



# Nitrogen-doped porous carbons by conversion of azo dyes especially in the case of tartrazine



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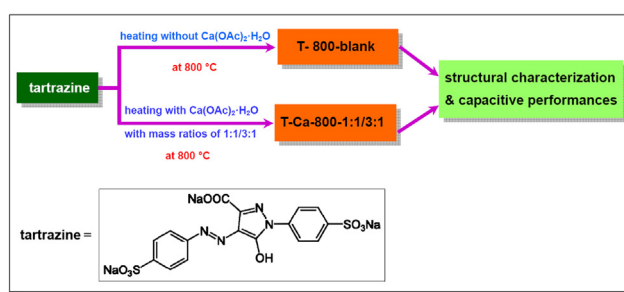
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## HIGHLIGHTS

- A direct carbonization method was developed for nitrogen-doped porous carbon.
- Tartrazine can serve as not only carbon source but also as nitrogen source.
- High surface areas and pore volumes are achieved with  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ .
- The carbon samples exhibit excellent capacitive behaviors.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Nitrogen-doped porous carbons possessing high surface areas and large pore volumes have been prepared by directly heating the mixture of tartrazine and  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  at 800 °C especially without further physical or chemical activation, where  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  serves as the hard template to regulate the surface area and pore structures. It reveals that the addition of  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  can remarkably improve the surface area and total pore volume. The **T-Ca-800-3:1** sample displays the highest BET surface area as  $1669 \text{ m}^2 \text{ g}^{-1}$  and largest total pore volume  $0.85 \text{ cm}^3 \text{ g}^{-1}$ , which is much larger than those without adding  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ . Furthermore, it exhibits excellent capacitive performances, including high specific capacitance (ca.  $224.3 \text{ F g}^{-1}$  at  $0.5 \text{ A g}^{-1}$ ), good rate capability (the retention of  $42.6\%$  at  $60 \text{ A g}^{-1}$ ) and good cycling stability (the retention of  $92.3\%$  within 5000 cycles).

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## 1. Introduction

Along with the increasing power demands of energy storage systems in the 21st century, supercapacitors have attracted much attention due to their pulse power supply, long cycle life ( $>100$  cycles), and high dynamic of charge propagation [1–3]. Among the

reported electrode materials, carbon materials have gained considerable interest because of high electrical conductivity, low cost and multiple forms and allotropes, as well as broad chemical stability in acidic or basic solutions [4,5]. More importantly, Simon et al. found that electrochemical double layer capacitors (EDLCs) are able to operate from  $-50$ – $100$  °C on the base of the combination of exohedral nanostructured carbon (nanotubes and onions) electrode and a eutectic mixture of ionic liquids [6]. Consequently, using carbon as the active material, EDLCs represent more than 80% of the commercially manufactured ECs today [7].

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Among the carbon electrodes, porous carbons are of great importance especially due to their high surface area and large pore volume, providing an extensively large electrode/electrolyte interface for charge storage [8]. Xu et al. prepared porous carbons by direct carbonization of poly(vinylidene chloride) (PVDC) without adding any templates, having BET surface area about  $1200 \text{ m}^2 \text{ g}^{-1}$  [9]. However, in most cases, hard/soft templates are commonly indispensable for preparing porous carbons. For example, templating with zeolites, silica or silicates can yield micro/meso/macropores with a narrow pore size distribution, but such *ex-situ* template methods are both expensive and inefficient, requiring rigorous etching with HF or KOH to remove the templates [10]. Alternatively, other kinds of hard templates, including MgO [11],  $\text{Mg}(\text{OH})_2$  [12],  $\text{Ni}(\text{OH})_2$  [13],  $\text{CaCO}_3$  [14], have been developed to cater for the template removal utilizing relatively gentle acid such as HCl.

Azo compounds have the functional group  $\text{R}-\text{N}=\text{N}-\text{R}'$ , in which R and R' can be either aryl or alkyl. As a consequence of  $\pi$ -delocalization, aryl azo compounds have vivid colors, especially reds, oranges, and yellows. Therefore, they are used as dyes, commonly known as azo dyes. The development of azo dyes was an important step in chemical industry. Taking tartrazine as an example, it is a synthetic lemon yellow azo dye primarily used as a food coloring, but also can be used with Brilliant Blue FCF or Green S to produce various green shades [15]. Considering the particular structure containing phenyls and especially high content nitrogen, tartrazine is for the first time expected to prepare nitrogen-doped porous carbon at elevated carbonization temperatures.

Herein, we present a straightforward carbonization method to prepare nitrogen-doped porous carbons without further physical or chemical activation, using tartrazine as carbon source and calcium acetate as hard template. The mass ratio of tartrazine and calcium acetate was emphatically investigated. The correlative capacitive performances were measured by cyclic voltammetry and galvanostatic charge–discharge techniques.

## 2. Experimental

All the analytical chemicals were purchased from Sinopharm Chemical Reagent (Shanghai) Co. Ltd. and used as received without further treatment.

In present experiment, pure tartrazine was heated at  $800^\circ\text{C}$  for 2 h under Ar flow to obtain **T-800-blank** sample. On the other hand, tartrazine and  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  with mass ratios of 1:1 and 3:1 at

$800^\circ\text{C}$  for 2 h under Ar flow to obtain **T-Ca-800-1:1/3:1** samples. The schematic routes and the unit structure of tartrazine are depicted in Fig. 1.

### 2.1. Typical synthetic procedure for T-Ca-800-3:1 sample

Tartrazine and  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  powder (mass ratio of 3:1) were ground adequately and then placed in a porcelain boat, flushing with Ar flow for 30 min, and further heated in a horizontal tube furnace up to  $800^\circ\text{C}$  at a rate of  $5^\circ\text{C min}^{-1}$  and maintained at  $800^\circ\text{C}$  for 2 h under Ar flow. The resultant product was immersed with dilute HCl solution to remove soluble/insoluble substances, which was further washed with adequate deionized water until  $\text{pH} = 7$ . Finally, the sample was dried under vacuum at  $120^\circ\text{C}$  for 12 h to obtain the **T-Ca-800-3:1** sample.

Regarding the synthetic procedure for **T-Ca-800-1:1** sample, it is similar to that of **T-Ca-800-3:1** sample detailedly depicted above except for the mass ratio of tartrazine and  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  powder as 1:1.

Regarding the synthetic procedure for **T-Ca-blank** sample, it is similar to that of **T-Ca-800-3:1** sample without using  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ .

### 2.2. Characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX2500V with  $\text{Cu K}\alpha$  radiation. Field emission scanning electron microscopy (FESEM) images were taken with a Hitachi S-4800 scanning electron microscope. X-ray photoelectron spectra (XPS) were obtained on a VG ESCALAB MK II X-ray photoelectron spectrometer with an exciting source of  $\text{Mg K}\alpha$  (1253.6 eV). The specific surface area and pore structure of the carbon samples were determined by  $\text{N}_2$  adsorption–desorption isotherms at 77 K (Quantachrome Autosorb-iQ) after being vacuum-dried at  $150^\circ\text{C}$  overnight. The specific surface areas were calculated by a BET (Brunauer–Emmett–Teller) method. Cumulative pore volume and pore-size distribution were calculated by using a slit/cylindrical nonlocal density functional theory (NLDFT) model.

### 2.3. Electrochemical measurements

In order to evaluate the capacitive performances of the as-prepared carbon samples (*ca.* 4 mg) in electrochemical capacitors, a mixture of 80 wt% the carbon powder, 15 wt% acetylene black and

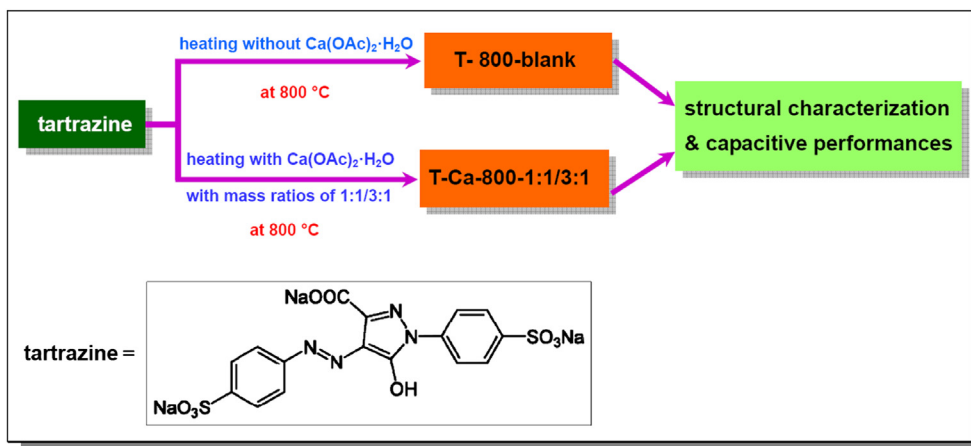


Fig. 1. Schematic illustration of the production of nitrogen-doped porous carbon by heating tartrazine with or without  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  at a designated carbonization temperature of  $800^\circ\text{C}$  for 2 h under Ar flow, in which  $\text{Ca}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  serves as hard template.

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