

Preparation, activity and mechanism of metallic Cu/TiO₂ nanotube arrays catalyst by fast solar drying method for photothermal CO₂ reduction

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Table S1 Some collected CO₂ photoreduction reaction rate data of TNTAs

Catalysts	Preparation method	Light source	Reducing agent	Reaction parameters	Main product
Pt/TiO ₂ NTAs [1]	Rapid microwave-assisted solvothermal approach	AM 1.5G sunlight	H ₂ O	Gas phase 1.0psi; 43±3°C	CH ₄ 36±6 μL · g ⁻¹ · h ⁻¹
CdS(Bi ₂ S ₃)/ TiO ₂ [2]	Hydrothermal and direct precipitation	500W Xe lamp	H ₂ O	Liquid phase RT(Room temperature)	CH ₃ OH 159.5 and 224.6 μmol · L ⁻¹ after 5h.
TiO ₂ NTAs [3]	Electrochemical anodization	-	H ₂ O	Liquid phase RT(Room temperature)	CH ₃ OH 10 nmol · cm ⁻² · h ⁻¹ C ₂ H ₅ OH 9 nmol · cm ⁻² · h ⁻¹
V, N co-doped TiO ₂	combination of	300-W Hg lamp	H ₂ O	Gas phase	CH ₄

nanotube arrays [4]	electrochemical anodization and hydrothermal reaction			RT(Room temperature)	$64.5 ppm \cdot cm^{-2} \cdot h^{-1}$
CuO/ TiO ₂ nanotube arrays [5]	anodization and electrodeposition	250W Xe lamp	H ₂ O	Liquid phase RT(Room temperature)	CH ₃ OH $8.3 \mu mol \cdot cm^{-2} \cdot h^{-1}$
TiO ₂ nanotube arrays [6]	Flame annealing	50 W LED lamp; AM 1.5 G, 100 mW cm ⁻²	H ₂ O	Liquid phase RT(Room temperature)	CH ₄ $156.5 \mu mol \cdot g^{-1} \cdot h^{-1}$
Am TNTAs [7]	Anodization	6 UV-light bulbs, each 16W	H ₂ O	Liquid phase RT(Room temperature)	CH ₄ $14.0 \mu mol \cdot g^{-1} \cdot h^{-1}$
TiO ₂ nanotube arrays [8]	Anodization	3 A-UV diodes	H ₂ O	Liquid phase RT(Room temperature)	CH ₄ About 14 $nmol \cdot m^{-2} \cdot h^{-1}$
CQD-modified TiO ₂ NTs [9]	Anodization	300W Xe lamp	H ₂ O	Liquid phase 10mL TEOA and 20mL H ₂ O RT(Room temperature)	CO and CH ₄ yields of 2.71 and 0.71 $\mu mol \cdot g^{-1} \cdot h^{-1}$
Cu ₂ O-loaded TiO ₂	Anodization	300 W Xe lamp	H ₂ O	Gas phase	CH ₃ OH

nanotube arrays [10]				RT(Room temperature)	
CN-TNTs [11]	Anodization and solid-state thermal condensation	Newport Class A solar simulator (AM 1.5 G one sun with an intensity of 100 mW cm ⁻²)	H ₂ O	aqueous solution of triethanolamine RT(Room temperature)	CO 14.97 $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$
Cu+/ TiO ₂ [12]	Anodization	Xe lamp with intensity of 136 mW cm ⁻²	H ₂ O	Gas phase 150 °C	CH ₄ 1.52 $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$

Detailed Experimental methods

Preparation of TiO₂ NTAs supported Cu nanoclusters catalysts

TiO₂ NTAs was prepared with classic anodization method. [32] The anodization device mainly contains a DC power and a thermostatic water bath. The Ti foil (purity>99.9%) was cut into 2.5*2.5*0.2 mm square pieces, then it was smoothed by the sandpaper, cleaned by ultrasonic with deionized water, ethanol and acetone for 15 min to remove the impurities. After ultrasound, the titanium sheet was put into the polishing liquid for about 3 min, and then taken out and cleaned with ethanol. The polishing liquid contains 10 mL of distilled water, 5 mL of concentrated nitric acid, 1 mL of 18 wt% NH₄F, 1 mL of 18% wt ammonia. After polishing, anodization was performed. A titanium foil is clamped on the anode, and a Pt sheet with the same size is used as an inert electrode. The position of the two electrodes should be adjusted to face each other and put together into the electrolyte. The electrolyte contained 0.3 g of NH₄F, 2 mL of deionized water, and 100 mL ethylene glycol. The DC voltage of anodization was adjusted to 50 V, and the electrolyte temperature was 45°C, and anodization was performed for about 25min. After anodization, it was cleaned in acetone and ethanol solution by sonication for 3 min and dried. The resulting mass of each TiO₂ nanotube arrays mass is around 0.01 g.

The procedure of Cu nanoclusters is following chemical reduction method. 0.5 g of polyvinylpyrrolidone was dissolved in 8 mL ultrapure water to form a solution. 1mL Cu(NO₃)₂ solution (1mol/L) and 1.76 g of ascorbic acid was sequentially added into the solution with stirring. Subsequently, the pH of the solution was adjusted to about 4.0, and placed in a constant temperature water bath pot with temperature 75 °C for different times to obtain Cu nanoclusters with different sizes (from 1nm, 3nm, 5nm to 7nm). The copper nanoclusters solution is stored at 4 °C for further experiments.

Detailed illustration of the home-made concentrating light reactor system

The home-made concentrating light systems can be seen in Figure S1 and S2. It is necessary to describe the reactor system in detail here, as a photoreactor is often a nonstandard equipment, especially for the photothermal reactor systems. At present, the reported reactor systems for the photothermal catalysis are generally divided into two genres. One is based on the original kettle reactor system, where a functional jacket is changed from being used to heat preservation to heating. The system is generally carried out in liquid phase and the catalyst dispersed uniformly in the reactor, leading to a CSTR. The degree of heating is limited, because high temperature easily vaporizes the water and hinders the light transmission. The decay of light will be more serious with temperature rising. The other is based on the heterogeneous thermal catalytic reactor, and a hole is dug on the wall of reactor and furnace so that the light beam can pass through. This reactor system can be heated to very high temperatures, and the reaction can take place in the gas phase. The problem is that the diameter of the hole is limited, and the catalyst is filled into the reactor in the form of a fixed bed, and the depth of penetration of light is needed to consider. Meanwhile, all the heat sources are from external. Our self-made photothermal reaction systems are somewhat different from the existing reaction systems. The heat resource is from the light conversion. In other words, we use concentrating light technology to concentrate a certain area range of light rays into a small area, which can get an enhanced light input, and also increase the temperature in the zone. This system is born from the thermocatalytic fixed-bed reaction system, the difference is

that it uses concentrated light as the source of energy driving force. At the same time, in order to be able to better receive the light, its reactor is kettle-type, and there is a light receiving window at the top of the kettle reactor. It's like a combination of two existing reaction systems, taking the reactor of one of the systems, and the other parts of the other system. Of course, in order to effectively increase the temperature in the reactor, we also increased the output power of the light source and added a concentrator component. Just as shown in Figure S1, the only different part from the thermocatalytic reaction system, a patio is opened on the left part of the system. From top to down, a 1000W light source is fixed at the top, and a Fresnel lens was settled under the light source, and a kettle reactor was put under the Fresnel lens. Both the site reactor and the lens can be adjusted up and down to obtain a different concentrating ratio.



Figure S1 The picture of the indoor reactor system with simulated light source

The Fresnel lens is made of PMMA and the reactor is made of stainless steel

with a quartz glass window at the top to receive the incident light. The diameter of the light source is about 20 cm, and the Fresnel lens diameter is about 20 cm too. The diameter of the window is about 8 cm. The volume of the reactor is 100 mL. The intensity of the light source is about 220 mW/cm² before concentrating. Since the light will form a spot of different sizes after concentrating, in order to well receive the light, the catalyst is pressed or trimmed into a round disc, the light shines on the upper surface of the catalyst disc. It is some kind of a fixed bed reactor, which is not the same as the traditional kettle type CSTR, where catalyst is often dispersed in aqueous solution, although it can be done the same way here. Depending on the concentrating degree, the light spot size will change, and the size of the catalyst disc can also change correspondingly. For convenient, the degree of light concentration can be expressed in terms of a light concentration ratio (CR), which is defined as the ratio of the incident area of the light source to the area of the catalyst disc.

Unlike the simulated light sources, which can be fixed at certain site, nature solar light from the sun moves all times of a day. The distance between solar light and the Fresnel lens is not changed, so what can be adjusted is the distance from the reactor to the Fresnel lens, which can adjust the concentration ratio. In order to ensure that solar light is vertically towards the Fresnel lens surface and reactor, not only does a sensor need to sense the solar light movement in direction, but also some power devices are needed to move and fine tune the lens and reactor. As shown in Figure S2, a framework fixed the Fresnel lens and the reactor together, and a solar light sensor is also fixed on the framework, two motors are equipped to provide the force to move

the framework attitude according to the guideline of the sensor.



Figure S2 The picture of the outdoor reactor system with nature solar light source

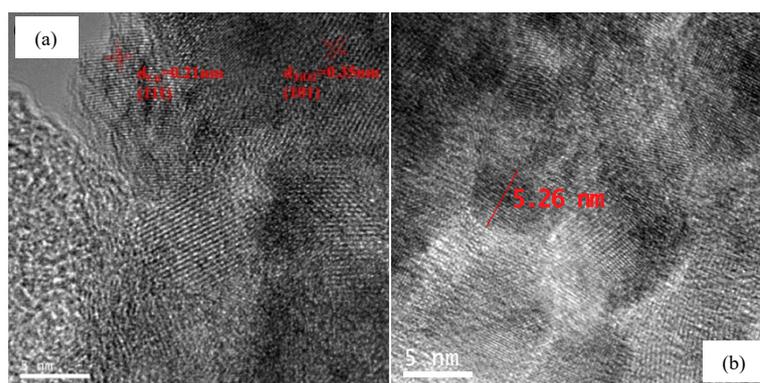


Figure S3 TEM images of fresh Cu/TiO₂ NTAs catalysts with different size of Cu nanoclusters. a) 3 nm; b) 5 nm

CO₂ content effect on the activity of Cu_{1nm}/TiO₂ NTAs under 1000 W Xe light

As the main reactants, CO₂ and H₂O content and ratio also may have effect on the reaction rate. Therefore, the photocatalytic reduction of CO₂ activity on Cu_{1nm}/TiO₂ NTAs at different water and CO₂ content with the same concentrating ratio (CR 16) was evaluated too.

CO₂ contents were set at 0.05 MPa, 0.1 MPa, 0.2 MPa, respectively. In Figure S4, it can be seen that either higher or lower of CO₂ contents is not favorable for the hydrocarbons yield. When charged with 0.05 MPa CO₂, the total yield is about 375 $\mu\text{mol} \cdot \text{g}^{-1}$ after 3 h reaction; when charged with 0.2 MPa CO₂, the total yield is about 121 $\mu\text{mol} \cdot \text{g}^{-1}$ after 3 h reaction. Both of them are lower than the yield of 570 $\mu\text{mol} \cdot \text{g}^{-1}$, charged with 0.1 MPa CO₂. The result is reasonable, according to the reaction rate equation. More interestingly, the content also influences the product distribution, at 0.1 MPa, there are more ethene and ethane formed.

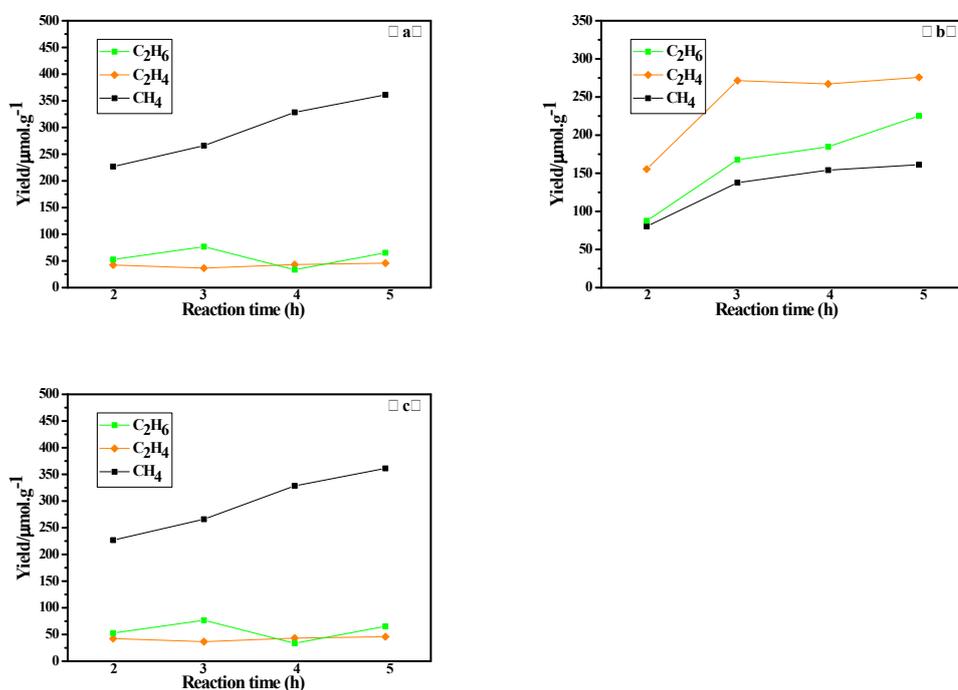


Figure S4 Yield of products on Cu_{1nm}/TiO₂ NTAs catalyst at different CO₂ contents (a)

0.05 MPa, (b) 0.1 MPa, (c) 0.2 MPa (CR 16; 2 mL H₂O)

Water content effect on the activity of Cu_{1nm}/TiO₂ NTAs under 1000 W Xe light

H₂O contents were set at 0.5 mL, 1.0 mL, 2 mL and 3 mL. The results are in Figure S5. At 1 mL of water, the total yield of the product was the highest, at 2644.37 $\mu\text{mol} \cdot \text{g}^{-1}$, and the content of ethane was relatively large, which was 743.8 $\mu\text{mol} \cdot \text{g}^{-1}$. At 2 mL of water, the production of ethylene and ethane products predominated, but the overall yield is lower than from 1 mL of water, which means that high water content is favorable for the formation of high hydrocarbons. Further, too much water is also not conducive to the formation of C₂ hydrocarbon products. The proportion of C₂ hydrocarbon products decreases significantly at a water volume of 3 mL. In general, at the time of the concentrator ratio, the change of water volume has a greater impact on the distribution of products, and not surprisingly, it also roughly corresponds to the characteristics of reaction kinetics.

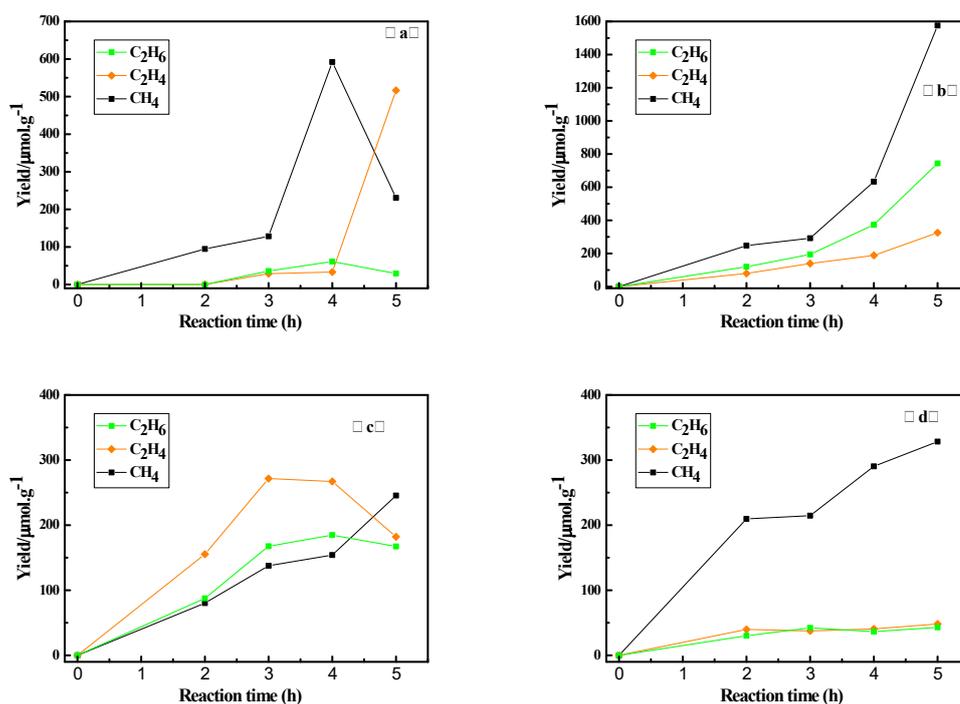


Figure S5 Yields of products on Cu_{1nm}/TiO₂ NTAs catalyst with different amounts of H₂O. (a) 0.5 mL (b) 1 mL, (c) 2 mL, (d) 3 mL (CR 16; CO₂ 0.1MPa)

Reaction kinetics and influence of reaction conditions

Nowadays, people are generally more concerned with the catalyst and its function mechanism, that is, what provides the high performance of the catalyst, but here we have to first analyze and strip out the influence of the reaction conditions, only then the relation between the structure and performance can be discussed conveniently.

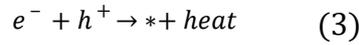
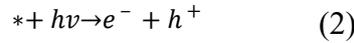
The effect of reaction environment and reaction conditions is still a very complex to distinguish as it includes the light intensity, the temperature, the pressure and the semiconductor. Fortunately, it can be reflected easily by reaction kinetics equation. It is known that the common reaction rate equation for CO₂ photoreduction

$$-r_{CO_2} = kI^\alpha \frac{P_{H_2O} P_{CO_2}}{(1 + K_2 P_{H_2O} + K_6 P_{CO_2})^2} \quad (1)$$

However, for concentrating solar light technology, there are more problems. The reaction order of light intensity α is decreasing with light intensity, which actually make the constant to be a variable factor. In particular, concentrating light will cause a Gaussian distribution of light intensity on the catalyst disc. The light intensity is the highest at the center of the catalyst, and decreases from center to around. It will almost be an impossible task to determine the α under different concentrating ratio without further consideration.

It is known that light is not a material and often treated as an energy. When the light participants into a reaction, it will work together with phonons of heat and form the “photothermal effect”. That is why is very hard to separate the general photothermal effect to “photo- effect” and “thermal effect” respectively. However, if the photon is treated as a reactant, the adsorption of photons on the active sites and the

recombination of electron-hole pairs could be analogue to be the adsorption/desorption process of a reactant on the catalyst surface.



Then according to the Langmuir adsorption theory, an adsorption isotherm equation will be obtained. The only thing is to consider it as a dissociative adsorption or non-dissociative adsorption. The reason to consider it as a non-dissociative adsorption is that one photon only can be transformed into one electron, while as a dissociative adsorption is that adsorption of one photon yields an electron and a hole at the same time. Nonetheless, according to the hypothesis, there would have

$$C_{e^-} = \frac{K_I I}{1 + K_I I} \quad \text{or} \quad C_{e^-} = \frac{K_I \sqrt{I}}{1 + K_I \sqrt{I}} \quad (4)$$

The reaction rate of CO₂ photoreduction equation will change to be

$$-r_{CO_2} = k(T) \frac{K_I I}{1 + K_I I} \frac{P_{H_2O} P_{CO_2}}{(1 + K_1 P_{H_2O} + K_2 P_{CO_2})^2} \quad \text{or} \quad -r_{CO_2} = k(T) \frac{K_I \sqrt{I}}{1 + K_I \sqrt{I}} \frac{P_{H_2O} P_{CO_2}}{(1 + K_1 P_{H_2O} + K_2 P_{CO_2})^2} \quad (5)$$

Considering that the CO₂ photoreduction is driven both by the electron and hole, it is inclined to use the later formula, and further considering the Gaussian distribution of the concentrating light intensity, we will see that the $-r_{CO_2}$ would change from the bound to the center of the catalyst disc with the light and temperature variation. At certain site, there is

$$(-r_{CO_2})_r = k(T_r) \frac{K_I \sqrt{I}_r}{1 + K_I \sqrt{I}_r} \frac{P_{H_2O} P_{CO_2}}{(1 + K_1 P_{H_2O} + K_2 P_{CO_2})^2} \quad (6)$$

Integral from the boundary to the center of the catalyst disc, and would yield a

reaction rate expressed by integral function of light and temperature. Especially, the $1/2$ order also reflects the constraints to light intensity. With the light intensity increases, the effect of light intensity on the reaction rate will decrease gradually. Then, with the recorded parameters T, P and I, the equation with 1000W lamp as the light source here can be formulated

Activity comparison of pure TiO₂ NTAs under 300 W and 1000 W Xe light

The light source in the paper uses a large power light source, which is different from 300 W or 500W Xe lamp in the major researches in the CO₂ photoreduction field. To build a bridge of understanding, CO₂ photoreduction activity under two light sources are compared. As shown in Figure S3, the main product is CH₄ under the two light resources. The CH₄ yield on the pure TiO₂ NTAs is about 1.26 $\mu\text{mol} \cdot \text{g}^{-1}$ after 5 h reaction, which is not very good, but still lines in the normal value range of reported results. Meanwhile, under 1000 W Xe lamp, the yield increases to about 74 $\mu\text{mol} \cdot \text{g}^{-1}$ after 5 h reaction. Compared with the result under 300 W Xe lamp, it has a clear increment.

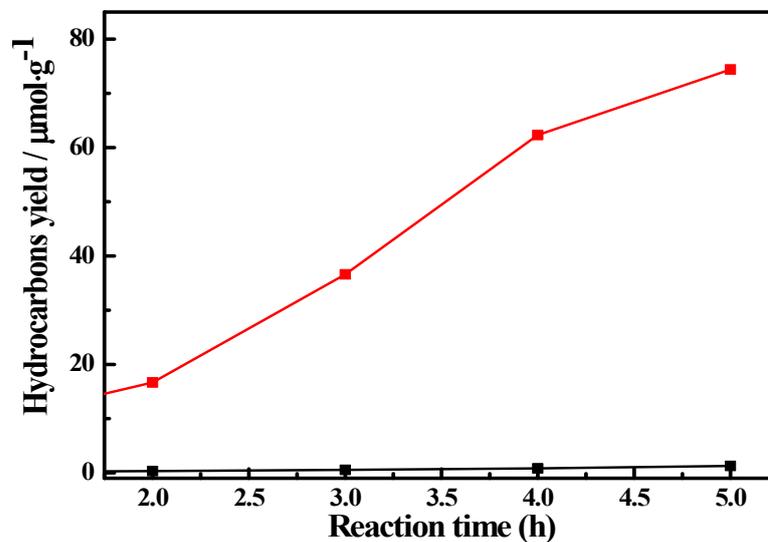


Figure S6 Hydrocarbons yield of pure TiO₂ NTAs catalyst under 300 W and 1000 W Xe lamp. (Initial CO₂ pressure 0.1 MPa; initial amount of H₂O 0.5 mL)

Table S2 Collected activity data under concentrating solar light

Catalysts	Light source	Reducing agent	Concentration ratio	Reaction parameters	Main product	Reaction rate/ $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$
(Ni, Fe)- N- C DSAC [13]	Xe lamp	H ₂ O	10	Liquid phase	CH ₄	135.35
				T ~ 150 °C	CO	86.16
				P ~ 0.1MPa	CH ₃ OH	59.81
Bi ₂ WO ₆ /WO ₃ [14]	Nature sunlight	H ₂ O	600	Gas phase	CH ₄	304.94
				T ~ 400 °C	C ₂ H ₄	62.70
				P ~ 1.1MPa	C ₂ H ₆	54.66
TiO ₂ nanotube arrays[15]	Nature sunlight	H ₂ O	800	Gas phase	CH ₄	861.1
				T 330-550 °C	C ₂ H ₄	100.8
				P 0.2-0.7 MPa	C ₂ H ₆	53.3
Fe ₂ O ₃ [16]	Nature sunlight	H ₂ O	600	Gas phase	CH ₄	1281.11
				T ~ 560 °C	C ₂ H ₄	85.46
				P ~ 1.1MPa	C ₂ H ₆	55.08
P25[17]	Nature sunlight	H ₂ O	800	Gas phase	CH ₄	3157.2
				T ~ 500 °C	C ₂ H ₄	511.6
				P ~ 1.1 MPa	C ₂ H ₆	1346.0

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