E/\mathrm{d}t, \qquad (1)$$

where Δi is the difference in current in forward and backward scans, $\mathrm{d}E/\mathrm{d}t$ is the potential scan rate, C is the specific electrical double layer capacitance, and A is effective surface area. For a glassy carbon electrode, the specific capacitance C is 55 $\mu F/cm^2$ [18], and Δi is 9×10^{-6} A/cm^2. As a result, the effective surface area is calculated to be about 1.636 cm^2 on a 1.0 cm^2 geometric substrate surface.

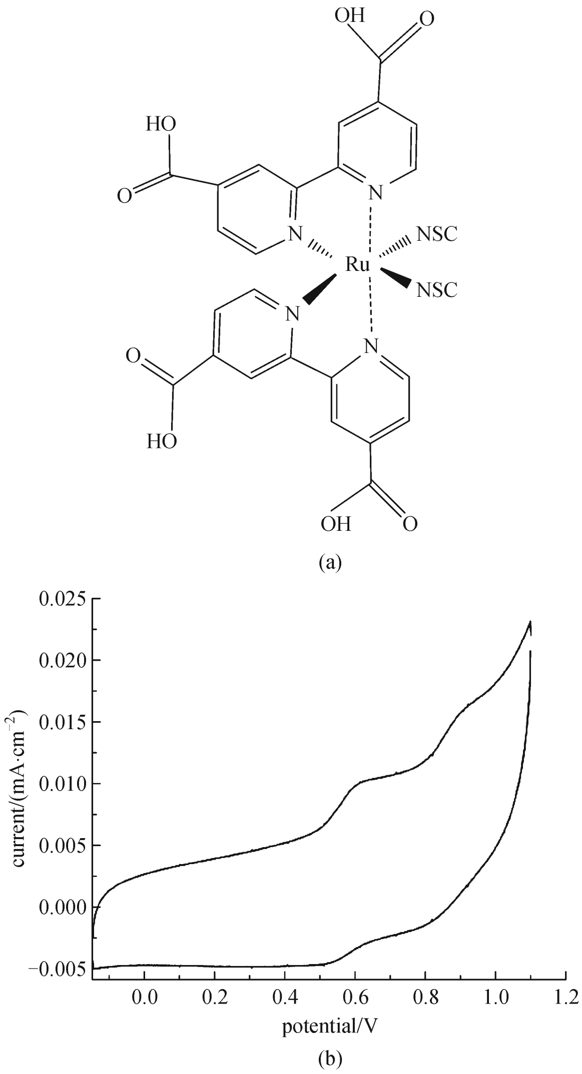

Fig. 1 Molecular structure of N719 dye and CV measurement in 0.1 mM Dye & 0.1 M LiClO4 acetonitrile solution taken with a scan rate of 50 mV/s using a platinum coil as a counter electrode, a Ag/AgCl(sat’d KCl) reference electrode, and a glassy carbon working electrode

Figure 2(a) shows a scanning electron microscopy (SEM) image at 45° perspective view of an as-grown VACNF array of about 5 m in length with a rather uniform vertical alignment. The density is about $1-2\times10^9$ CNF/cm^2, corresponding to an average nearest-neighbor distance of about 300–400 nm. Such three-dimensional (3-D) nanobrush structures offer sufficient open space for TiO_2 and dye molecule deposition. After deposition of TiO_2 for 60 min, we can observe the nanoneedles with the average diameter of 10–15 nm and length of 50–100 nm stacked on the CNF surface, as shown in Fig. 2(b). This provides a much larger surface area for dye molecules absorption, which is desired for higher DSSC efficiency.

To evaluate the effective surface area of the anodes, the vertically aligned carbon nanofiber array coated with

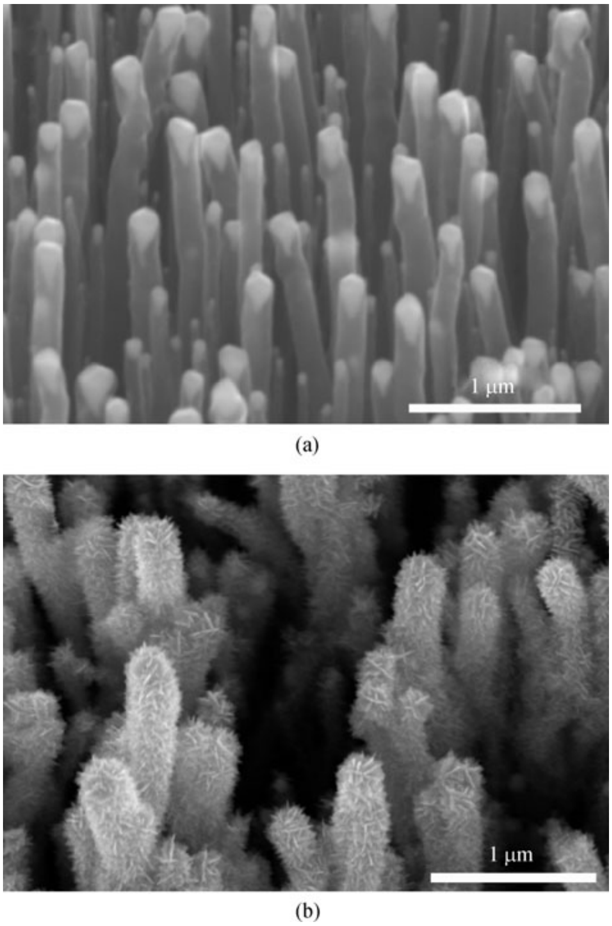

Fig. 2 (a) SEM image at 45° perspective view of a vertically aligned carbon nanofiber array; (b) vertically aligned carbon nanofiber array coated with anatase TiO_2 nanoneedles

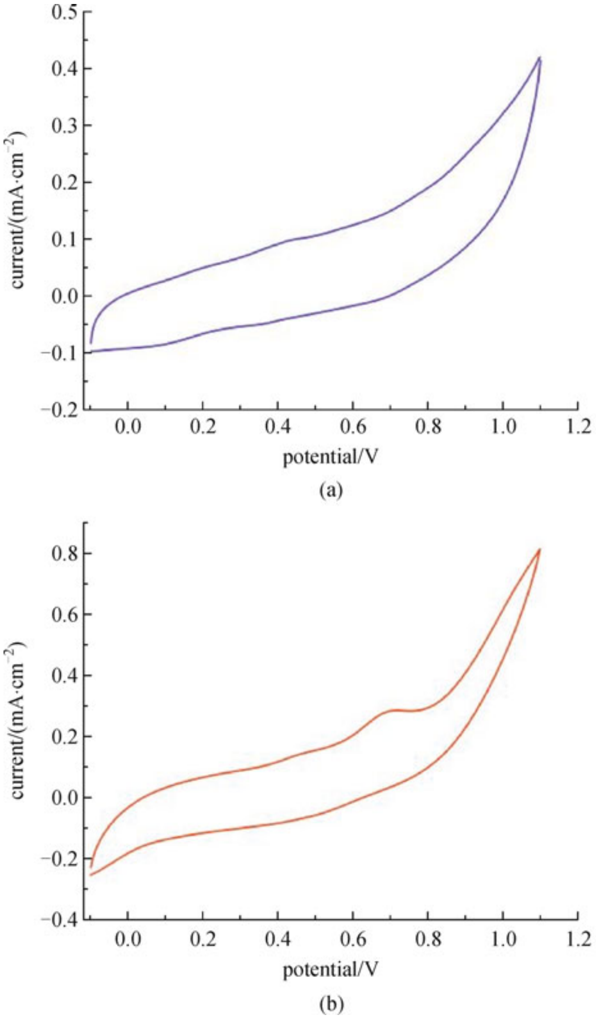

Fig. 3 (a) CV measurement in 0.1 M $LiClO_4$ acetonitrile solution taken with a scan rate of 50 mV/s using a platinum coil as a counter electrode, a Ag/AgCl(sat'd KCl) reference electrode, the vertically aligned carbon nanofiber array coated with anatase TiO_2 nanoneedles as the working electrode; (b) dye N719 absorption on the surface of vertically aligned carbon nanofiber array coated with anatase TiO_2 nanoneedles as the working electrode

anatase TiO_2 nanoneedles were used as the working electrode to check the CV behavior, as shown in Fig. 3(a). The capacity of anatase TiO_2 is about 90 $\mu F/cm^2$, which can be found on page 7720 of Ref. [19]. Following Eq. (1), we can calculate the effective surface area of the anode to be about 15 cm^2 on 1.0 cm^2 of geometric substrate surface. After absorption of dye N719 molecules, we observed an anodic peak at about 0.68 V which is due to the oxidation of dye molecules (see in Fig. 3(b)).

For comparison, the CV measurements with three working electrodes were shown in Figs. 4(a) and (b). According to Eq. (1), the effective surface area increases to 21 cm^2 on 1.0 cm^2 of substrate, as derived from CV in Fig. 4(a), with dye absorbing on the surface of the VACNF array that is coated with anatase TiO_2 nanoneedles. This value is 12.8 times larger than that of glassy carbon electrodes.

From the charge-discharge current, we can calculate an effective surface area around 21 cm^2 of TiO_2 nanoneedles coating on the VACNF array on 1.0 cm^2 of geometric surface. Furthermore, we can calculate the total surface area from transmission electron microscope (TEM) image. As shown in Fig. 6, CNF has the diameter of 100 nm, length of 5 μm, and the needle-shaped TiO_2 nanostructure has the mean diameter of 15 nm and the mean length of 100 nm was deposited onto the surface of CNF. The orientation of the nanoneedles is random. The density of TiO_2 nanoneedle is about 1×10^{11} cm^{-2} derived from the TEM image. The surface area of a single CNF is

$$A_{\mathrm{CNF}} = 2\pi RL = 1.57 \times 10^{-8}\ \mathrm{cm}^2,$$

and the total area of CNF array on 1 cm^2 geometric area is

$$\begin{aligned} A_{\mathrm{CNF,\,array}} &= A_{\mathrm{CNF}} \times (\text{density of CNFs}) + 1\ \mathrm{cm}^2 \\ &= 1.57 \times 10^{-8} \times 10^{9}\ \mathrm{cm}^2 + 1\ \mathrm{cm}^2 = 16.7\ \mathrm{cm}^2. \end{aligned}$$

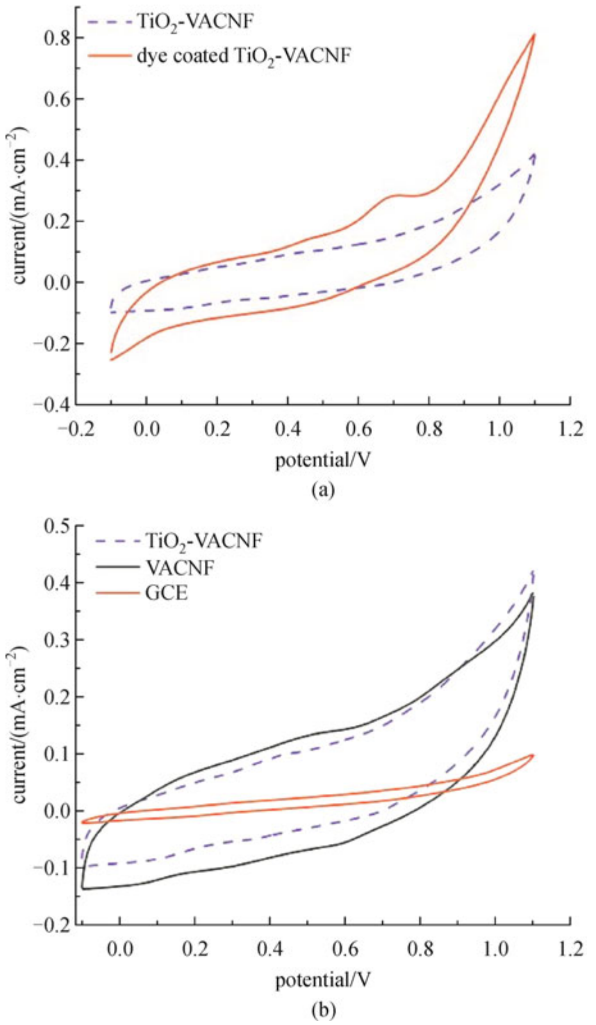

Fig. 4 (a) CV measurement in 0.1 M $LiClO_4$ acetonitrile solution taken with a scan rate of 50 mV/s using a platinum coil as a counter electrode, a Ag/AgCl (sat'd KCl) reference electrode, the vertically aligned carbon nanofiber array coated with anatase TiO_2 nanoneedles as the working electrode (blue line), dye N719 absorption on the surface of vertically aligned carbon nanofiber array coated with anatase TiO_2 nanoneedles as the working electrode (red line); (b) CV measurement in 0.1 M $LiClO_4$ acetonitrile solution taken with a scan rate of 50 mV/s, the vertically aligned carbon nanofiber array coated with anatase TiO_2 nanoneedles as the working electrode (blue line), the vertically aligned carbon nanofiber array (black line); a glassy carbon working electrode (red line)

Thus the surface enhancement factor is 16.7. By CNF alone, the surface area is not so great. For Gratzel cells, the surface enhancement factor for a 10 m thick TiO_2 NP film is claimed to be about 1000. This is why ZnO NW and TiO_2 NT based solar cells have much lower efficiency than Gratzel cells. After coating with TiO_2 nanoneedles, we can estimate the roughness factor using the similar method. The surface area of a single TiO_2 nanoneedle is

$$
\begin{aligned}
A_{\mathrm{TiO_2}} &= 2\pi RL \\
&= 2\times 3.14\times 7.5\times 10^{-7}\times 100\times 10^{-7}\ \mathrm{cm}^2 \\
&= 4.71\times 10^{-11}\ \mathrm{cm}^2,
\end{aligned}
$$

and the total area of TiO_2 nanoneeldes on a single CNF is

$$
\begin{aligned}
A_{\mathrm{TiO_2/CNF}} &= (\text{density of TiO}_2\text{ nanoneedles}) \\
&\quad \times (\text{nanoneedle surface area}) \\
&\quad \times (\text{single CNF surface area}) \\
&\quad + (\text{CNF surface area}) \\
&= (10^{11}\ \mathrm{TiO_2/cm^2})\times(4.71\times10^{-11}\ \mathrm{cm^2}) \\
&\quad \times (1.57\times10^{-8}\ \mathrm{cm^2}) + (1.57\times10^{-8}\ \mathrm{cm^2}) \\
&= 8.96\times10^{-8}\ \mathrm{cm^2}.
\end{aligned}
$$

So the roughness factor is

$$A_{\mathrm{TiO_2/CNF}}/A_{\mathrm{CNF}} = 8.96\times10^{-8}/1.57\times10^{-8} = 5.71.$$

The total area of a TiO_2-coated CNF array on 1 cm^2 of geometric area is

$$
\begin{aligned}
A_{\mathrm{TiO_2/CNF}} &= (A_{\mathrm{TiO_2/CNF}})\times(\text{Density of CNF}) + 1\ \mathrm{cm}^2 \\
&= 8.96\times10^{-8}\ \mathrm{cm}^2\times10^{9} + 1\ \mathrm{cm}^2 = 90.6\ \mathrm{cm}^2.
\end{aligned}
$$

In addition, from the redox wave (see in Figs. 5(a) and (b)), we can get charge $Q = 4.96\times10^{-4}$ C. Since Q = neF, the value of n can be calculated as 5.14×10^{-9} mol of dye. From Ref. [20], the dye N-719 molecule occupies an area of about 116–155 Å^2. Therefore, the dye molecules would occupy only about 36 cm^2 if they are closely packed area, namely their surface coverage is only 0.397 monolayer, which is far less than a close-packed monolayer. In order to increase the dye absorption, the surface of TiO_2 nanoneedles on CNFs needs to be chemically activated for stronger dye adsoption.

4 Conclusions

In conclusion, we have demonstrated an electrochemical method for the analysis of dye adsorption on vertically aligned carbon nanofiber arrays coated with TiO_2 nanoneedles for dye-sensitized solar cells. The electrochemical method can detect activities of chemical species and determine the coverage of the dye on the surface of TiO_2 coating. The low efficiency of dye-sensitized solar cell is due to low dye absorption (0.397 monolayer) on the surface of TiO_2 nanoneedles, which may also induce the current leakage and lower the efficiency of solar cells. To improve the performance of our dye-sensitized solar cell, chemical treatment of the TiO_2 surface is needed induce stronger binding of dye molecules with Ti atoms to fully cover the TiO_2 surface. This electrochemical method can be also applied to detect other chemical species.

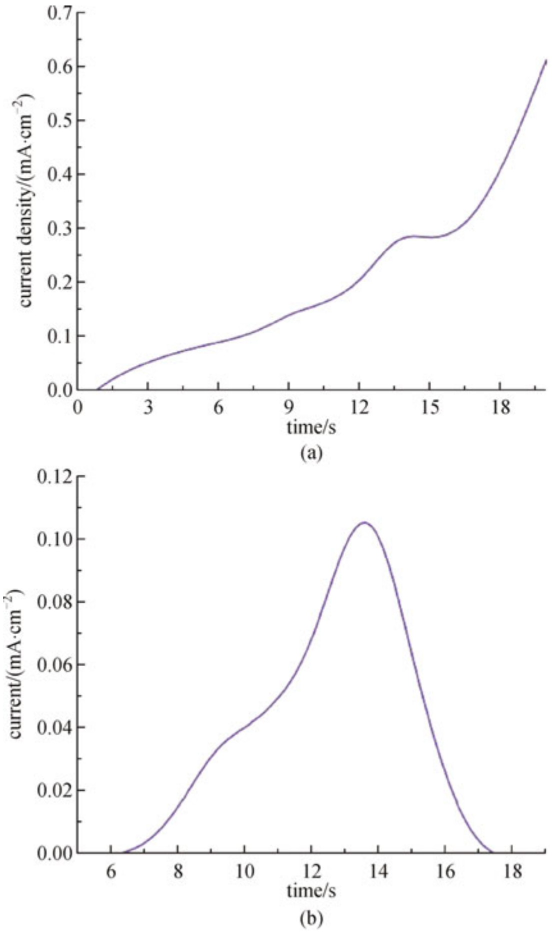

Fig. 5 (a) Current-time plot of forward curve of a cyclic voltammogram with dye N719 adsorbed on surface of a vertically aligned carbon nanofiber array coated with anatase TiO_2 nanoneedles as working electrode; (b) same plot after baseline fitting and subtraction from (a)

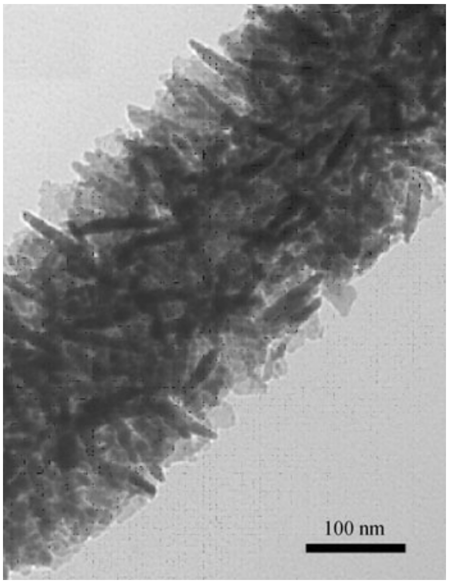

Fig. 6 Carbon nanofiber coated with TiO_2 nanoneedles

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