



Short Communication

Stabilizing the titanium-based metal organic frameworks in water by metal cations with empty or partially-filled d orbitals

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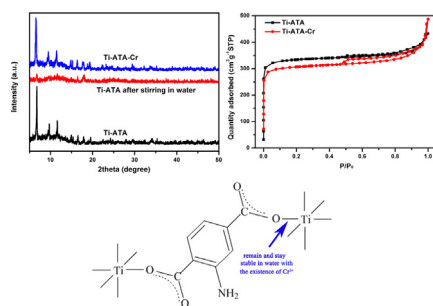
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GRAPHICAL ABSTRACT

The Ti-based MOF, Ti-ATA, is unstable in water, but its stability in water is greatly enhanced without sacrificing its porosity and photocatalytic activity by treating it in aqueous solutions containing metal ions with empty d orbitals (Y^{3+} , La^{3+} , Ce^{3+} , Nd^{3+} and Tm^{3+}) or partially-filled d orbitals (Cr^{3+}).



ARTICLE INFO

Article history:

Received 12 June 2018

Revised 6 August 2018

Accepted 15 August 2018

Available online 17 August 2018

Keywords:

Ti-based MOFs

Enhancing the stability in water

Metal cations with empty or partially-filled d orbitals

ABSTRACT

Though titanium-based metal-organic frameworks (MOFs) are declared to be relatively water stable, their framework gradually collapses in water within days due to the attack of OH^- to $O-Ti-O$ bond. For practical applications of titanium-based MOFs, it is crucial to solve their instability problem in water. We searched for a simple and efficient method to enhance the stability of titanium-based MOFs in water by using Ti-ATA (ATA = 2-aminoterephthalate ion) as a representative titanium-based MOF. Here, we show that the stability of Ti-ATA in water is greatly improved nearly without affecting its porosity and photocatalytic activity by treating it with aqueous solutions containing metal ions of empty d orbitals (Y^{3+} , La^{3+} , Ce^{3+} , Nd^{3+} and Tm^{3+}) or partially-filled d orbitals (Cr^{3+}).

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1. Introduction

MOFs consisting of metal clusters and organic linkers have a wide range of potential applications, which include gas

adsorption/separation, catalysis, magnetism, proton conduction and drug delivery [1–9]. A crucial issue facing the applications of MOFs is their stability in water [10–13]. For example, use of the MOFs such as HKUST-1 and MOF-5 in aqueous solution is impracticable because they are unstable in water [14,15]. Titanium is often chosen to construct MOFs for its high catalytic activity, but Ti-based MOFs are somewhat unstable in water [16–18]. The

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structure of a Ti-based MOF usually collapses gradually after being stirred in water, which in turn decreases its photocatalytic activity [19]. In designing stable MOFs, the hard soft acid base concept is often invoked [20]. Here, we report a very simple and efficient method to enhance the stability of a representative Ti-based MOF, Ti-ATA (ATA = 2-aminoterephthalate ion) in water for days, without sacrificing its porosity and photocatalytic activity. The stability of Ti-ATA in water is greatly improved when it is treated with aqueous solutions containing metal ions M^{n+} with empty d orbitals (Y^{3+} , La^{3+} , Ce^{3+} , Nd^{3+} and Tm^{3+}) or partially-filled d orbitals (Cr^{3+}).

2. Results and discussion

For convenience of our discussion, we use the notation Ti-ATA-M to refer to the Ti-ATA treated with aqueous solution containing the metal ions M^{n+} (Y^{3+} , La^{3+} , Ce^{3+} , Nd^{3+} , Tm^{3+} and Cr^{3+}). We first compare the structures of Ti-ATA and Ti-ATA-Cr. As shown in Fig. 1a, the powder X-ray diffraction (XRD) patterns of Ti-ATA-Cr are identical to that of the parent Ti-ATA [19], indicating that Ti-ATA-Cr and Ti-ATA have the same framework structure, and the Cr of Ti-ATA-Cr does not substitute for the Ti in Ti-ATA. The energy dispersive X-ray spectrum (EDS) of Ti-ATA-Cr proves the presence of Cr in Ti-ATA-Cr (Fig. S1) with the Cr/Ti atom ratio of 0.16. The latter is the maximum amount of Cr that one can upload in Ti-ATA, because this ratio is not further increased even when more Cr^{3+} ions are added in the starting solution. This suggests that only the surfaces of Ti-ATA particles are affected by Cr^{3+} ions. The content of Cr^{3+} in Ti-ATA-Cr was also determined using ICP-AES. The concentration of Ti and Cr were determined to be 29.55 and 5.13 mg/L, respectively under our experimental conditions. Therefore, the Cr/Ti atom ratio was 0.16, which was consistent with the EDS data.

The scanning electron microscopy (SEM) images of Ti-ATA and Ti-ATA-Cr are presented in Fig. 1b–d. Even after 4 days of being stirred in water, the morphology and particle size of Ti-ATA-Cr still remain the same as those of the as-prepared Ti-ATA. Whereas, the nanocube morphology of the as-prepared Ti-ATA is destroyed into much smaller nanoparticles after 4 days of being stirred in water. The stabilizing effect of Cr on Ti-ATA is further checked under harsh conditions, namely, hydrothermal treatment at 120 °C as well as stirring in acidic (pH = 3.0), neutral (pH = 7.0) and alkaline (pH = 11) solutions for 10, 15 and 20 days. The powder XRD patterns reveal that Ti-ATA is unstable, but Ti-ATA-Cr remains stable even under these harsh conditions (Fig. S2).

To check how the porous structure of Ti-ATA is modified by the introduction of Cr, we compare the N_2 adsorption-desorption isotherms at 77 K of Ti-ATA and Ti-ATA-Cr (Fig. 1e). At high relative pressure P/P_0 , both Ti-ATA and Ti-ATA-Cr show a high adsorption, indicating the presence of accumulation pores. Both samples display typical type-IV isotherms with a type H3 hysteresis loop, indicating the existence of irregular mesoporous structure. Compared with Ti-ATA, Ti-ATA-Cr displays an obvious promotion of mesoporosity, which is beneficial to improve the diffusion of small guest molecule, and restrain the decomposition of the MOF framework structure [21,22]. Therefore, it is reasonable that Ti-ATA-Cr is more stable than Ti-ATA in water. The BET surface area of Ti-ATA and Ti-ATA-Cr are calculated to be 1053.3 and 920.2 m^2/g , respectively. Thus, the introduction of Cr preserves the porous framework structure of Ti-ATA with only a small decrease in the BET surface area.

Ti-ATA has been applied to photocatalytic hydrogen evolution reaction (HER). The photocatalytic HER activities over Ti-ATA and Ti-ATA-Cr show that Ti-ATA-Cr and Ti-ATA exhibit the same HER rate in the first two hours (Fig. 2). The HER rate over Ti-ATA decreases gradually so that there is almost no increase in the H_2 evolution after 4 h of reaction, implying the collapse of the framework structure of Ti-ATA. However, Ti-ATA-Cr displays steady and

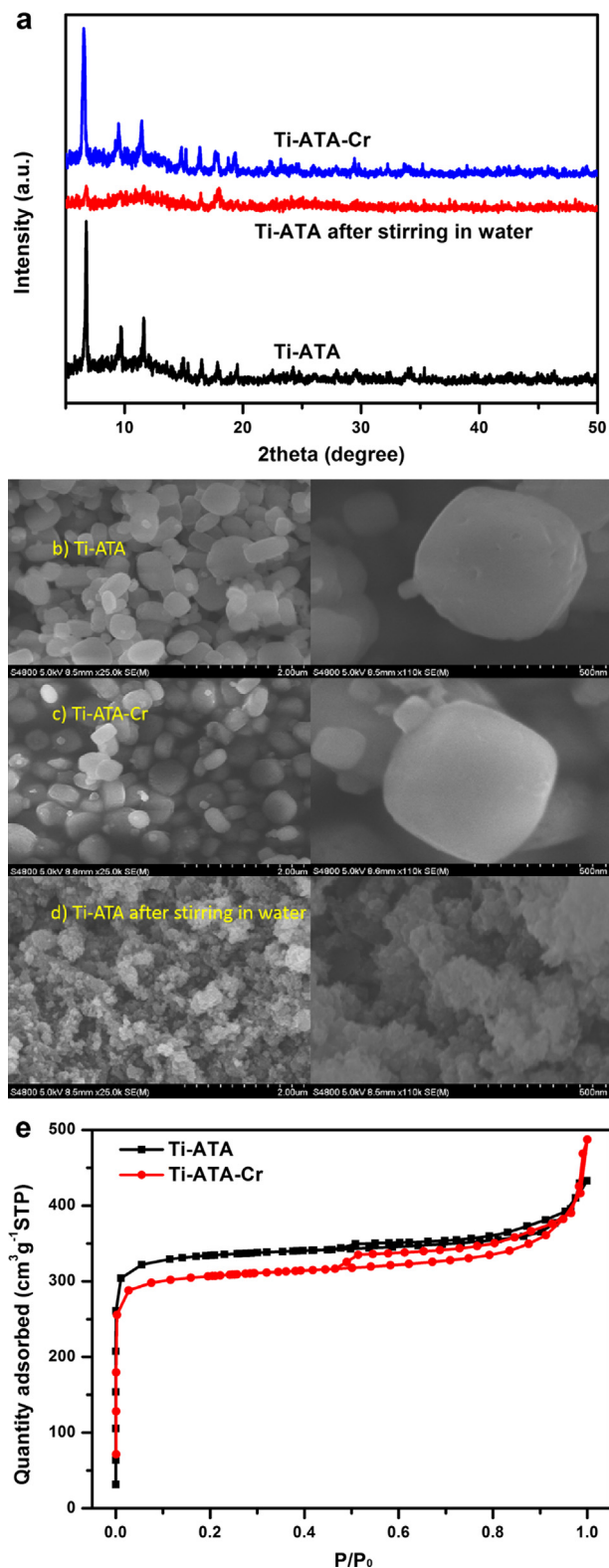


Fig. 1. (a) Powder XRD patterns of Ti-ATA and Ti-ATA in the absence and presence of Cr^{3+} after stirring in water for 4 days. (b) SEM image of as-prepared Ti-ATA. (c, d) SEM images of Ti-ATA-Cr and Ti-ATA after being stirred in water for up to 4 days. (e) N_2 adsorption/desorption isotherms of as-prepared Ti-ATA and Ti-ATA-Cr as a function of the relative pressure P/P_0 .

stable H_2 evolution even with 20 h of continuous reaction. Consequently, the introduction of Cr does not decrease the photocatalytic activity of Ti-ATA, and Ti-ATA-Cr is indeed much more stable than Ti-ATA.

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