

Supporting Information for

In Situ Synthesis of TiO₂-Doped Mesoporous Silica from Coal Fly Ash for the Photocatalytic Degradation of Dyes

Bangda Wang^{a,b}, Yuexi Zhou^c, Lei Li^{a,b}, Hui Xu^{a,b}, Yinglong Sun^{a,b}, Yunsan Du^d and Yi

Wang^{a,b,}*

(^a School of Environment, Tsinghua University, Beijing 100084, China)

(^b Key Laboratory for Solid Waste Management and Environment Safety (Tsinghua University), Ministry of Education of China, Tsinghua University, Beijing 100084, China)

(^c Chinese Research Academy of Environmental Sciences, Beijing 100012, China)

(^d CNPC Northeast Refining & Chemical Engineering Co., LTD, Dalian 116023, China)

Corresponding Author

* Yi Wang. E-mail: yi_wang@tsinghua.edu.cn. Tel: +86-10-62773313

Experimental S1. Desilication of coal fly ash

The composition of the coal fly ash was analyzed by XRF, and the chemical composition is shown in Table.S1. The coal fly ash is mainly composed of SiO_2 and Al_2O_3 . In addition, the coal fly ash contains a small amount of transition metal oxides such as Fe_2O_3 and TiO_2 .

Table S1. Chemical composition of raw coal fly ash.

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2
Content (%)	55.54	35.84	4.24	2.99	1.23

The mineral phase analysis of coal fly ash. As the mineral phase analysis of coal fly ash shown in Fig. S1, the crystal phases belong to mullite and corundum. The uplift area at 2θ at $20\text{-}25^\circ$ (amorphous state) belongs to the amorphous silica.

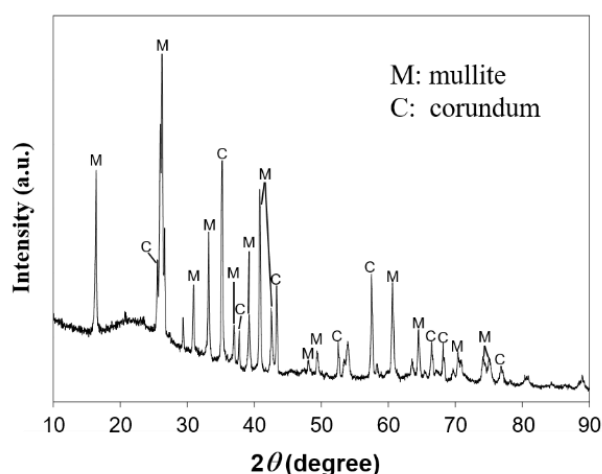


Figure S1. XRD pattern of coal fly ash.

Mix 200 g of coal fly ash with 500 g of 20% NaOH solution in a high pressure reactor (ash to NaOH base ratio of 2:1), and react at 120°C for 2 h. After the mixture is cooled to room temperature, it is filtered to obtain desilication liquid and desilicated ash. The desilication liquid is used for the synthesis of mesoporous materials. A total of 20 desilication experiments were carried out. The results of desilication experiments are listed in Table.S2.

Table S2. Results of various desilication experiments.

Number	CFA (g)	NaOH a.q.(g)	Desi-ash (g)	Mass ratio
1	200	500	160.65	0.80
2	200	500	170.16	0.85
3	200	500	163.77	0.82
4	300	750	249.65	0.83
5	300	750	243.71	0.81
6	200	500	160.24	0.80
7	200	500	160.61	0.80
8	200	500	161.05	0.81
9	200	500	160.53	0.80
10	200	500	168.00	0.84
11	200	500	165.75	0.83
12	200	500	166.53	0.83
13	200	500	167.61	0.84
14	200	500	168.80	0.84
15	200	500	164.47	0.82
16	200	500	167.25	0.84
17	200	500	165.67	0.83
18	200	500	169.85	0.85
19	200	500	167.40	0.84
20	300	750	251.55	0.84

Note: CFA denotes coal fly ash; NaOH a.q. denotes 20% NaOH solution; Desi-ash denotes the mass of coal fly ash after desilication; Mass ratio denotes the ratio of Desi-ash to CFA.

It can be seen from Table.S2 that in the desilication stage, the mass loss of coal fly ash before and after the reaction is between 15% and 20%. Select the two desilicated ash (No.11 and No.17) for component analysis. The results are shown in Table.S3.

Table S3. Chemical compositions of coal fly ash after desilication.

Number	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	TiO ₂
11	35.66	52.28	5.88	4.27	1.23
17	34.80	55.30	5.64	5.17	1.32

Comparing the results of Table.S1 and Table.S3, it can be seen that after the desilication process, the Si component in the coal fly ash is well extracted, so that the Al in the coal fly ash is enriched. At the same time, the composition of the desilication liquid is analyzed, and the components in the desilication liquid are obtained in Table

S4.

Table S4. Element concentration of desilication solution (mg/L).

Element	Si	Fe	Ti	Ca	Al
Concentration	44	0.073	0.14	0.043	1.56

It can be seen from Table 6 that the desilication liquid contains a large amount of Si, and its concentration is as high as 44 mg/L, and the desilication liquid also contains a small amount of Fe, Ti, Ca and the like. The composition analysis of the desilication liquid further proves that the desilication has a good effect of removing Si enriched Al.

Experimental S2. Determination of zero potential of TDMS.

The pH-dependence of potential of TDMS materials in the aqueous solution was determined by the following procedure: 0.500 g samples of TDMS were added to 50.0 mL of deionized water in ten 100-mL plastic beakers. The pH of the solutions was adjusted using a pH meter to 1.2, 2.4, 3.2, 4.2, 6.3, 7.9, 9.1 and 10.1 with 1 M HCl and 0.1 M NaOH, as needed. The suspended samples were shaken for 12 h in a revolving water bath to reach equilibrium, and the resulting pH and zeta potential of each sample was then measured. The zero potential was defined as the point where the zeta potential was zero, and the relevant pH was defined as zero potential pH.

Experimental S3. Determination of acid orange II and rhodamine B.

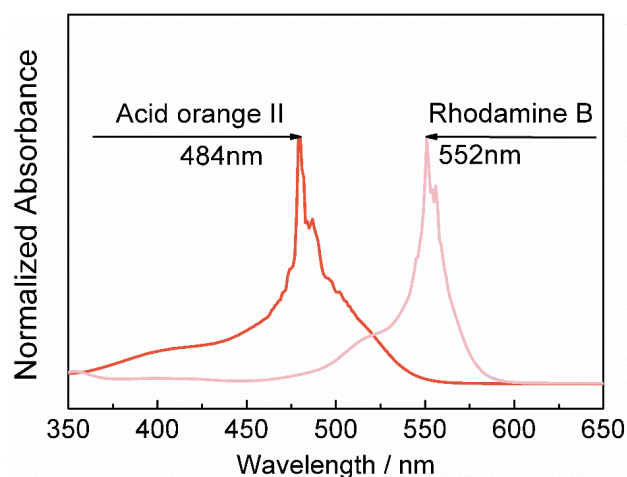


Figure S2. Spectral pattern of acid orange II and rhodamine B.

Fig. S2 shows the absorption spectra of acid orange II and Rhodamine B. The maximum absorption wavelength of acid orange II is 484 nm. The maximum absorption wavelength of rhodamine B is 552 nm. Therefore, the absorbance value of the solution is measured at the maximum absorption wavelength, respectively, so that the concentration of the dye in the solution can be judged.

Experimental S4. Preparation and characterization of mesoporous silica without TiO_2 .

Preparation of material

Herein, mesoporous silica without TiO_2 denotes SiO_2 . The preparation of SiO_2 : 1 g of P123 was first dissolved in 450 mL of distilled water and 50 mL of the desilication solution was added in and the solution was then stirred for 30 min. After that, the pH of the solution was adjusted to approximately 5 with HCl and stirring was continued for 10 min. During this process, a flocculent gel mixture was produced, and then the mixture was placed in a water bath at 60 °C for 48 h. Then, the mixture was filtered and the obtained solids were stirred in ethanol at 80 °C for 8 h to remove the surfactants.

The solid obtained by filtering and drying was finally calcined at 550 °C for 4 h to remove organic surfactant.

Characterization of material

The microstructure of SiO₂ is obtained via SEM. As shown in Figure S3, SiO₂ shows amorphous aggregate microstructure. The XRF result shown in Table S5 also reveals the purity of SiO₂. The chemical structure of SiO₂ is studied via FTIR (Figure 2 in the manuscript).

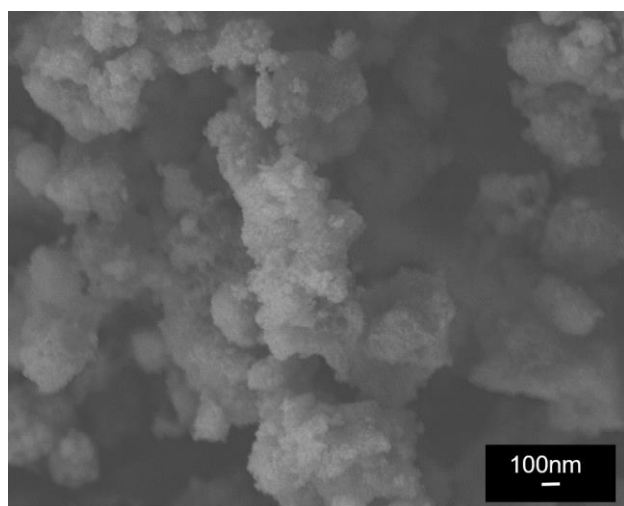


Figure S3. SEM image of mesoporous silica.

Table S5. Chemical composition of mesoporous silica by XRF

	SiO ₂	Na ₂ O	other
Content (%)	98.56	1.29	0.15

Experimental S5. The effect of initial dye concentration on removal kinetics.

Fig.S4 shows the decoloration rate versus time for acid orange II with different initial concentrations. The larger diagram denotes initial concentration of acid orange II with 50 ppm and the smaller diagram denotes 100 ppm. It can be seen from the Fig.S3

that at the initial concentration of 50 ppm, the decoloration rate reaches 99% within 30 min. However, when the initial concentration of acid orange II increased to 100 ppm, under the same photocatalytic conditions, the decoloration rate reaches 99% within 6 hours. This shows that higher initial concentration will significantly slow down the decoloration kinetics. A lower initial concentration will result in sufficient discoloration faster.

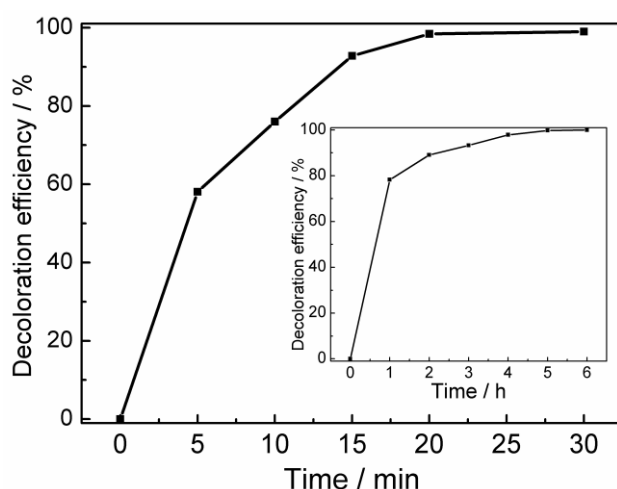


Figure S4. The decoloration rate vs. time at different initial acid orange II concentration. The larger diagram denotes initial concentration of acid orange II with 50 ppm and the smaller diagram denotes 100 ppm.

Experimental S6. Adsorption experiments for dye

The large specific surface area and abundant pore structure facilitate the adsorption of the dye on the material and improve the removal of the dye. In order to study the contribution of adsorption to dye removal, we compared the adsorption effects of TDMS and commercial TiO_2 on acid orange II and rhodamine B without UV lamp illumination. The dosage of the adsorbent was 2 g/L, the adsorption time was within 96 h, and the decolorization rate of the dye solution was sampled at different time. The adsorption kinetics are shown in Figure S5. The adsorption of the dyes on the materials

reaches equilibrium after 48 h. The slow kinetics may be attributed to the large dye molecules. When the adsorption equilibrium is reached, the decolorization rate of both TDMS and commercial TiO_2 for oranges are very low, with 2.1 and 4.6%, respectively. For Rhodamine B, the adsorption effect of both TDMS and TiO_2 is better than that of acid orange II, with 21.9 and 13.4%, respectively. It is worth noting that the photocatalysis experiments are proceeded within 6 hours (See Figure 5 in the manuscript), during this period, the adsorption amount of dye on TiO_2 is higher than that of TDMS, but the photocatalytic property of TDMS is better than TiO_2 . This result indicates that the improvement of photocatalytic effect of TDMS is not due to the increase of adsorption effect, the reason can be attributed to the improved nano-dispersion of TiO_2 component in TDMS.

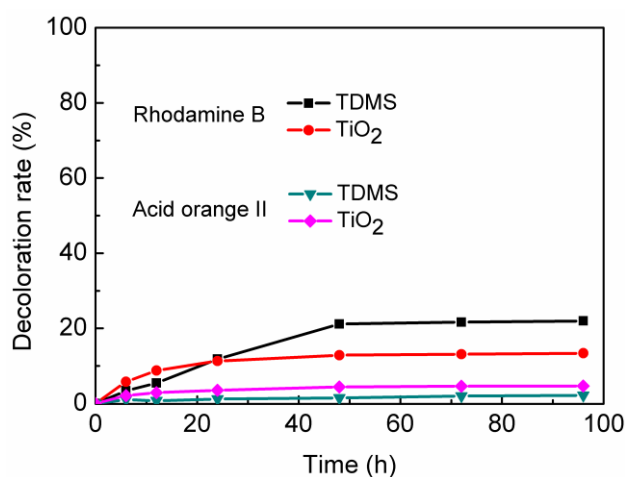


Figure S5. Adsorption kinetics of adsorbents for dyes.