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Template-free synthesis of high-yield phosphonated tin oxides with high specific surface area

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ABSTRACT

High-yield porous phosphonated tin oxides (SnEDTMP) were successfully synthesized through a facile hydrothermal route with $SnCl_4{\cdot}5H_2O$ as tin source, ethylene diamine tetra(methylene phosphonic acid) (EDTMP) as the organophosphorus and NaOH as the pH regulator. Without any additive template during synthetic process, the obtained product had a high specific surface area of 377 m^2/g, which was considered to stem from the aggregation of nanoparticles resulting in sufficient void spaces. It was found that the order of NaOH added during synthetic process could effectively dominate the aggregation of nanoparticles such to form tight or loose accumulation, which was the key to successful preparation of high-specific-surface-area phosphonated tin oxides.

1. Introduction

Various tin-contained compounds, because of their Lewis-acidic and redox properties from tin species, have been widely used in photocatalytic degradation of organic dyes [1], photovoltaic devices [2], rechargeable lithium batteries [3,4], gas-sensing materials [5], and so on. Phosphonating the tin-contained compounds to form organic-inorganic hybrid structures would enrich their functionalities and widen their potential application prospects in many aspects, such as heterogeneous catalysis, adsorption, ion exchange, and as supports [6–9].

To improve application performance of phosphonated tin oxides, incorporating porosity to fabricate materials with high specific surface areas would be a feasible strategy. Surfactant templating routes have been developed to serve this purpose. For example, in 2005 Fujiwara et al. [10] fabricated mesoporous hybrid tin phenylphosphonate with a specific surface area of 371 m^2/g in the presence of anionic surfactant sodium dodecylsulfate. In 2012, Dutta et al. [11] synthesized a hybrid porous tin (IV) phosphonate with $SnCl_5{\cdot}5H_2O$ as tin source, pentaethylenehexamine-octakis-(methyl phosphonic acid) hexadecasodium salt solution as the phosphonate source and cetyl trimethylammonium bromide as the structure directing agent. This material showed a BET surface area of 723 m^2/g, and good catalytic activity in one-pot liquid phase oxidation of cyclohexanone to adipic acid under eco-friendly conditions. In 2016, Wang et al. reported a category of porous tin (IV) phosphonates, showing specific surface areas in the range of 27–168 m^2/g, in presence of nonionic templating agent F127 through solvothermal treatment [9]. For templating synthesis strategy, surfactant molecules have to be further removed whether by acid-ethanol extraction or by calcination. This method would make tedious synthetic steps and lead to increased cost, as well as bring environmental pollution in the post-treatment. Surfactant-free synthesis of such kind of materials with high specific surface area is intriguing. However, the related reports are rare [12].

In this research, high-yield porous phosphonated tin oxide (SnEDTMP) was hydrothermally synthesized with $SnCl_4{\cdot}5H_2O$ as tin source, ethylene diamine tetra(methylene phosphonic acid) (EDTMP) as the organophosphorus and NaOH as the pH regulator. Without any surfactant templating agent or organic solvent involved in the hydrothermal media, SnEDTMP with a high specific surface area of 377 m^2/g could be obtained by simply controlling the adding order of NaOH in the synthetic process.

2. Materials and methods

The typical synthesis of porous phosphonated tin oxides could be described as follows. An EDTMP aqueous solution was prepared by dissolving 0.76 g of EDTMP into 25 mL of water and then NaOH (0.56 g) was added under stirring. Afterward an aqueous solution of $SnCl_4{\cdot}5H_2O$ (1.78 g in 5 mL of H_2O) was added dropwise. The mixture was continuously stirred at 45 °C for 2 h and then trans-

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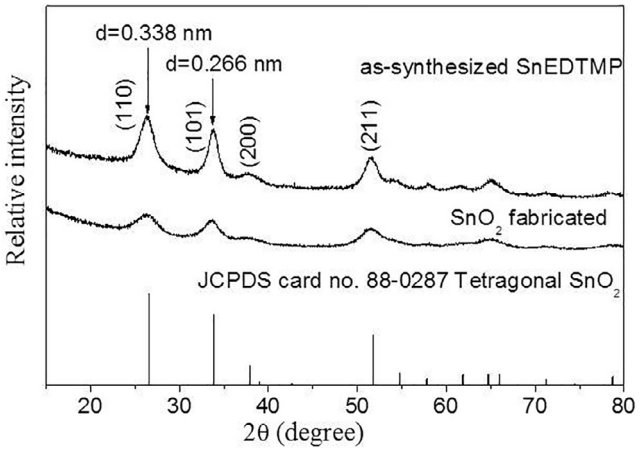

Fig. 1. XRD patterns of as-synthesized SnEDTMP and SnO_2 fabricated.

ferred into an autoclave aging at 120 °C for 24 h. Finally white powder were collected by filtering, washed with water and dried at 80 °C. The as-prepared material was designated as SnEDTMP. For the purpose of comparison, SnO_2 sample was prepared following the processing described above without addition of phosphorus.

Details about the material characterizations can be found in Supplementary material.

3. Results and discussion

The XRD pattern of SnEDTMP (Fig. 1) gives four typical peaks at 2θ values of 26.38°, 33.76°, 37.61° and 51.4°, corresponding to (1 1 0), (1 0 1), (2 0 0), and (2 1 1) reflections, respectively, which evidently revealed the presence of a tetragonal SnO_2 crystalline structure. The as-obtained SnEDTMP contained tetragonal SnO_2

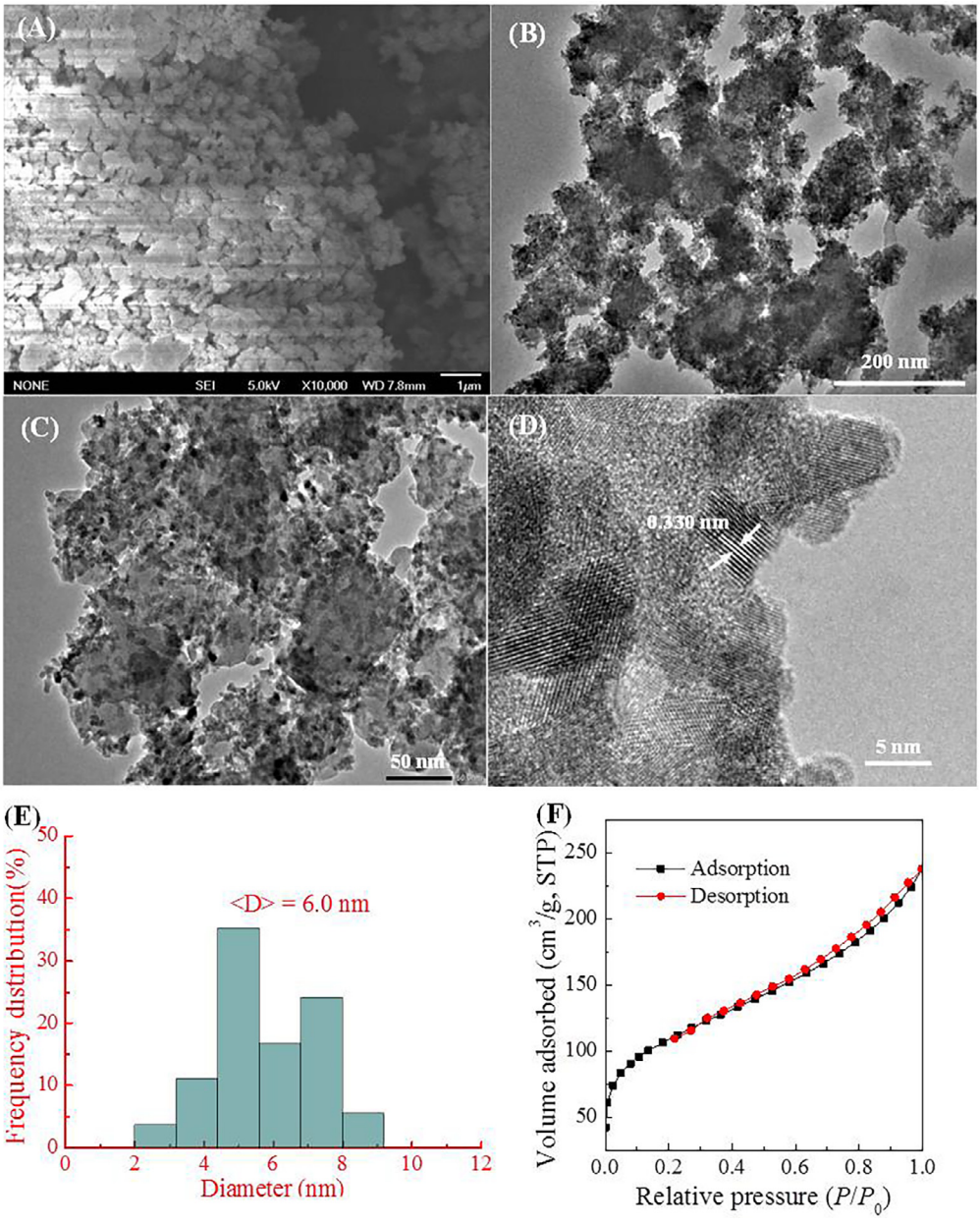

Fig. 2. (A) SEM image, low- (B, C) and high-resolution (D) TEM images, (E) the corresponding particle size distribution from (C), and (F) N_2 adsorption-desorption isotherms, of SnEDTMP.