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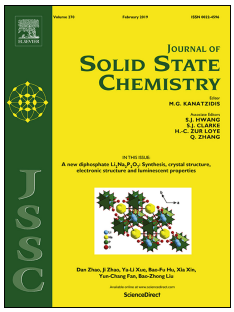

Zeolitic Imidazolate Framework-67@Cellulose aerogel for rapid and efficient degradation of organic pollutants

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PII: S0022-4596(20)30451-5

DOI: https://doi.org/10.1016/j.jssc.2020.121621

Reference: YJSSC 121621

To appear in: *Journal of Solid State Chemistry*

Received Date: 8 July 2020

Revised Date: 22 July 2020

Accepted Date: 25 July 2020

Please cite this article as: Y. Wu, W. Ren, Y. Li, J. Gao, X. Yang, J. Yao, Zeolitic Imidazolate Framework-67@Cellulose aerogel for rapid and efficient degradation of organic pollutants, *Journal of Solid State Chemistry* (2020), doi: https://doi.org/10.1016/j.jssc.2020.121621.

Y. Wu and W. Ren synthesized the MOFs and wrote the paper; Y. Li measured the degradation performance; J. Gao, X. Yang and J. Yao designed and supervised the experiments.

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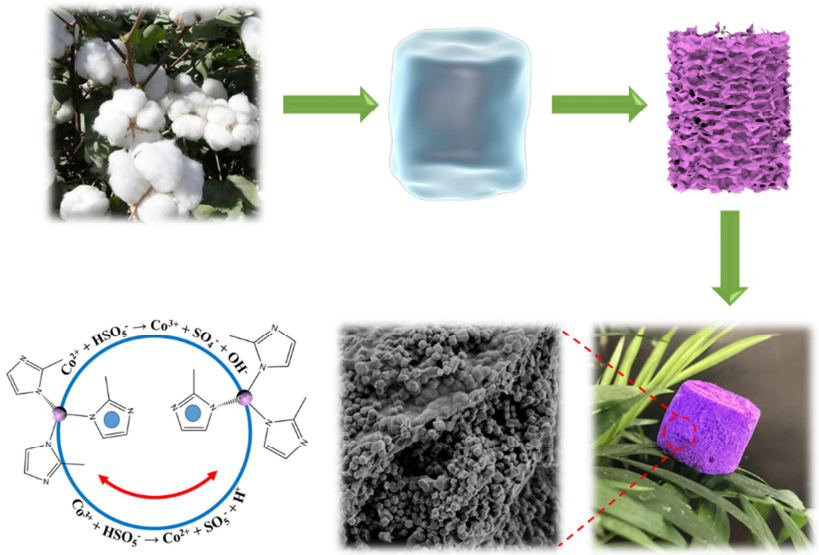

Facile doping method is developed to fabricate the ZIF-67@CAs. The strategy can effectively disperse MOFs uniformly. The ZIF-67@CAs combines the degradation performance of MOFs and the shape ability of aerogels, which can effectively improve the degradation performance. The degradation mechanism shows that ZIF-67@CAs can effectively purify organic pollutants in water. The strategy can be applied to various MOF catalysts in wastewater treatment and thereby expanding their application in a wider range of fields.

Zeolitic Imidazolate Framework-67@Cellulose Aerogel for Rapid and Efficient Degradation of Organic Pollutants

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Abstract: Metal-organic frameworks (MOFs) can efficiently degrade stubborn organic pollutants via advanced oxidation process. However, it is essential to find ways to shape MOFs if its promise of practical application is to be realized. Herein, we develop a Zeolitic Imidazolate Framework-67 (ZIF-67)@cellulose aerogel (denoted as ZIF-67@CA) by a facile doping method. The strategy enhances actual macroscopic shape ability and external hierarchical porosity. Cellulose can provide mechanical flexibility to shape MOFs and promote recycle efficiency after water treatment. The novel doping method increases the loading and dispersibility of ZIF-67, which further increases the potential for the degradation of organic pollutants. ZIF-67@CA can take advantage of the accessible surface area and metal catalytic sites of ZIF-67 to activate peroxymonosulfate (PMS) efficiently and promote its degradation of p-nitrophenol (PNP) and tetracycline hydrochloride (TC). The degradation rate of organic pollutants is up to 80% within only 20 min. Furthermore, ZIF-67@CA exhibits excellent pH stability and recyclability so that it can be reused in harsh environments. Therefore, the low-cost and environmental-friendly production method can effectively recycle high-performance MOFs and expand its applications in a wider range of fields.

Keywords: metal-organic frameworks; doping method; cellulose aerogel; advanced oxidation process; organic pollutant

1. Introduction

Recently, water pollution is considered as one of the most serious environmental problems, which has caused a huge impact on human life and health. Toxic substances

and organic pollutants in wastewater such as p-nitrophenol (PNP) and tetracycline hydrochloride (TC) not only destroy ecosystems but also pose a great threat to aquatic life and even human beings [1]. Thus, the efficient and cost-effective biological approached are urgently developed to remove pollutants from toxicity and recalcitrance. Various technologies have been proposed to remove pollutants from water, such as adsorption [2], oxidation [3], photocatalysis degradation [4], electrodegradation [5] and advanced oxidation processes (AOPs) [6]. Given high efficiency, wide application range and chemical stability, AOPs have caused widespread concern by using hydroxyl radicals (•OH) and sulfate radical anions ($SO_4^{\bullet-}$) as powerful oxidizing species [7]. Specially, the generated $SO_4^{\bullet-}$ from the activation of peroxymonosulfate (PMS) exhibit efficient degradation rate of organic pollutants due to its high redox potential (2.5-3.1 V), high selectivity and wide operating pH range [8]. Currently, the solid catalysts including transition metals (e.g. Co, Fe, Mn and Cu) are used as activators of PMS [9]. Although these catalysts show good degradation properties, the secondary pollution of the toxic ion dissolution and the difficulty in separation and recovery limit their practical applications [10]. Thus, lots of efforts have been done to overcome those above mentioned defects. Recently, metal-organic frameworks (MOFs) have attracted great attention as promising heterogeneous catalysts due to their high specific surface areas, tunable porous structure, and modifiability [11]. Meanwhile, transition metal based MOFs exhibit ultrahigh activity for activating PMS, which can be beneficial to promote the degradation reaction [12]. For example, Zeolitic Imidazolate Framework-67 (ZIF-67) coordinated by cobalt ion

and dimethylimidazole, which can obtain through facile method and provide cobalt ion to activate PMS. However, MOF particles are not easy to be separated from the suspension, which greatly affect their recovery and reusability, and hinder their practical applications. Thus, it is urgent to develop environmental friendly and recyclable supporting substrates to collect MOF particles.

Cellulose aerogels (CAs) have been considered as one of the most potential supporting materials for water treatment in view of their low-cost, biodegradability, aqueous stability and recyclability [13]. As supporting substrates, cellulose aerogels have the following characteristics: (a) the porous structure effectively promotes the adsorption of wastewater; (b) the stable physical and chemical properties make sure that they can work in complex environments; (c) the good mechanical stability endows CAs with excellent recyclability to achieve the separation and recovery of catalysts [14]. MOFs@cellulose composites have been developed for wastewater treatment in recent years [15]. However, loading MOFs on cellulose aerogels for degradation of organic pollutants is quite challenging and rare studies were reported.

In our present work, a facile doping method is developed to fabricate the ZIF-67@CA with high loading (44.7 wt%). The composite materials possess excellent catalytic degradation ability of MOFs, and combines the plasticity and the external hierarchical porosity of cellulose aerogel. ZIF-67@CA showed excellent degradation performance (up to 80% within 20 min) for both PNP and TC. In addition, ZIF-67@CA presented outstanding pH tolerance and cyclical stability, which is of great significance for practical applications. Our method provides a low-cost,

sustainable and scalable platform for the full utilization and recycling of MOFs materials.

2. Results and Discussions

In view of the harmfulness of organic pollutants and the difficulty of self-degradability, it is necessary to develop new catalytic materials, which are highly efficient, degradable and recyclable [16].

The ZIF-67@CA was prepared by a novel and simple doping method (the details were presented in Supporting Information). This method is extremely beneficial for increasing the load of ZIF-67 and uniform dispersion of ZIF-67. Meanwhile, the appearance morphology of ZIF-67@CA is more controllable. The obtained ZIF-67@CA is showed in Figure 1, the bright purple of ZIF-67@CA is consistent with that of ZIF-67, and the ZIF-67@CA maintain a well-defined shape with the excellent properties of aerogels.

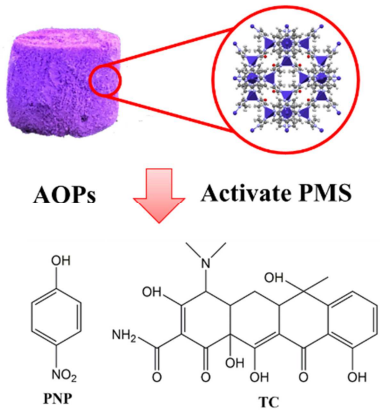

Figure 1. Photograph of ZIF-67@CA and the scheme of ZIF-67, PNP and TC structures.

2.1 Characterization of ZIF-67@CA

The powder X-ray diffraction (XRD) was used to demonstrate the crystal structure of ZIF-67 in the aerogels. As shown in Figure 2a, the cellulose aerogels show a broad

diffraction peaks around 20°, which is a typical crystalline structure for the cellulose. The XRD patterns of ZIF-67@CA is similar to that of ZIF-67 powder, indicating the pure phase of ZIF-67 is successfully loaded on the aerogels. Furthermore, the microscopic morphology of ZIF-67@CA was observed by scanning electron microscopy (SEM). The porous structure of the aerogel is well presented in Figure 2b and abundant ZIF-67 crystals are attached to the pore walls of the aerogel unhindered, indicating the successful fabrication of ZIF-67@CA and the aerogel structure is not destroyed by the doping method. In Figure 2c, the loading of ZIF-67 is significantly increased, this will be further confirmed by thermogravimetric analysis (TGA). Microscopic shape integrity and uniform distribution of ZIF-67 demonstrate the simplicity and efficiency of the doping method (Figure 2d).

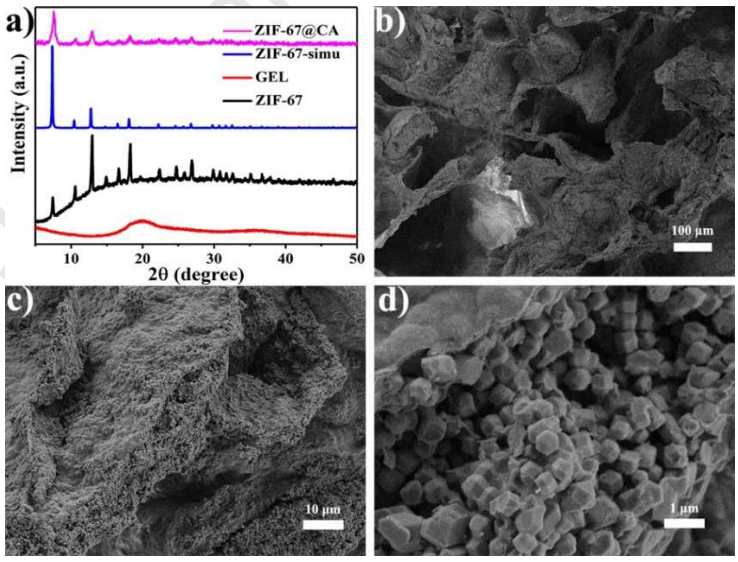

Figure 2. (a) XRD patterns; (b-d) Scanning electron micrograph at different magnifications.

Nitrogen adsorption isotherm analysis was conducted to investigate the specific surface area and pore structure of ZIF-67 as shown in Figure S1. The curve exhibits a typical type I isotherm, which provides the evidence of mesoporous structure. The specific surface area of ZIF-67 is up to 1639.6 m^2 g^{-1}, and the pore size distribution

curve illustrates that the average pore diameter of ZIF-67 is 2.1 nm. The loading of ZIF-67 was calculated by TGA (Figure S2 and Table S1) and the calculation method of the load amount was obtained from the formula in the literature [17]. The ZIF-67@CA prepared by doping method possesses a higher loading (44.7 wt%) and the loading amount can be regulated. After the doping of ZIF-67, the porosity of ZIF-67@CA increased from 45.7% (pure CA) to 87.3% (Table S2). The doubled porosity demonstrated that doping method would not block the pore structure of aerogel at all.

2.2 The degradation performance of ZIF-67@CA

The degradation properties of ZIF-67@CA were studied by degrading two typical pollutants TC and PNP, which were the representative of antibiotics and phenolic contaminants respectively. The ZIF-67@CA/PMS system was used to study the contaminant degradation performance. As shown in Figure 3, there is no change in the concentration of the pollution using only PMS, indicating that the PMS alone cannot generate free radicals to degrade the pollutants. Meanwhile, the ZIF-67@CA have no significant degradation performance without PMS (the slight drop can be attributed to the adsorption on the surface of the aerogel). The ZIF-67@CA and PMS system exhibits excellent degradation performance and the degradation rate reaches up to 80%. It is worth noting that ZIF-67@CA/PMS completes degradation only in 20 minutes. Since ZIF-67@CA is prepared by doping method contained more ZIF-67, more PMS in the system are activated and more free radicals are provided. In addition, there is no interaction between cellulose aerogel and PMS and the slight decrease in cellulose aerogel/PMS system is attributed to the adsorption of cellulose aerogel.

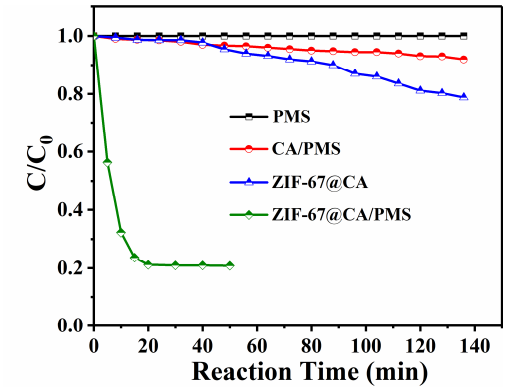

Figure 3. The degradation efficiency of ZIF-67@CA/PMS system in PNP.

We further explored the degradation properties of ZIF-67@CA. To investigate the degradation performance of ZIF-67@CA in different amount of PMS, different doses of PMS were added to the ZIF-67@CA/PMS system. Figure 4a and b show the degradation performance of ZIF-67@CA toward PNP and TC in different doses of PMS, respectively. The results demonstrate that the increase of PMS has a positive effect on the degradation performance of ZIF-67@CA for different types of contaminants.

2.3 The degradation efficiency of ZIF-67@CA in different environments

Complex water environment is one of the important factors affect the practical usability of cellulose composite aerogel. Thus, the effect of pH on the degradation of composite aerogels was investigated in the pollution of PNP and TC, respectively. Figure 4c and d show the degradation performance of ZIF-67@CA on organic pollutants PNP and TC at the pH range of 4-9, respectively. It is obvious that pH conditions have no significant effect on the degradation of pollutants PNP and TC, indicating that ZIF-67@CA/PMS system have excellent pH resistance. Even in an

alkaline environment, the degradation process can be carried out stably with ZIF-67@CA/PMS system.

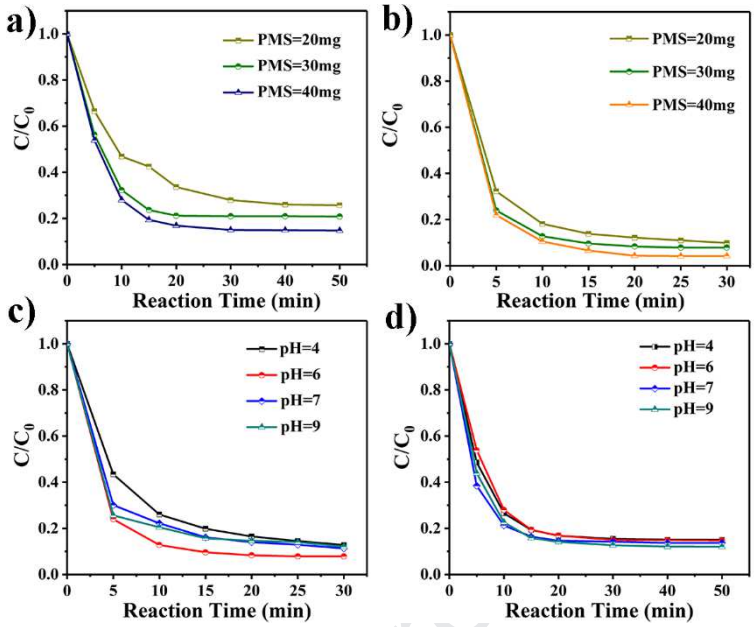

Figure 4. The degradation efficiency of ZIF-67@CA toward PNP (a) and TC (b) in the presence of different amounts of PMS. The degradation efficiency of ZIF-67@CA toward PNP (a) and TC (b) in different pH.

.2.4 Recyclability of ZIF-67@CA

As another critical parameter, the recyclability of ZIF-67@CA plays a crucial role of whether the ZIF-67@CA can work efficiently and reduce the cost in practical applications. Thus, the recyclability of ZIF-67@CA was investigated in PNP and TC as shown in Figure S3. The degradation performance of ZIF-67@CA remains at around 90% after 3 cycles without obvious decrease. Meanwhile, there is no significant change in the structure and morphology of the reusable ZIF-67@CA (Figure S4 and S5), demonstrating the superior stability and reusability of ZIF-67@CA. The excellent degradation performance, stable structures and environmental friendliness of ZIF-67@CA have realistic guiding significance for the development of pollution treatment.

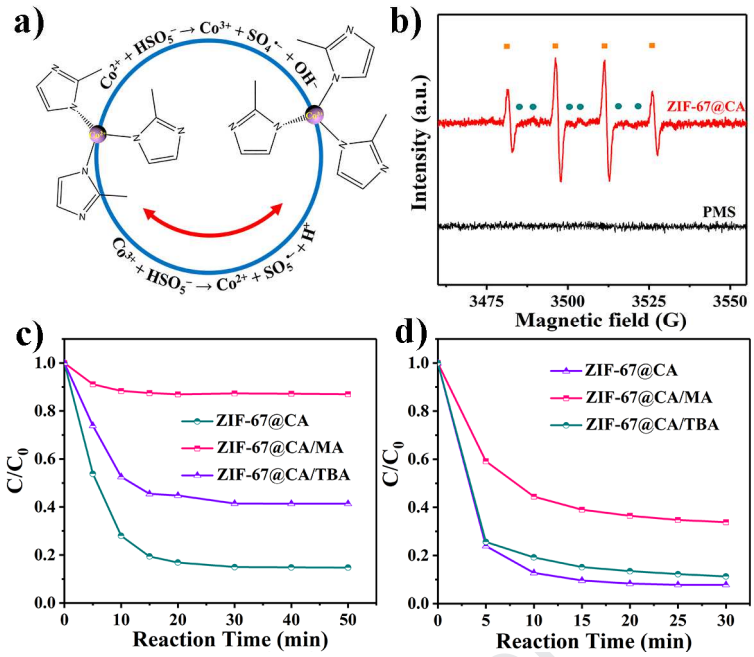

Figure 5. (a) Mechanism schematic of ZIF-67@CA/PMS system to generate free radicals. (b) EPR spectrum of ZIF-67@CA/PMS system for the removal of PNP. (c) and (d) Effect of capture agent on degradation of PNP and TC, respectively. (PNP solution = 20 mg L^{-1}; TC solution = 20 mg L^{-1}; PMS = 600 mg L^{-1}; ZIF-67@CA = 600 mg L^{-1}; TBA = 1 mL; MA = 1 mL; pH = 6; T = 25°C).

2.5 Degradation mechanism of ZIF-67@CA

In ZIF-67@CA/PMS system, the cobalt ions of ZIF-67 play a crucial role to active PMS. As shown in Figure 5a, the cobalt ions react with HSO_5^- to generate $SO_4^{\bullet-}$ and •OH through changing the state between Co^{2+} and Co^{3+} [18]. The $SO_4^{\bullet-}$ with strong oxidation potential effectively degrades PNP and TC into intermediates and further converts to non-toxic small molecules. Meanwhile, electron paramagnetic resonance (EPR) test demonstrate the generation of $SO_4^{\bullet-}$ and •OH in Figure 5b. A large number of free radicals were generated while adding ZIF67@CA/PMS to PNP solution, while there was no response in an environment with only PMS. Furthermore, two different free radicals were detected in the system: the peaks with an intensity ratio of 1:2:2:1 represent •OH (DMPO-•OH: $\alpha_H = \alpha_N$ = 14.9 G), and the peaks around the signals of •OH belonged to DMPO-$SO_4^{\bullet-}$ (α_N = 13.2G, α_H = 9.6G, α_H = 1.48G, α_N =

0.78G) suggesting the existence of $SO_4^{\bullet-}$ [19]. The result proved that $SO_4^{\bullet-}$ and •OH were the key for the degradation of organic pollutants. In addition, in order to distinguish the dominant role of specific radicals in the degradation of pollutants, tert-butanol (TBA) and methanol (MA) were used to capture •OH and $SO_4^{\bullet-}$ in both PNP and TC, respectively. As shown in Figure 5c, the contaminants were not substantially removed when MA was added, while the removal rate of the contaminants was greatly increased when TBA was added, suggesting that $SO_4^{\bullet-}$ played a major role and •OH was auxiliary in the degradation of PNP. Furthermore, when TBA was added in TC solution with PMS, ZIF-67@CA showed nearly no effect on the degradation of TC. On the contrary, the degradation performance was greatly affected when the MA was added (Figure 5d). The results may attribute to the complexity and stability of TC structure, compared with the weaker oxidizing •OH, the $SO_4^{\bullet-}$ showed a strong oxidizing ability to decompose TC, thereby achieving the degradation of TC.

3. Conclusion

In brief, we innovatively developed a simple doping method and successfully synthesized high MOFs loading hybrid aerogels. MOFs@CA provide external pores, controllable loading amount and superior recyclability. Furthermore, doping method largely increases the loading of hybrid aerogels (44.7 wt%) and efficiently improves the degradation ability of pollutants. The degradation rate of organic pollutants is up to 80% within 20 min in ZIF-67@CA/PMS system, and it can be widely used in various

pH range of pollutants. Thus, the low-cost and environmentally friendly production method may effectively expand its applications in a wider field in the future.

Supporting Information

The experimental details, SEM, BET, XRD and TGA of the samples.

Acknowledgments

This work was supported by the Zhejiang Provincial Natural Science Foundation of China (LY20E020001), National Natural Science Foundation of China (51672251). J.G. acknowledges the Fundamental Research Funds of Zhejiang Sci-Tech University (2019Q007).

Notes

The authors declare no competing financial interest.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: