



# ZrO<sub>2</sub>/carbon aerogel composites: A study on the effect of the crystal ZrO<sub>2</sub> structure on cationic dye adsorption



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## ABSTRACT

In this study, ZrO<sub>2</sub>/carbon aerogel (CA) composites with different amounts of monoclinic and tetragonal ZrO<sub>2</sub> crystallites were successfully prepared by varying the quantity of HMTA in the hydrothermal synthesis. Monoclinic ZrO<sub>2</sub> (m-ZrO<sub>2</sub>) structures are successfully transformed to tetragonal ZrO<sub>2</sub> (t-ZrO<sub>2</sub>) structures by increasing the amount of HMTA from 0.187 to 1.683 g. As a result, ZrO<sub>2</sub>/CA (H 1.683) samples with the addition of 1.683 g of HMTA possess only the t-ZrO<sub>2</sub> structure. Furthermore, ZrO<sub>2</sub>/CA (H 1.683) samples possess the highest adsorption capacity for cationic RhB dyes with positive charges, which is attributed to these samples having the largest negative surface charge (−42 mV at pH 7). As a result, ZrO<sub>2</sub>/CA (H 1.683) samples have a large potential for use in the industrial removal of the cationic RhB dye. This work provides a basis for the concept of crystalline structure design to improve organic dye adsorption.

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## 1. Introduction

ZrO<sub>2</sub> is a well-known ceramic material with three different crystalline structures: monoclinic, tetragonal and cubic. These structures are used for various applications, including solid oxide electrolytes [1], drug delivery [2,3], catalysis [4,5], solar cells [6] and adsorption [7,8]. The crystalline structure of ZrO<sub>2</sub> is very important for applications. Take the adsorption application for example; compared with the monoclinic ZrO<sub>2</sub> structure (m-ZrO<sub>2</sub>), tetragonal ZrO<sub>2</sub> (t-ZrO<sub>2</sub>) possesses a larger negative surface charge, which results in a better adsorption capacity for cationic dyes, such as RhB dyes. However, m-ZrO<sub>2</sub> structure is thermally stable below 1200 °C, while the t-ZrO<sub>2</sub> structure is stable between 1200 °C and 2300 °C. Furthermore, cubic ZrO<sub>2</sub> (c-ZrO<sub>2</sub>) is thermally stable above 2300 °C [9], which means that t-ZrO<sub>2</sub> and c-ZrO<sub>2</sub> structures are hardly prepared at low temperatures. Some strategies to prepare t-ZrO<sub>2</sub> and c-ZrO<sub>2</sub> structures at low temperatures have been reported in the literature. c-ZrO<sub>2</sub> structures with an excess of oxygen vacancies were successfully prepared by yttrium doping to form cubic yttria-stabilized zirconia (YSZ) [10]. The t-ZrO<sub>2</sub> and c-ZrO<sub>2</sub> nanocrystallites were successfully fabricated in ammonia solutions using a femtosecond laser ablation process [11]. Tahir et al. [12] successfully synthesized c-ZrO<sub>2</sub> nanoparticles in aqueous NaOH solutions at high pH using a hydrothermal process. The results indicate that t-ZrO<sub>2</sub> and c-ZrO<sub>2</sub> crystallites are

favored for growth at high pH values and OH<sup>−</sup> concentrations. In our previous study [13], ZrO<sub>2</sub>/carbon aerogel (CA) composites with t-ZrO<sub>2</sub> structures were successfully synthesized with the assistance of phenol formaldehyde (PF) resins that formed during the hydrothermal process. Compared with pure m-ZrO<sub>2</sub> nanoparticles, negatively charged t-ZrO<sub>2</sub>/CA composites avoid the particle aggregations, leading to a larger specific surface area and a better adsorption capacity for cationic dyes.

In this study, ZrO<sub>2</sub>/CA composites with different amounts of m-ZrO<sub>2</sub> and t-ZrO<sub>2</sub> phases could be controllably generated by the formation of PF resins and adding different amounts of hexamethylenetetramine (HMTA). The effect of the ZrO<sub>2</sub> crystal structure on the adsorption capacity for cationic dyes, such as RhB dyes, was investigated in this work. The results show that t-ZrO<sub>2</sub> possesses a greater negative surface charge, which leads to a better adsorption capacity for cationic dyes, such as RhB dyes. This work illustrates the concept of crystalline structure design for organic dye adsorption.

## 2. Experimental

### 2.1. Chemicals

Zirconyl chloride octahydrate (ZrOCl<sub>2</sub>·8H<sub>2</sub>O, 99%, Merck Company), hexamethylenetetramine (HMTA, 95%, ECHO-Chemical Company) and phenol (99%, ECHO-Chemical Company) were used for the preparation of the ZrO<sub>2</sub>/CA composites. Rhodamine B dyes (RhB, 95%, Sigma-Aldrich Company), and de-ionized water were

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**Table 1**

ZrO<sub>2</sub> percentage, percentage of monoclinic and tetragonal crystallites, pore volume, specific surface area and surface charges in the ZrO<sub>2</sub>/CA samples as a factor of different amounts of HMTA (0.187 g, 0.561 g and 1.683 g).

	ZrO <sub>2</sub> percentage (%)	M (%)	T (%)	Pore volume (cm <sup>3</sup> /g)	Specific surface area (m <sup>2</sup> /g)	Surface charge (mV) (pH 7)
ZrO <sub>2</sub> /CA (H 0.187)	27.6	88.4	11.6	0.15	146.5	−19.3
ZrO <sub>2</sub> /CA (H 0.561)	46.9	43.6	56.4	0.35	337.6	−27.0
ZrO <sub>2</sub> /CA (H 1.683)	46.1	0	100	0.41	275.7	−42.0

used for the dye absorption experiments. Eye, face or body contacts with RhB dyes should be avoided during the dye absorption experiments.

## 2.2. Synthesis of ZrO<sub>2</sub>/CA composites

The preparation of ZrO<sub>2</sub>/CA composites was followed according to our previous studies [13]. Briefly speaking, ZrO<sub>2</sub>/CA composites were obtained by the carbonization of ZrO<sub>2</sub>/phenol formaldehyde (PF) resins at 800 °C for 6 h under a nitrogen atmosphere. For the ZrO<sub>2</sub>/PF nanostructures, ZrOCl<sub>2</sub> (1.1 g), phenol (0.502 g) and three different amounts of HMTA (0.187, 0.561 and 1.683 g) were allowed to react together at 180 °C for 24 h in a hydrothermal process. The resulting ZrO<sub>2</sub>/PF nanostructures with different amounts of HMTA (0.187, 0.561 and 1.683 g) were further heated at 800 °C for 6 h to form the ZrO<sub>2</sub>/CA (H 0.187), ZrO<sub>2</sub>/CA (H 0.561) and ZrO<sub>2</sub>/CA (H 1.6831) samples, respectively.

## 2.3. RhB dyes adsorption test

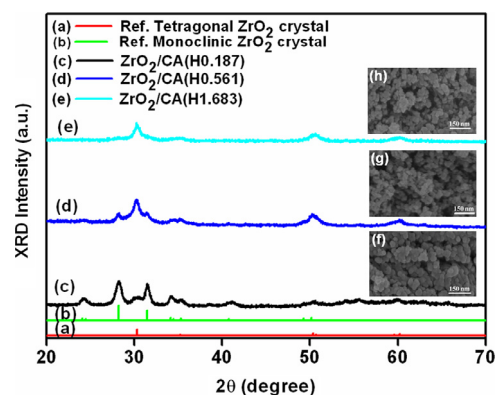
ZrO<sub>2</sub>/CA (H 0.187), ZrO<sub>2</sub>/CA (H 0.561) and ZrO<sub>2</sub>/CA (H 1.6831) samples were utilized for the adsorption of RhB dyes. A total of 10 mg of ZrO<sub>2</sub>/CA (H 0.187), ZrO<sub>2</sub>/CA (H 0.561) or ZrO<sub>2</sub>/CA (H 1.6831) was immersed in 100 ml of RhB dye solutions with differing concentrations at pH 7. The resulting mixtures were further stirred at room temperature for 24 h to reach equilibrium. After a centrifugal separation, the remaining RhB concentration was measured using a UV–visible spectrophotometry, and this concentration was used to obtain the adsorption isotherms. For the regeneration procedures of ZrO<sub>2</sub>/CA composites, the used ZrO<sub>2</sub>/CA adsorbents were stirred in 100 ml of ethanol solution for 2 h. After centrifugation separation, the washed ZrO<sub>2</sub>/CA adsorbents were further used for the second cycle of the dye adsorption.

## 2.4. Characterizations

The surface morphology and the crystalline phases of the ZrO<sub>2</sub>/CA samples were examined via field-emission scanning electron microscopy (FESEM, Hitachi, S-4800N) and powder X-ray diffraction (PXRD, PANalytical X'Pert PRO, PW3040/60), respectively. The t-ZrO<sub>2</sub> crystalline size of ZrO<sub>2</sub>/CA (H 0.187), ZrO<sub>2</sub>/CA (H 0.561) and ZrO<sub>2</sub>/CA (H 1.6831) samples was calculated using the Scherrer equation as follows:  $d = \frac{0.9\lambda}{B \cos \theta}$ . Where, d is the crystalline size of t-ZrO<sub>2</sub> phase,  $\lambda$  is X-ray wavelength,  $\theta$  is the Bragg angle and B is the line broadening at half the maximum intensity (FWHM) of the Bragg angle, respectively. The specific surface area and pore volume of the ZrO<sub>2</sub>/CA samples were measured based on N<sub>2</sub> adsorption/desorption isotherms (BET, Micromeritics ASAP 2020). The functional groups in the as-prepared samples were characterized using Fourier Transform Infrared spectroscopy (FTIR, Perkin-Elmer Inc., Spectrum One). The concentration of RhB dye in solution was measured via UV–visible spectrophotometry (Hitachi, U-3900/U-3900H).

## 3. Results and discussion

The crystalline structures and surface morphologies of ZrO<sub>2</sub>/CA (H 0.187), ZrO<sub>2</sub>/CA (H 0.561) and ZrO<sub>2</sub>/CA (H 1.683) samples were



**Fig. 1.** XRD patterns for the reference (a) tetragonal and (b) monoclinic ZrO<sub>2</sub> crystals, and the ZrO<sub>2</sub>/CA structures with different amounts of HMTA: (c) 0.187 g, (d) 0.561 g and (e) 1.683 g. FESEM images of the ZrO<sub>2</sub>/CA structures with different amounts of HMTA: (f) 0.187 g, (g) 0.561 g and (h) 1.683 g.

first investigated by FESEM and XRD, as shown in Fig. 1. The reference diffraction patterns for t-ZrO<sub>2</sub> and m-ZrO<sub>2</sub> phases are included in Fig. 1(a) and (b), respectively. Fig. 1(c) and (d) are the XRD diffraction patterns of ZrO<sub>2</sub>/CA (H 0.187) and of ZrO<sub>2</sub>/CA (H 0.561) samples. The diffraction peaks produced by the ZrO<sub>2</sub>/CA (H 0.187) and ZrO<sub>2</sub>/CA (H 0.561) samples agree well with those of the reference m-ZrO<sub>2</sub> and t-ZrO<sub>2</sub> crystals, indicating the presence of mixed monoclinic and tetragonal crystalline phases in these samples. Surprisingly, as the quantity of HMTA was increased to 1.683 g, the observed diffraction peaks of the ZrO<sub>2</sub>/CA (H 1.683) samples (Fig. 1(e)) corresponded only to those of the tetragonal reference, implying the existence of a pure tetragonal phase in ZrO<sub>2</sub>/CA (H 1.683) sample. The monoclinic (M%) and tetragonal (T%) crystallite percentages of the three ZrO<sub>2</sub>/CA samples were calculated in the manner following our previous study [13], and the results are listed in Table 1. The monoclinic crystallite percentages are 88.4, 43.6 and 0% for the ZrO<sub>2</sub>/CA (H 0.187), ZrO<sub>2</sub>/CA (H 0.561) and ZrO<sub>2</sub>/CA (H 1.683) samples, respectively. Furthermore, the tetragonal crystallite percentages are 11.6, 56.4 and 100% for the ZrO<sub>2</sub>/CA (H 0.187), ZrO<sub>2</sub>/CA (H 0.561) and ZrO<sub>2</sub>/CA (H 1.683) samples and the t-ZrO<sub>2</sub> crystalline sizes determined by the Scherrer equation are 6.9, 8.5 and 10.8 nm for the ZrO<sub>2</sub>/CA (H 0.187), ZrO<sub>2</sub>/CA (H 0.561) and ZrO<sub>2</sub>/CA (H 1.683) samples, respectively. A possible mechanism for the ZrO<sub>2</sub> monoclinic to tetragonal phase transition was discussed in our previous study [13]. Briefly speaking, higher HMTA concentrations produce more OH<sup>−</sup> ions in the reaction solution, and the growth of symmetric tetragonal crystallites are favored at higher OH<sup>−</sup> concentrations [11,12]. The FESEM images of the three samples (Fig. 1(f–h)) reveal their porous structure. The specific surface areas of the ZrO<sub>2</sub>/CA (H 0.187), ZrO<sub>2</sub>/CA (H 0.561) and ZrO<sub>2</sub>/CA (H 1.683) samples are 146.5, 337.6 and 275.7 m<sup>2</sup>/g (Table 1), respectively, as obtained from N<sub>2</sub> adsorption/desorption isotherms. The pore volumes of the ZrO<sub>2</sub>/CA (H 0.187) (0.15 cm<sup>3</sup>/g), ZrO<sub>2</sub>/CA (H 0.561) (0.35 cm<sup>3</sup>/g) and ZrO<sub>2</sub>/CA (H 1.683) (0.41 cm<sup>3</sup>/g) samples are also obtained from N<sub>2</sub> adsorption/desorption isotherms, as shown in Table 1.

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