

Contents lists available at ScienceDirect

Journal of Solid State Chemistry



journal homepage: www.elsevier.com/locate/jssc

Titanium metal-organic framework nanorods for highly sensitive nitroaromatic explosives detection and nanomolar sensing of Fe³⁺



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ARTICLE INFO

Keywords. Titanium Metal-organic framework Luminescent sensing Nitroaromatic explosives Metal ions sensing Fluorescent test paper

ABSTRACT

Fe³⁺ is the fourth most important transition metal ion in biological systems. Also, nitro-aromatics is a class of compounds which is highly explosive and toxic. Therefore, selective detection of Fe^{3+} and nitro-aromatics is of great significance for human health and environmental protection. In this work, we reported a rare example of Ti-MOF material (ZSTU-1) for highly sensitive and selective luminescent sensing of nitroaromatic explosives and nanomolar level of detection of Fe^{3+} . To the best of our konwledge, ZSTU-1 is the first report of Ti-MOFs for highly efficient sensing of nitroaromatic explosives, and realized excellent sensing properties for PA (2,4,6-trinitrophenol) in both liquid and vapor phase. In liquid, the detection limit for PA can reach 12.3 µM (2.8 ppm) and the Ksv is calculated to be 3.586×10^4 M⁻¹. The most important is that there have been very few MOF-based sensors reach the nanomolar level of detection Fe^{3+} with the detection limit calculated to be 63.8 nM (approximately 3.6 ppb) and the Ksv value of ZSTU-1 nanorod is $2.69 \times 10^6 \,\mathrm{M}^{-1}$. In addition, the detection of Fe³⁺ and nitroaromatic explosives was carried out in fluorescent test paper which could be used for rapid detection of these substances by naked eyes. These results demonstrate the advantages of titanium-based MOFs for the detection of Fe^{3+} and nitroaromatic explosives, and can contribute to develop a high performance and visible to the naked eyes fluorescent sensor for detection of specific substances that are vital in biological systems.

1. Introduction

Fe³⁺ is the fourth most important transition metal ion in biological systems, and it is also an indispensable metal ion in human life activities and environment [1]. For instance, Fe³⁺ plays an important role in transporting and exchanging oxygen in the blood [2]. The excess and deficiency of Fe³⁺ in the human body may cause series of diseases [3]. At the same time, Fe^{3+} is also a common pollutant in water. Excessive Fe^{3+} in drinking water may also lead to human health problems [4]. Also, nitro-aromatics is a class of compounds in which a hydrogen on the benzene ring is substituted with a nitro group, such as nitrobenzene (NB), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), p-nitrophenol (PNP), 2,4,6-trinitrophenol (PA), etc [5]. They are widely used in the explosives industry, the dye industry and the pharmaceutical industry [6], and are highly explosive and toxic [7]. Therefore, selective detection of Fe³⁺ and nitro-aromatics is of great significance for human health and environmental protection. However, conventional methods for detecting

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https://doi.org/10.1016/j.jssc.2019.07.053

Received 9 July 2019; Received in revised form 25 July 2019; Accepted 30 July 2019 Available online 30 July 2019 0022-4596/© 2019 Elsevier Inc. All rights reserved.

Fe³⁺ and nitro-aromatics include ion mobility spectrometry (IMS) [8], mass spectrometry (MS) [9], and plasma desorption mass spectrometry (PDMS) [10], etc. These detection methods have high accuracy and sensitivity, but they suffer from high cost and lack portability [11]. Therefore, it is crucial to develop a low-cost, high-efficiency, portability and fast-response fluorescence sensing method to detect Fe³⁺ and nitro-aromatics.

Metal-organic framework materials (MOFs) are highly crystalline organic-inorganic hybrid materials with 1D, 2D, or 3D structures formed by metal ions or metal clusters and organic ligands self-assembled by coordination bonds [12]. MOFs show great potential in many fields, such as hydrogen storage, gas adsorption and separation, drug delivery, catalytic reactions, medical imaging, sensors and other fields have important applications [13]. MOF are excellent materials for luminescent detection of metal ions and other organic small molecules pollutants based on several advantages [14]: (a) the highly conjugated linkers are usually adopted in MOF frameworks which provide good luminescent properties and attract conjugated analytes through π - π interaction; (b) the coordination interaction between organic ligands and metal ions could provide good rigidity of the ligands, hence enhance the MOFs' luminescent intensity; (c) the variety of the choice and the feasibility of the functionalization of the ligands makes the specific interactions between the MOFs and the goal analytes.

Among diverse MOFs, Ti(IV) and Zr(IV) based MOFs consititued by high valence metal ions and organic ligands provide strong metalcarboxylate bonds and rigid frameworks, and also demonstrated excellent photocatalytic properties [15]. Previously we have devoted great efforts to explore novel Ti(IV) based MOFs [16] and also develop highly efficient Fe³⁺ sensing based on Ti(IV) MOF nanosheets NTU-9 [2]. The NTU-9 nanosheets exhibited specific sensing of Fe³⁺ with the modest detection limit performance of $0.45 \,\mu$ M. Given the half-filled d orbits of the outer electronic structure of Fe³⁺ and the electron deficient properties of the nitro-aromatics molecules, we speculate that if we can incorporate a rich electron organic ligand with higher electron donating ability, it can lead to more efficient electron transfer between the Ti-MOF materials and the goal analytes, thus we should be able to target novel Ti(IV) based MOFs sensors with much higher sensitivity.

Triphenylamine and its derivatives are an important class of organic luminescent materials which generally have high hole and electron transport capabilities. They also show strong electron donating behavior due to the strong electron donating ability of the nitrogen atom in the center of the triphenylamine molecules. The larger groups around the nitrogen atom and the larger steric hindrance factors increase the stability of the triphenylamine [17]. Thus triphenylamine and its derivatives are widely used in organic solar cells and dye-sensitized solar cells [18]. Recently we have utilized triphenylamine molecules as organic ligands and synthesized a series of Ti-MOFs with 1D Ti-O rods structure which show excellent photocatalytic H₂ production performance [15b]. Herein, we report the rare example of Ti-MOF material, $Ti_6(\mu_3-O)_6(\mu_2-OH)_6(TCA)_2(H_2O)(DMF)_2$ (ZSTU-1, $H_3TCA = tri-carbox$ ylic acids 4,4',4"-nitrilotribenzoic acid) for highly sensitive and selective luminescent sensing of nitroaromatic explosives and nanomolar detection of Fe³⁺. To the best of our knowledge, there have been very few MOF-based sensors reach the nanomolar level of detection limit for Fe³⁺. and this is the first report of Ti-MOFs for highly efficient sensing of nitroaromatic explosives.

2. Experimental section

2.1. Materials and general methods

All the chemicals were commercially available and not otherwise processed and purified. Power X-ray diffraction patterns were recorded on a Bruker D8 Advanced diffractometer equipped with Cu K α radiation ($\lambda = 1.542$ Å) at a scan rate of 5°/min and a scan range of 3°–50°. The size and morphology of **ZSTU-1** nanorods were determined by transmission electron microscopy (TEM, JEM-2100) and field emission scanning electron microscopy (FE-SEM, Vltra55, Carl Zeiss). Fluorescence measurements were taken on a F-4600 fluorescence spectrometer. The PL lifetime was taken on Fluorolog HORIBA JOBIN YVON.

2.2. Synthesis

2.2.1. Synthesis of ZSTU-1 nanorod

According to the reference work [15b], **ZSTU-1** nanorods were synthesized by solvothermal method. H_3TCA (4,4',4"-tricarboxytriphenylamine) (1.7 g, 4.51 mmol), TPOT (isopropyl titanate) (1.55 mL, 5.2 mmol) were dissolved in absolute DMF 25 mL, and the mixture was taken to and sealed in 50 mL Teflon-lined autoclave, which was heated at 180 °C for 24 h. After cooled to room temperature, the mixture was washed by DMF and methanol several times. And then the yellow crystalline powder was obtained.

2.3. Metal ions sensing

The metal salts analytes for luminescent sensing experiments are LiNO₃, AgNO₃, KNO₃, Mg(NO₃)₂, Mn(NO₃)₂, Ni(NO₃)₂, Zn(NO₃)₂, Ca(NO₃)₂, Co(NO₃)₂, Cu(NO₃)₂, Cr(NO₃)₃, Fe(NO₃)₃.

Ultrasonic treatment of dried powder of **ZSTU-1** nanorods (10 mg) in 100 mL H₂O obtained an aqueous suspension of **ZSTU-1** nanorods. The PL spectrum was carried out by adding 50 μ L aqueous solutions of 10^{-4} M metal ions (Li⁺, Ag⁺, K⁺, Mg²⁺, Mn²⁺, Ni²⁺, Zn²⁺, Ca²⁺, Co²⁺, Cu²⁺, Cr³⁺, Fe³⁺) to 2 mL **ZSTU-1** nanorods aqueous solution.

2.4. Small molecule sensing

The small molecule analytes used for luminescent sensing experiments are H_2O , methanol, ethanol, acetone, aniline, methylbenzene, DMF, phenol, nitrobenzene, 2,4-DNT, 2,6-DNT, PNP, 1.22% PA.

The dried powder of **ZSTU-1** nanorods (10 mg) was sonicated in 100 mL of ethanol to obtain a suspension of **ZSTU-1** nanorods. The PL spectrum was carried out by adding 50 µL ethanol solution of 10^{-1} M small molecules (H₂O, MeOH, acetone, aniline, methylbenzene, DMF, phenol, NB, 2,4-DNT, 2,6-DNT, PNP, 1.22% PA, among them, the concentration of 1.22% PA was 5.32×10^{-2} M) to 2 mL **ZSTU-1** nanorods ethanol solution.

2.5. The nitro-aromatics vapor sensing

A 20 mL vial containing 1 ml of 1.22% PA solution was placed in a glass vial and allowed to stand at room temperature for several days to ensure equilibrium vapor pressure was reached. Approximately 2 mg of **ZSTU-1** nanorods powder was thinly coated to the glass slide, and then the slide was placed in a glass bottle and exposed to saturated steam at room temperature. The slides were removed from the bottles for a specific period of time and their solid state emission spectra were collected immediately.

2.6. The fluorescent photograph of test paper

The experimental filter paper was selected as the carrier of **ZSTU-1** nanorod. The procedure for preparing the fluorescence sensor was as follows: the experimental filter paper was cut into squares of $1.5 \times 1.5 \text{ cm}^2$ size, and completely immersed in a **ZSTU-1** nanorods ethanol solution (10 mg/20 mL) for several hours at room temperature, and dry at 60 °C. For the nitroaromatic explosives and Fe³⁺ dispersed in the aqueous sample, they were transferred by a pipette to test paper respectively.

3. Results and discussion

The Ti-MOF materials ZSTU-1 was prepared according to previously reported methods [16b]. Briefly, the ZSTU-1 material was obtained by the reaction of titanium isopropoxide [Ti(i-OPr)₄] with the ligand H₃TCA in DMF. As shown in Fig. 1, the diffraction peaks of the sample is consistent with the simulation mode, indicating the pure phase of the synthesized product. In the **ZSTU-1**, the Ti⁴⁺ is connected by hydrolysis oxygen atom to form the Ti₆O₆ cluster, then the Ti₆ clusers are connected by the ligand TCA to constitute a regular hexagon shape (as shown in Fig. 2a), forming a 2D layer structure. The 2D layer structure was further connected via hydrolysis μ_2 -OH to form a porous 3D MOF structure with infinite 1D SBU chains (Fig. 2b). It is worth noting that the 2D layers has a vertical c-axis orientation and the distance between the 2D layer is approximately 3.3877 Å. The transmission microscopy (TEM) and scanning electron microscopy (SEM) were performed to examined the morphology of the ZSTU-1. The measurements show that the sample exhibits nanorod morphology with the size of approximately 50 nm (Fig. 2c and d).

The above nanorod feature of ZSTU-1 encouraged us to examine its



Fig. 1. The experimental and simulated powder XRD patterns of **ZSTU-1** naorod and Powder X-ray patterns of **ZSTU-1** nanorod immersed in 10^{-3} M 2,4-DNT, 2,6-DNT, PNP,0.122%PA, 10^{-4} M Fe³⁺ and water.

potential application in luminescent sensing. The **ZSTU-1** nanorods dispersed in water and EtOH exhibit photoluminescence (PL) properties with fluorescence peaks at 464 nm and 461 nm (Fig. S1†), respectively, which is almost the same with the fluorescence peaks of the free ligand H₃TCA located at 460 nm (Fig. S2†). The PL properties of **ZSTU-1** nanorod could be attributed to the fluorescence of the coordinated ligand TCA in the framework. The uniform nanoscale particle size makes **ZSTU-1** nanorods material highly dispersive in water and ethanol, forming stable MOF suspensions; the high valence Ti(IV) and organic ligands provide strong metal-carboxylate bonds which lead to the water stability of this MOF. Moreover, **ZSTU-1** nanorods material also exhibits strong luminescence emission.

The above advantages of **ZSTU-1** nanorods material encouraged us to explore its potential ability as a sensor towards organic small molecules in ethanol solution. The addition of a small amount of organic small

molecules $(2.44 \times 10^{-3} \text{ mol/L}, \text{ the concentration of PA}$ is $1.30\times 10^{-3}\,\text{mol/L})$ has different effects on the luminescence intensity of the dispersed nanorods in ethanol (Fig. 3a). The analytes such as methanol, water, aniline, methylbenzene, N,N-dimethylformamide (DMF), acetone, phenol do not substantially affect the luminescence intensity of ZSTU-1 nanorods ethanol solution, while the nitro-aromatics molecules have a significant quenching effect on ZSTU-1 nanorods, indicating that ZSTU-1 nanorods material can be used to detect small amounts of nitroaromatics molecules. It is interesting that ZSTU-1 nanorods material show different quenching effects for different nitro-aromatics molecules. The quenching effect of nitrobenzene (NB), 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) on MOF solution is small, while the quenching effect of *p*-nitrophenol (PNP) and 2,4,6-trinitrophenol (PA) is significantly higher than the former three (Fig. S3[†]). The quenching effect of different nitro-aromatic molecules decreased in the order $PA > PNP > 2,4-DNT \approx 2,6-DNT > NB$. In particular, PA has the strongest quenching effect on MOF solution, when 238.3 ppm PA is added, the fluorescence intensity of **ZSTU-1** nanorods solution is almost completely quenched (Fig. 3b). Noticeably, the ZSTU-1 nanorods material displays a linear response with PA concentration in the low concentration range. The quenching efficiency of PA can be quantitatively explained by using the Stern-Volmer equation. The relationship between the $(I_0/I-1)$ and the concentration of PA was calculated using the Stern-Volmer equation $(I_0/$ I) = 1 + Ksv[M] and plotting the S–V plots, where I₀ and I are the fluorescence intensities of ZSTU-1 nanorods and ZSTU-1 nanorods with PA, [M] is the concentration of PA, and Ksv is the quenching coefficient. The estimated *Ksv* is 3.585×10^4 M⁻¹ (Fig. 3c). And the detection limit of PA is calculated to be 12.3 µM (2.81 ppm) by fluorescence titration (Fig. S4[†]). Such detection sensitivity is superior to some reported MOFs (Table S2). Furthermore, the study on the effect of mixed organic small molecules on the luminescence of ZSTU-1 nanorods was also carried out, it was found that the addition of nitro-aromatics to ZSTU-1 nanorods ethanol solution with other organic small molecules had almost no interference on the quenching efficiency of MOF (Fig. S6b[†]). The result showed that the ZSTU-1 nanorods material could detect nitro-aromatics efficiently in the presence of interfering organic small molecules.

In order to examine the potential of **ZSTU-1** nanorod material to be multiresponsive fluorescent sensor, the sensing performance of aqueous



Fig. 2. The structure of (a) along ab plane, (b) along ac plane, (c) The TEM image of ZSTU-1 nanorods, (d) The SEM image of ZSTU-1 nanorods. Color scheme of (a) and (b): carbon, black; nitrogen, blue; oxygen, red; metal (Ti), green. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 3. (a) Fluorescence intensity of 5×10^{-6} mol different organic small molecule (among them, the amount of PA was 2.66×10^{-6} mol) added to **ZSTU-1** nanorods ethanol solution at 460 nm emission; (b) the PL spectra of **ZSTU-1** nanorods with different amounts of PA; (c) SV curve of PA, inset: a photograph showing the original fluorescence (left) and the quenching fluorescence (right) upon addition of 50 µL of 0.122% PA (UV light, 365 nm); (d) Photograph of fluorescence response after 5 µL of 1.22% PA was added to paper sensor under 365 nm UV light.

solution of **ZSTU-1** nanorods material towards different metal ions was further explored. It is interesting that the addition of 50 µL of different metal ions with a concentration of 10^{-4} M (approximately equal to 2.5×10^{-6} mol/L, 0.14 ppm) has different effects on luminescence intensity of **ZSTU-1** nanorods material dispersed in water (Fig. 4a). Analytes such as Li⁺, Ag⁺, K⁺, Ni²⁺, Zn²⁺, Ca²⁺, Cu²⁺, Mg²⁺, Mn²⁺, Co²⁺, Cr³⁺ do not substantially affect the luminescence intensity, while Fe³⁺ has a significant quenching effect to the luminescence intensity of the dispersed **ZSTU-1** nanorods aqueous solution. It is worthy to note that the different queching effect allow **ZSTU-1** nanorods material to discern Fe³⁺

from Cu²⁺, which is highly challenging for molecular-based fluorescent sensor materials [19]. The fluorescence intensity of the dispersed **ZSTU-1** nanorods aqueous solution can be obviously quenched by adding only 0.03 ppm of Fe³⁺. The addition of about 0.08 ppm of Fe³⁺ can quench the fluorescence intensity to less than half of the original fluorescence intensity, and the addition of 0.27 ppm Fe³⁺ can completely quench the fluorescence of **ZSTU-1** nanorods aqueous solution (Fig. 4b). The quenching efficiency of Fe³⁺ ion can be quantitatively explained by using the Stern-Volmer equation. In the low concentration region, the *Ksv* plot for Fe³⁺ was linear in nature and *Ksv* value of the **ZSTU-1** nanorods



Fig. 4. (a) Fluorescence intensity of 5×10^{-9} mol different metal ions added to **ZSTU-1** nanorods aqueous solution at 460 nm emission; (b) **ZSTU-1** nanorod PL spectra with different amounts of Fe³⁺; (c) SV curve of Fe³⁺, inset: a photograph showing the original fluorescence (left) and the quenching fluorescence (right) upon addition of 50 µL of 10^{-4} M Fe³⁺ (UV light, 365 nm); (d) Photograph of fluorescence response after 5 µL of 10^{-4} M of Fe³⁺ was added to paper sensor under 365 nm UV light.

aqueous solution was found to be $2.69 \times 10^{6} \, M^{-1}$ (Fig. 4c). The detection limit of Fe³⁺ is calculated to be 63.8 nM (3.57×10^{-3} ppm, approximately 3.6 ppb) (Fig. S5†). This value is one of the highest among the reported MOF-based Fe³⁺ sensors (Table S1). Furthermore, the study on the effect of mixed metal ions on the luminescence of **ZSTU-1** nanorods was also carried out, it was found that the addition of Fe³⁺ to **ZSTU-1** nanorods aqueous solution with other metal ions had almost no interference on the quenching efficiency of MOF (Fig. S6a†). The result showed that the **ZSTU-1** nanorods material could detect Fe³⁺ efficiently in the presence of interfering ions.

The addition of Fe³⁺ and nitro-aromatics molecules lead to the quenching effect of the **ZSTU-1** nanorod material, while the fluorescence lifetime of **ZSTU-1** nanorods has almost no change (Fig. S8†,Tables S3 and S4), indicating that there is no coordination between the MOF and the analytes. PXRD and FT-IR were also carried out to investigate the structural change and interaction between the MOF and the analytes. The powder XRD patterns of **ZSTU-1** nanorods material immersed in the solution of different analytes was identical with that of the original one (Fig. 1), indicating that the structure of **ZSTU-1** nanorods material remained the same. Also the absorption peak remained the same for the FT-IR before and after immersed in the solution of different analytes, confirming that there was no coordination between the nitro-aromatics/ Fe³⁺ and the MOF (Fig. S9†).

Based on previous pioneering work on MOF-base sensing material for nitro-aromatics detection [5d,20], the quenching mechanism process mainly includes photoinduced electron transfer (PET) and fluorescence resonance energy transfer (FRET). Based on our measured absorption spectra and energy level conduction bands of the nitro-aromatics and ZSTU-1 nanorods, we speculate that the fluorescence quenching mechanism for nitro-aromatics is mainly a combination of PET and FRET. In the PET mechanism, the electrons on the ZSTU-1 nanorod material were excited under the excitation light, which was excited from the HOMO level to the LUMO level, then transferred to the LUMO level of the nitro-aromatics with the electron-deficient nitro group, and this process caused MOF fluorescence quenching [14e], as shown in Fig. S10⁺. Moreover, the emission spectrum of the ZSTU-1 nanorods material and the absorption spectrum of the nitro-aromatics and Fe³⁺ overlap effectively, indicating that the fluorescence resonance energy transfer process may also occur during the fluorescence quenching process [11,21]. It can be clearly seen from Fig. S11⁺ that the absorption spectrum of PA (compared with other nitro-aromatics) have a maximum overlap with the emission spectrum of ZSTU-1 nanorods material. This maximum spectral overlap may result in most efficient energy transfer between ZSTU-1 nanorods material and PA, resulting in highly efficient fluorescence quenching. For nitro-aromatics, the order of the overlapping parts of the spectrum is as follows: PA > PNP>2,4-DNT≈2,6-DNT, which agrees with the experimental different quenching efficiencies for different nitro-aromatics. Therefore, both electron transfer and energy transfer contribute to the efficient quenching of ZSTU-1 nanorod material by nitro-aromatics.

In addition, the UV–Vis absorption spectrum of different metal ions (Fig. S12†) showed that Fe^{3+} ions in aqueous solution exhibit much stronger UV–Vis adsorption ability in the 300–400 nm range. The competition of absorption of the light source energy is responsible for the luminescent quenching effect [22]. Also considering the half-filled 3d orbitals in Fe³⁺, the fluorescent queching upon Fe³⁺ may attributed to the electron transfer from **ZSTU-1** nanorods to Fe³⁺ [2].

It is worth noting that the **ZSTU-1** nanorods material is not only responsive to nitro-aromatics in the liquid phase, but also sensitive in the gas phase. As expected, a significant decrease in fluorescence intensity was observed within 30 min, and after 150 min, the intensity decreased by approximately 50% (Fig. S13†). The detecting gas phase of nitro-aromatics with solid powder provides us a highly sensitive and cost-effective approach to directly detect the vapor of nitro-aromatics.

Due to the good sensing effect of **ZSTU-1** nanorod on Fe^{3+} and nitroaromatics, the detection of Fe^{3+} and nitro-aromatics was carried out in fluorescent test paper. The fluorescent test paper of **ZSTU-1** nanorod emitted blue light under ultraviolet light (365 nm), when a spot of Fe³⁺ and PA solution was added to test paper respectively, a clear dark spot appeared immediately (Figs. 3d and 4d). These results demonstrate that the fluorescent test paper has a faster fluorescence response and is visible to the naked eye.

4. Conclusions

In this work, we have targeted a rare example of nanoscale luminescent titanium metal-organic framework **ZSTU-1** nanorods material with strong electron donating ability groups in the ligand for highly sensitive and selective sensing of Fe³⁺ and nitro-aromatics. The **ZSTU-1** nanorods material exhibits highly efficient sensing performance, realizing the nanomolar detection of Fe³⁺ with the detection limit of only 63.8 nM (approximately 3.6 ppb), which is one of the best value for MOF-based Fe³⁺ sensor materials. The **ZSTU-1** nanorods material also show sensitive sensing performance toward nitro-aromatics both in liquid and vapor phase, with the detection limit for PA of only 12.3 μ M (approximately 2.81 ppm). In addition, we prepared a simple fluorescent test paper for rapid and visual detection of Fe³⁺ and nitro-aromatics in the filed. This work may help to explore new Ti-MOF sensing materials for targeted applications in the environment and human health.

Notes

The authors declare no competing financial interest.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51602301) and Natural Science Foundation of Zhejiang Province (No. LY19E020007). J. G. acknowledges the financial support from the Fundamental Research Funds of Zhejiang Sci-Tech University (2019Q007).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://do i.org/10.1016/j.jssc.2019.07.053.

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