

Article

# Direct Coal Liquefaction with Fe<sub>3</sub>O<sub>4</sub> Nanocatalysts Prepared by a Simple Solid-State Method

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**Abstract:** Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by a simple solid-state method under ambient conditions. The obtained nanoparticles, with small size and large surface area, were used as a catalyst for direct coal liquefaction (DCL). The results display that high conversion and oil yield were achieved with the nanocatalysts in direct liquefaction of two kinds of coals, i.e., Heishan coal and Dahuangshan coal. The effects of the temperature, initial H<sub>2</sub> pressure, and holding time on conversion and product distribution have been investigated in the catalytic hydrogenation of Dahuangshan coal. The optimal reaction condition for DCL in which conversion and oil yield are 96.6 and 60.4 wt % was determined with Fe<sub>3</sub>O<sub>4</sub> nanocatalysts. This facile solid-state route is beneficial for scale-up synthesis of iron-based catalysts with good performance for DCL.

**Keywords:** Fe<sub>3</sub>O<sub>4</sub> nanoparticles; solid-state synthesis; direct coal liquefaction; catalysis

## 1. Introduction

Nowadays, it the issue of how coal is used efficiently and cleanly is of increasing concern, because of the rapid depletion of fossil fuels and the deterioration of the environment [1,2]. Direct coal liquefaction (DCL), which is one means processing coal into liquids, has received an increasing amount of attention [3]. It is critical to further improve the efficiency and reduce the cost of DCL processes, in view of its pervasive application [4]. As one of the valid methods, the development of catalysts with high efficiency, which could promote coal conversion and decrease reaction severity, has been considered by researchers [5,6].

In the past several decades, many kinds of catalysts have been studied for DCL [7–10]. Iron-based catalysts are predominant among them, because they are low-cost, abundant, and disposable [11,12]. However, they usually show lower catalytic activity toward DCL, which is unfavorable for the transformation from coal to liquids. As a consequence, some approaches have been developed to improve the performance of iron-based catalysts, such as decreasing the particle size of catalysts and enhancing dispersion of catalysts in the reaction system [13–16]. In particular, nanosized iron-based materials show superior catalytic activity for DCL [17,18]. Recently, Fe<sub>3</sub>O<sub>4</sub> nanoparticles capped with oleic acid have been prepared by our group by thermal decomposition and solution-based dehydration process, respectively [19,20]. The nanocatalysts displayed higher activity toward DCL than commercial Fe<sub>3</sub>O<sub>4</sub> powders. In particular, a large-scale synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles was achieved through the solution-based dehydration method, which is beneficial for practical DCL applications [20]. However, a large volume of organic solvent is involved in this method, which raises the cost, and is potentially harmful to the environment. Hence, it is still necessary to find a greener way that is feasible for large-scale production of iron-based catalysts with high activity in DCL.

In this paper, a simple solid-state method is applied to the preparation of  $\text{Fe}_3\text{O}_4$  nanoparticles at room temperature. The method is green, solvent-free, and conducive to large-scale synthesis of products with nanosize. The obtained  $\text{Fe}_3\text{O}_4$  nanoparticles are used as catalysts for hydroconversion of two Chinese coals. The effects of the temperature, initial  $\text{H}_2$  pressure, and holding time on conversion and product distribution are investigated in detail for liquefaction of Dahuangshan coal. The optimal reaction condition for DCL with  $\text{Fe}_3\text{O}_4$  nanocatalysts is determined.

## 2. Experimental Section

### 2.1. Starting Materials

All chemicals were used as received, without further purification. Ferric(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 98.0%), ferrous (II) chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , 99.7%), and sodium hydroxide ( $\text{NaOH}$ , 96.0%) were purchased from Zhiyuan Chemical Reagents Co., Ltd. (Tianjin, China). The raw coals in this study were obtained from the Heishan mine and Dahuangshan mine in the Xinjiang Autonomous Region of China. Their proximate analysis and ultimate analysis results are given in Table 1. The coals used in DCL were ground to fine particles with about 200 mesh.

**Table 1.** Proximate and ultimate analysis of two Chinese coals.

Coal	Proximate Analysis <sup>1</sup> (wt %)			Ultimate Analysis (wt %, daf <sup>2</sup> )					H/C
	M <sub>ad</sub>	A <sub>d</sub>	V <sub>daf</sub>	C	H	O <sup>3</sup>	N	S	
Heishan	1.48	3.76	35.08	81.24	4.47	9.29	0.79	0.46	0.66
Dahuangshan	1.22	17.57	48.34	63.17	3.63	14.30	1.11	0.20	0.69

<sup>1</sup> M<sub>ad</sub>, moisture content of air-dried coal; A<sub>d</sub>, ash content of air-dried coal; V<sub>daf</sub>, volatile content of dry ash-free coal.

<sup>2</sup> daf, dry ash-free coal. <sup>3</sup> Obtained by difference.

### 2.2. Preparation of $\text{Fe}_3\text{O}_4$ Nanoparticles

$\text{Fe}_3\text{O}_4$  nanoparticles were prepared through a solid-state chemical reaction. In a typical experiment,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (10.8 g, 40 mmols) and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (4.0 g, 20 mmols) were mixed by grinding in an agate mortar at room temperature. Subsequently,  $\text{NaOH}$  (6.4 g, 160 mmols) was added into the mixtures. After grinding for about 30 min, the color of mixtures changed from yellow to black. The resulting solid products were washed with distilled water and absolute ethanol several times, then dried at 80 °C for 3 h.

### 2.3. Characterization

The crystal structure of the obtained samples was characterized by X-ray diffraction (XRD) using a Bruker D8 X-ray diffractometer (Bruker Corporation, Karlsruhe, Germany) with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). A field emission scanning electron microscope (FESEM) image was obtained on a Hitachi S-4800 scanning electron microscope (Hitachi Limited, Tokyo, Japan) with an accelerating voltage of 15 kV. A transmission electron microscope (TEM) image and high-resolution transmission electron microscope (HRTEM) image were obtained on a JEOL JEM-2010F electron microscope (JEOL, Tokyo, Japan) with an accelerating voltage of 200 kV. The Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halender (BJH) results were obtained from an Autosorb IQ surface area and porosity analyzer (Quantachrome Instruments, Boynton Beach, FL, USA).

### 2.4. Reaction of DCL

Liquefaction reactions were conducted in a 0.5 L batch-stirred autoclave. The process of DCL catalyzed by  $\text{Fe}_3\text{O}_4$  nanoparticles and the separation procedure of products were similar to the previous studies [19,20]. In a typical experiment, 10.0 g of coal, 20.0 g of tetralin as a solvent,  $\text{Fe}_3\text{O}_4$  nanoparticles (Fe is 1.4 wt % of dry and ash-free (daf) coal) as a catalyst, and sulfur (S/Fe mole ratio is 1.8) as a

cocatalyst were mixed and charged into the reactor. After replacing air in the autoclave with H<sub>2</sub> (99.99%), the reactor was pressurized with H<sub>2</sub> to 6 MPa at room temperature and heated to 430 °C. Then, the mixture was stirred with 300 rpm for 60 min at that temperature. After the autoclave was rapidly cooled by blowing to room temperature, the resulting liquid and solid product was extracted in sequence with *n*-hexane and tetrahydrofuran (THF) in a Soxhlet extractor (Hualikexi Co., Ltd., Urumqi, China). The *n*-hexane-soluble (HS), *n*-hexane-insoluble but THF-soluble, and THF-insoluble substances were defined as oil, asphaltene and pre-asphaltene (APA), and residue, respectively. Different reaction temperatures (410, 420, 440, and 450 °C), initial H<sub>2</sub> pressures (4, 5, 7, and 8 MPa), and holding times (30, 45, 75, and 90 min) for the catalytic hydrogenation of Dahuangshan coal were also conducted. The conversion, oil yield, APA yield, and gas yield of coal were determined using the following equations:

$$\text{conversion/wt \%} = [1 - (W_r - W_{\text{ash}} - W_c)/W_{\text{daf}}] \times 100 \quad (1)$$

$$\text{oil yield/wt \%} = [(W_{\text{HS}} - W_s)/W_{\text{daf}}] \times 100 \quad (2)$$

$$\text{APA yield/wt \%} = (W_{\text{APA}}/W_{\text{daf}}) \times 100 \quad (3)$$

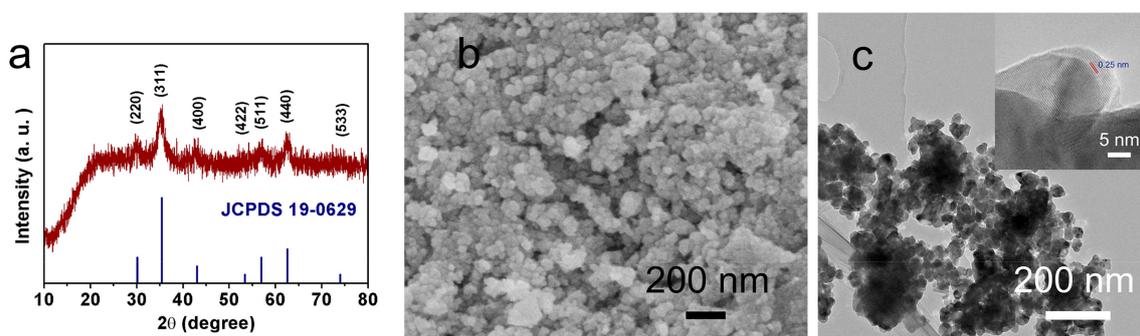
$$\text{gas yield/wt \%} = \text{conversion} - \text{oil yield} - \text{APA yield} \quad (4)$$

where  $W_{\text{daf}}$  is the weight of dry and ash-free coal;  $W_r$  is the weight of the residue;  $W_{\text{ash}}$  is the weight of ash;  $W_c$  is the total weigh of Fe<sub>3</sub>O<sub>4</sub> and sulfur;  $W_{\text{HS}}$  is the weight of HS substances;  $W_s$  is the weight of solvent; and  $W_{\text{APA}}$  is the weight of APA. The reported coal conversion and product yields for DCL are the average values of at least two equivalent experiments, and the error bars are indicated in Figure 2.

### 3. Results and Discussion

#### 3.1. Structure and Morphology Characterization of Nanocatalysts

The structure and morphology of the as-prepared samples were investigated by XRD, FESEM, and TEM. In Figure 1a, it can be seen that all peaks of the XRD pattern are indexed to Fe<sub>3</sub>O<sub>4</sub> with the cubic structure (JCPDS No. 19-0629). Peaks resulting from impurities were not observed in the XRD results, confirming the pure phase of the product. The broader diffraction peaks also imply a fine grain size in the Fe<sub>3</sub>O<sub>4</sub> sample. Figure 1b displays the representative FESEM image of the obtained Fe<sub>3</sub>O<sub>4</sub>. Many spherical particles with a size of 20–100 nm can be observed. In the TEM image of the sample in Figure 1c, the structural information is further confirmed. The fringe spacing of 0.25 nm shown in the HRTEM image (Figure 1c, inset) agrees well with the (311) plane of cubic Fe<sub>3</sub>O<sub>4</sub>.



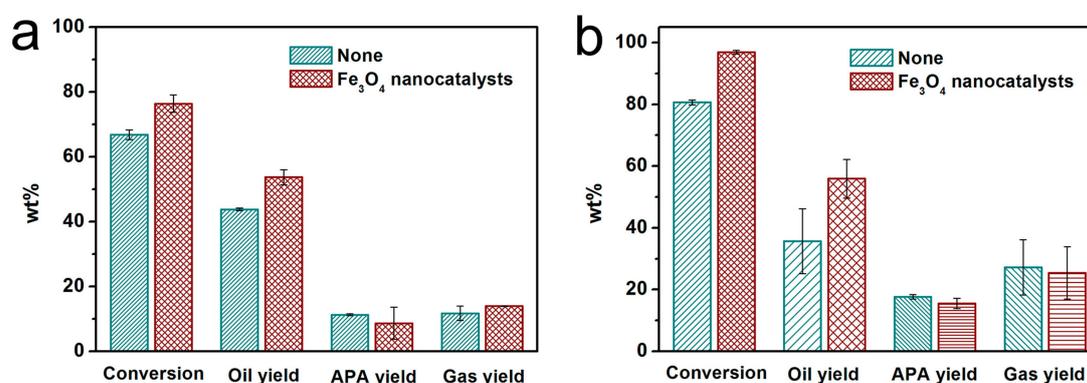
**Figure 1.** (a) XRD pattern; (b) Typical FESEM image; (c) TEM image of as-synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

The Fe<sub>3</sub>O<sub>4</sub> nanoparticles were obtained through the solid-state chemical reaction among reactants in a one-pot process under ambient conditions. Expensive and toxic organic solvents were not involved

in the method. The method for the synthesis of  $\text{Fe}_3\text{O}_4$  nanoparticles is facile, green, cost-effective, and easy to scale-up, which are beneficial for the application in many fields.

### 3.2. Catalytic Properties of $\text{Fe}_3\text{O}_4$ Nanoparticles in DCL

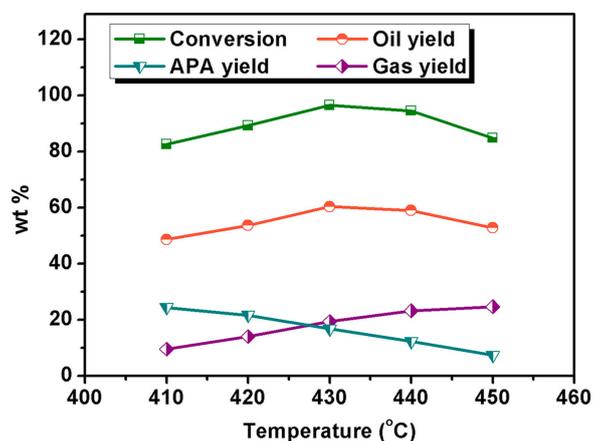
The catalytic performances of the as-prepared  $\text{Fe}_3\text{O}_4$  nanoparticles for DCL were investigated. Figure 2 shows the results of catalytic hydrogenation of two Chinese coals, i.e., Heishan coal and Dahuangshan coal. It is observed that low conversion (66.8 wt %), oil yield (43.8 wt %), and gas yield (11.7 wt %) for Heishan coal were presented in the absence of catalysts. With the addition of  $\text{Fe}_3\text{O}_4$  nanoparticles, the conversion, oil yield, and gas yield of Heishan coal increased to 76.4, 53.8, and 13.9 wt %, respectively. The APA yield dropped to 8.7 wt % with the nanocatalysts, while it was 11.3 wt % without catalysts. It is obvious that  $\text{Fe}_3\text{O}_4$  nanoparticles exhibited high catalytic activity toward DCL, and the transform from APA to oil was promoted by the  $\text{Fe}_3\text{O}_4$  nanocatalysts, which possess enhanced selectivity for oil components. Similarly, in the liquefaction of Dahuangshan coal, conversion and oil yield increased by 16.3 and 20.2 wt %, respectively, with  $\text{Fe}_3\text{O}_4$  nanoparticles compared to liquefaction without catalysts. The superior catalytic activity of  $\text{Fe}_3\text{O}_4$  nanoparticles may be attributable to their small size and large specific surface area. Based on the result of nitrogen adsorption-desorption isotherm measurement (Figure S1), it can be seen that the  $\text{Fe}_3\text{O}_4$  nanoparticles manifested a surface area of  $143.0 \text{ m}^2/\text{g}$  and a pore volume of  $0.168 \text{ cm}^3/\text{g}$ . The large surface area and pore volume of the  $\text{Fe}_3\text{O}_4$  nanoparticles are of great benefit to full contact between coal and catalyst, which will promote the catalytic hydrogenation of coal. Furthermore, it reveals that the conversion and oil yield of Dahuangshan coal are higher than that of Heishan coal with  $\text{Fe}_3\text{O}_4$  nanoparticles. The larger  $V_{\text{daf}}$  (i.e., volatiles based on dry and ash-free coal) and H/C (atomic ratio of hydrogen to carbon) of Dahuangshan coal (Table 1) are beneficial for its hydrogenation, which leads to a higher transformation efficiency of Dahuangshan coal for DCL. In addition, an increased gas yield was observed in the liquefaction of Dahuangshan coal. This may be ascribed to the higher oxygen content, which forms carbon oxides during the direct liquefaction of Dahuangshan coal.



**Figure 2.** Results of the direct liquefaction of (a) Heishan coal and (b) Dahuangshan coal with  $\text{Fe}_3\text{O}_4$  nanocatalysts.

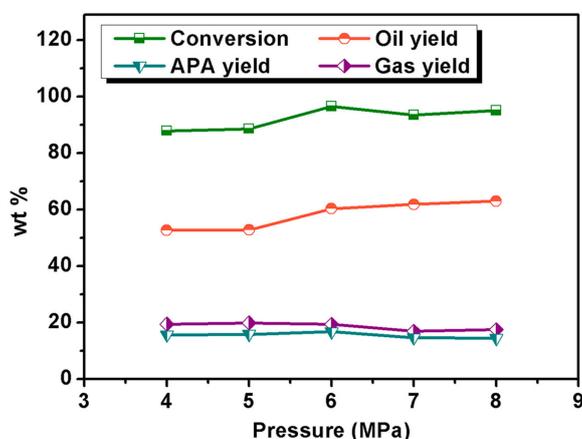
The liquefaction performance of Dahuangshan coal was further studied in light of the fact that Dahuangshan coal showed more suitable properties for DCL than Heishan coal. The effects of the temperature, initial  $\text{H}_2$  pressure, and holding time on conversion and product distribution of Dahuangshan coal were investigated in detail. The temperature, which affects the behaviors of coal pyrolysis and radical formation, is an important factor during liquefaction [21]. Direct liquefaction of Dahuangshan coal with  $\text{Fe}_3\text{O}_4$  nanocatalysts was studied at several temperatures between 410 and 450 °C. As shown in Figure 3, the conversion and oil yield increase with the rise in temperature, and they reach the maximum values of 96.6 wt % and 60.4 wt %, respectively, at 430 °C. But the 84.8 wt % of conversion and 52.8 wt % of oil yield are obtained at 450 °C. They decrease with a further rise in

temperature from 430 to 450 °C. The reason for this may be that the proper temperature is required for the matching between generated radicals and active hydrogen. Hence, the free radicals can be stabilized by activated hydrogen in the solvent of the liquefaction, thus the retrogressive reaction is suppressed. Moreover, it can be seen that the APA yield decreases with the rise of temperature, while the gas yield increases. The high temperature is beneficial for the formation of small-molecule gas products.



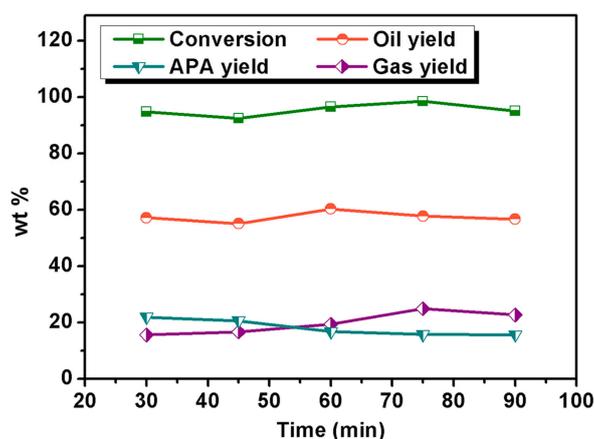
**Figure 3.** Results of the catalytic hydrogenation of Dahuangshan coal with  $\text{Fe}_3\text{O}_4$  nanoparticles at different temperatures.

The amount of  $\text{H}_2$ , which is regarded as a source of active hydrogen, is also of importance for DCL. A high  $\text{H}_2$  pressure is beneficial, as it suppresses retrogressive reactions and promotes hydrogenation. Nevertheless, economic considerations are also necessary. Figure 4 shows the results of catalytic hydrogenation of Dahuangshan coal with  $\text{Fe}_3\text{O}_4$  nanoparticles under different initial  $\text{H}_2$  pressure at 430 °C. The conversion increases with initial  $\text{H}_2$  pressure between 4 and 6 MPa, and then changes smoothly with further increase in pressure. Meanwhile, it can be observed that an increase of initial  $\text{H}_2$  pressure from 4 to 6 MPa causes an increase in the oil yield. However, when the pressure is over 6 MPa, the oil yield changes little. In addition, the APA yield and gas yield are almost constant in all ranges of the initial  $\text{H}_2$  pressure. The higher  $\text{H}_2$  pressure is beneficial for the reaction between radical fragments and active hydrogen, which improves the liquefaction of coal. However, the operating severity and manufacturing cost are raised in the high pressure. Thus, a moderate  $\text{H}_2$  pressure (6 MPa for this work) is favorable in the practical DCL.



**Figure 4.** Results of the catalytic hydrogenation of Dahuangshan coal with  $\text{Fe}_3\text{O}_4$  nanoparticles in different initial  $\text{H}_2$  pressures.

Holding time is another factor that could influence product distribution in DCL. Figure 5 demonstrates the variations of conversion and yields versus the holding time in the liquefaction of Dahuangshan coal with  $\text{Fe}_3\text{O}_4$  nanoparticles at 430 °C. It reveals that the conversion and oil yield float with the prolonging of holding time. The maximum values of conversion and oil yield are exhibited at 75 min and 60 min, respectively. It is also noted that the gas yield increases with the extension of holding time and reaches the maximum value at 75 min, while the APA yield decreases continuously with the increase of holding time. Although a longer holding time at the target temperature is good for conversion and gas yield, the highest oil yield is shown at a moderate holding time. This implies that longer reaction times will benefit the transformation from coal to gas products. Therefore, it is confirmed that the moderate holding time of 60 min is suitable for the coal-to-oil, and the high oil yield of 60.4 wt % is obtained by  $\text{Fe}_3\text{O}_4$  nanocatalysts.



**Figure 5.** Results of the catalytic hydrogenation of Dahuangshan coal with  $\text{Fe}_3\text{O}_4$  nanoparticles in different holding times.

The optimal reaction condition for DCL with  $\text{Fe}_3\text{O}_4$  nanocatalysts is determined based on the above studies. A good result of the liquefaction of Dahuangshan coal is obtained with initial  $\text{H}_2$  pressure of 6 MPa at 430 °C for 60 min. The conversion, oil yield, APA yield, and gas yield are 96.6, 60.4, 16.8, and 19.4 wt % under those conditions, respectively. The results of DCL catalyzed by various nanomaterials are shown in Table S1. It indicates that the  $\text{Fe}_3\text{O}_4$  nanoparticles prepared by the solid-state route are one of worthy catalysts for DCL. The ease of production of  $\text{Fe}_3\text{O}_4$  nanocatalysts makes them potential candidates in practical DCL.

#### 4. Conclusions

In conclusion, a facile and green method has been used for the synthesis of  $\text{Fe}_3\text{O}_4$  nanoparticles.  $\text{Fe}_3\text{O}_4$  particles with sizes of 20–100 nm were prepared by a solid-state chemical reaction under ambient conditions. The obtained nanoparticles exhibited superior catalytic performance in the direct liquefaction of two Chinese coals. The optimal result for DCL was achieved at 430 °C for 60 min with an initial  $\text{H}_2$  pressure of 6 MPa. The conversion, oil yield, APA yield, and gas yield were 96.6, 60.4, 16.8, and 19.4 wt %, respectively, in the catalytic hydrogenation of Dahuangshan coal under the conditions. This simple solid-state method is applicable to large-scale synthesis of  $\text{Fe}_3\text{O}_4$  nanocatalysts for DCL.

**Supplementary Materials:** The following are available online at [www.mdpi.com/1996-1073/10/7/886/s1](http://www.mdpi.com/1996-1073/10/7/886/s1), Figure S1: Nitrogen adsorption-desorption isotherm of  $\text{Fe}_3\text{O}_4$  nanoparticles, Table S1: Summary of catalytic activities for the direct coal liquefaction with various catalysts.

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**Author Contributions:** All authors conceived and designed the experiments; Yizhao Li performed the experiments and wrote the paper; all authors analyzed the data and approved the manuscript.

**Conflicts of Interest:** The authors declare no conflict of interest.

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