# **Green Chemistry**



View Article Online

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**Cite this:** *Green Chem.*, 2021, **23**, 1766

# Hybridization of MOFs and ionic POFs: a new strategy for the construction of bifunctional catalysts for CO<sub>2</sub> cycloaddition<sup>†</sup>

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A new strategy toward constructing a bifunctional catalyst for  $CO_2$  cycloaddition has been developed based on post-synthetic modification of CUS-based metal–organic frameworks (MOFs) with ionic porous organic frameworks (POFs) to form MOF@iPOF core–shell hybrid materials. Based on this strategy, two new MOF@iPOF core–shell hybrid materials,  $Cu_3(BTC)_2@iPOF-TB-Br^-$  and  $Cu_3(BTC)_2@iPOF-TM-Br^-$ , are synthesized for the first time by feasible encapsulation of a  $Cu_3(BTC)_2$  core within an ionic POF shell. Because of the synergetic role of dual functional sites including CUS as a Lewis acid in the MOFs and the Br<sup>-</sup> anion as the nucleophile in the ionic POFs,  $Cu_3(BTC)_2@iPOF-TB-Br^-$  and  $Cu_3(BTC)_2@iPOF-TM-Br^-$  demonstrate excellent catalytic performance for the CO<sub>2</sub> cycloaddition under co-catalyst free mild conditions (60 °C, 0.5 MPa CO<sub>2</sub>, 24 h). Moreover, these core–shell bifunctional catalysts can not only realize the synergy of two functional sites, but also maintain the porosity of hybrid materials for improving the mass transfer rate and catalytic efficiency.

Received 31st December 2020, Accepted 25th January 2021 DOI: 10.1039/d0gc04425c

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#### Introduction

With the large consumption of fossil energy, anthropogenic emission of CO<sub>2</sub> has been considered as the primary factor to cause global warming and subsequent climate change.1 In spite of its adverse environmental effects, CO<sub>2</sub> is indeed an abundant, renewable, inexpensive and nontoxic C1 resource, which can be converted into diverse value-added industrial products.<sup>2</sup> Therefore, compared with simple CO<sub>2</sub> capture and storage (CCS),<sup>3</sup> CO<sub>2</sub>-involved chemical synthesis has been considered with much more promise. In the context of CO<sub>2</sub> fixation, the cycloaddition of CO<sub>2</sub> and epoxide to synthesize cyclic carbonates is one of the most important and successful reactions, because of the efficient resource utilization and the diversity of products, which have wide applications in fine chemicals.<sup>4</sup> However, due to the inherent thermodynamic and kinetic stability of  $CO_2$ , it is challenging to activate  $CO_2$  and realize its transformation under mild conditions, especially at low temperatures and pressures. So far, various catalysts or catalytic systems have been explored for the CO2 cycloaddition reaction.<sup>5</sup> In general, homogeneous catalysts are widely used

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to produce cyclic carbonates in industry, such as metal halides, alkali metal salts, quaternary ammonium salt, metal-salen complexes and so on,<sup>6</sup> but they often suffer from harsh reaction conditions, complicated purification processes, and weak recyclability. Therefore, it is of significance to develop efficient, economical and recyclable heterogeneous catalysts for  $CO_2$  conversion under mild conditions.

Metal-organic frameworks (MOFs) with high surface areas, adjustable pore sizes and various functionalities have attracted tremendous attention.<sup>7</sup> As the capture of CO<sub>2</sub> has already been widely studied in MOFs,<sup>8</sup> it has recently been studied for their use as catalysts for the conversion of CO<sub>2</sub> into high-value chemicals.9 In recent years, many MOFs with coordinatively unsaturated metal sites (CUSs) as effective Lewis acid catalysts have been tested in the cycloaddition of CO<sub>2</sub> with epoxides some remarkable results have been achieved.<sup>10</sup> and Unfortunately, these single functional MOF catalysts usually require the addition of tetrabutylammonium bromide (TBAB) as a co-catalyst to obtain optimal efficiency. To overcome this disadvantage, ionic liquid (IL) functional groups have been incorporated into many CUS-based MOFs to accomplish the synergistic effect of the Lewis acid and nucleophilic halogen ions. Recently, several strategies have been developed for introducing multiple IL functional groups into MOFs, which include the following: (1) using ionic ligands to construct specific MOFs;<sup>11</sup> (2) post-synthetic modification (PSM) of special ligands of MOFs to graft IL functional groups;<sup>12</sup> and (3) in situ polymerization of ILs in the pores or cages of MOFs.<sup>13</sup> However, these strategies often suffer from some problems, such as requirement of complicated ionic ligand preparation

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<sup>†</sup>Electronic supplementary information (ESI) available: Additional figures. See DOI: 10.1039/d0gc04425c

processes, special active groups (*e.g.* –Br, –NH<sub>2</sub>, and imidazole) at the ligands for PSM, and extremely high chemical stability of MOFs. Besides, the appearance of IL functional groups in the pores of MOFs will result in a decrease in specific surface area and pore volume, which weakens the advantages of porous MOFs, such as the high adsorption capacity for  $CO_2$  and rapid diffusion of reactants or products. To maintain the porosity of functional MOF catalysts, the exploration of a new modification strategy is of great importance.

Recently, MOF-based core-shell hybrid materials have been prepared by encapsulating MOFs within porous organic frameworks (POFs), which are also a famous type of porous material and can exhibit outstanding properties.14 These reported MOF@POF core-shell hybrid materials could possess the structural traits and properties of their individual components; besides, the synergistic enhancement of performances is often achieved in these hybrid materials.<sup>15</sup> Herein, we put forward a strategy for constructing MOF@iPOF core-shell bifunctional catalysts by integration of CUS-based MOFs with ionic POFs, to form heterogeneous catalysts with extra high activity for CO<sub>2</sub> cycloaddition under co-catalyst free mild conditions (60 °C, 0.5 MPa CO<sub>2</sub>, 24 h). Moreover, these core-shell bifunctional catalysts can not only realize the synergy of two functional sites, but also solve the problem of pore blockage for current MOF heterogeneous catalysts, thus improving the mass transfer rate and catalytic efficiency. This project is of great significance for developing highly efficient CO<sub>2</sub> cycloaddition catalysts and provides a new perspective to develop MOF@iPOF core-shell hybrid materials for various applications.

#### **Results and discussion**

To establish a proof of principle for our core-shell PSM strategy, we synthesized two MOF@iPOF core-shell hybrid materials and examined their catalytic performance in the cycloaddition of CO<sub>2</sub>. A typical Lewis acid MOF, Cu<sub>3</sub>(BTC)<sub>2</sub>, was chosen in our experiment due to its simple synthetic method and excellent adsorption capacity for CO2.<sup>16</sup> Besides, the admissible stability of Cu<sub>3</sub>(BTC)<sub>2</sub> allowed us to employ a polymerization method to coat ionic POFs onto it. Two mainchain imidazolium-based ionic POFs were chosen as shells to construct the composite because of their IL functional sites and mild synthesis process. The synthetic route of MOF@iPOF core-shell hybrid materials is schematically illustrated in Scheme 1. Quaternization polymerization of tris(4-(1H-imidazol-1-yl)phenyl)amine (TIPA) and 1,3,5-tris(bromomethyl) benzene (TB) or 2,4,6-tris(bromomethyl)mesitylene (TM) in the presence of the as-prepared  $Cu_3(BTC)_2$  gave rise to Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TM-Br<sup>-</sup>. Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TB-Br<sup>-</sup> or Scanning electron microscopy (SEM) images reveal that the bare  $Cu_3(BTC)_2$  exhibits a smooth and clean surface with an octahedral shape (Fig. 1A and B). After hybridization, obtained Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TB-Br<sup>-</sup> the and Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TM-Br<sup>-</sup> inherit the octahedral profile from the Cu<sub>3</sub>(BTC)<sub>2</sub> cores and have relatively rough ionic POF shells (Fig. 1C-F). These results validate the successful synthesis of MOF@iPOF hybrid materials with a core-shell structure. Transmission electron microscopy (TEM) images further show that ionic POF shells can be distinguished by a lighter contrast than that of the inner Cu<sub>3</sub>(BTC)<sub>2</sub> cores, and the thickness of the shell is about 200 nm (Fig. S3<sup>†</sup>). The images of the corresponding elemental mapping show that Br and N are mainly located at the exterior shells, but Cu and O are densely distributed in the internal cores (Fig. S4<sup>†</sup>), which is consistent with the aforementioned morphology of Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TB-Br<sup>-</sup> and Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TM-Br<sup>-</sup>.

To investigate the crystallinity and structural features of  $Cu_3(BTC)_2$ @iPOF-TB-Br<sup>-</sup> and  $Cu_3(BTC)_2$ @iPOF-TM-Br<sup>-</sup> hybrid materials, comprehensive characterization was performed. As shown in Fig. 2A, powder X-ray diffraction (PXRD) patterns



Scheme 1 Synthetic routes of MOF@iPOF core-shell hybrid materials.



Fig. 1 The SEM images of  $Cu_3(BTC)_2$  (A and B),  $Cu_3(BTC)_2@iPOF-TB-Br^-$  (C and D), and  $Cu_3(BTC)_2@iPOF-TM-Br^-$  (E and F).



Fig. 2 (A) PXRD spectra of  $Cu_3(BTC)_2$  (a),  $Cu_3(BTC)_2@iPOF-TB-Br^-$  (b), and  $Cu_3(BTC)_2@iPOF-TM-Br^-$  (c); (B) FT-IR spectra of  $Cu_3(BTC)_2$  (a),  $Cu_3(BTC)_2@iPOF-TB-Br^-$  (b), and  $Cu_3(BTC)_2@iPOF-TM-Br^-$  (c).

show that the crystallinity of  $Cu_3(BTC)_2$  is well maintained in  $Cu_3(BTC)_2$ @iPOF-TB-Br<sup>-</sup> and  $Cu_3(BTC)_2$ @iPOF-TM-Br<sup>-</sup>, and no additional diffraction peaks from iPOF-TB-Br<sup>-</sup> or iPOF-TM-Br<sup>-</sup> are detected, revealing that ionic POFs are amorphous. Moreover, the Fourier-transform infrared (FT-IR) spectrum was used to characterize the composition of these MOF@iPOF core-shell hybrid materials (Fig. 2B). The peaks of  $Cu_3(BTC)_2$  are well maintained, and the new peaks at 1508 and 1070 cm<sup>-1</sup> are ascribed to the vibration of the imidazolium ring. The occurrence of the FT-IR adsorption band at 1272 cm<sup>-1</sup> for  $Cu_3(BTC)_2$ @iPOF-TB-Br<sup>-</sup> and  $Cu_3(BTC)_2$ @iPOF-TM-Br<sup>-</sup> corres-



Fig. 3 (A) Br 3d XPS spectra of TB (a) and  $Cu_3(BTC)_2@iPOF-TB-Br^-$  (b); (B) Br 3d XPS spectra of TM (a) and  $Cu_3(BTC)_2@iPOF-TM-Br^-$  (b); (C) N 1s XPS spectra of TIPA (a),  $Cu_3(BTC)_2@iPOF-TB-Br^-$  (b), and  $Cu_3(BTC)_2@iPOF-TM-Br^-$  (c).

ponds to the stretching vibration of C–N, further proving the successful combination of  $Cu_3(BTC)_2$  and ionic POFs.

To verify the existence of Br- anions and imidazolium species in the MOF@iPOF core-shell hybrid materials, X-ray photoelectron spectroscopy (XPS) was performed. As shown in Fig. 3A and B, the XPS analysis of organic monomers, TB and TM show the binding energy of Br 3d at 70.1 eV. Br 3d of Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TB-Br<sup>-</sup> and Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TM-Br<sup>-</sup> show the binding energy at 68.0 eV and 68.1 eV, with a significant downshift compared to the typical Br atom, indicating that the Br in these MOF@iPOF core-shell hybrid materials is negatively charged.<sup>13,17</sup> Furthermore, the N 1s test of TIPA presents two clear peaks at 398.5 and 400.6 eV (Fig. 3C), which are related to the two different nitrogen environments, that is the N atom in the triphenylamine and the N atom in the imidazole ring. In contrast, the N 1s binding energies of Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TB-Br<sup>-</sup> and Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TM-Br<sup>-</sup> show an obvious increase, indicating the positively charged N in the ionic POF shells.<sup>11a</sup>

The thermal stability of all samples and the content of ionic POF coating were assessed by thermogravimetric analysis (TGA) and elemental analysis (Fig. S5<sup>†</sup> and Table S1<sup>†</sup>). There are two rapid mass losses occurring at 320 °C and 350 °C, corresponding to the structural collapse of ionic POFs and Cu<sub>3</sub>(BTC)<sub>2</sub> respectively. Besides, according to the results of elemental analysis, the ionic POF shells content could be calculated roughly, which is about 24% of the total weight. To evaluate the pore character, the N2 sorption of all the samples is investigated at 77 K, and type I adsorption curves are observed (Fig. 4A). The Brunauer-Emmett-Teller (BET) surface areas decrease from 1454 m<sup>2</sup> g<sup>-1</sup> of bare  $Cu_3(BTC)_2$  to 974 and  $m^2$  $g^{-1}$ Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TB-Br<sup>-</sup> 927 of and Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TM-Br<sup>-</sup>, respectively. Nevertheless, the decrease in BET surface areas after ionic POF coating is reasonable, because the ionic POF shells account for about 24% of the total weight and do not have a large surface area as the  $Cu_3(BTC)_2$  structure. In addition, compared with the single



Fig. 4 (A) N<sub>2</sub> adsorption/desorption isotherms at 77 K; (B) CO<sub>2</sub> adsorption/desorption isotherms at 273 K; (C) CO<sub>2</sub> adsorption/desorption isotherms at 295 K. Cu<sub>3</sub>(BTC)<sub>2</sub> (black), Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TB-Br<sup>-</sup> (green), and Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TM-Br<sup>-</sup> (blue).

microporosity of bare Cu3(BTC)2, ionic POF shells contain a number of mesopores, which suggests that reactants or products can easily pass through the mesoporous ionic POF shells (Fig. S6<sup>†</sup>). The CO<sub>2</sub>-adsorption behaviors were also analysed for all the samples at 273 and 295 K (Fig. 4B and C). Compared to the CO<sub>2</sub> uptake of Cu<sub>3</sub>(BTC)<sub>2</sub> (261 cm<sup>3</sup> g<sup>-1</sup> at 273 K and 161 cm<sup>3</sup> g<sup>-1</sup> at 295 K),  $Cu_3(BTC)_2$  (iPOF-TB-Br)and Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TM-Br<sup>-</sup> exhibited a slightly lower CO<sub>2</sub> adsorption uptake of 231 cm<sup>3</sup> g<sup>-1</sup> and 220 cm<sup>3</sup> g<sup>-1</sup> at 273 K, 141  $\mbox{cm}^3\mbox{ g}^{-1}$  and 132  $\mbox{cm}^3\mbox{ g}^{-1}$  at 295 K. However, the  $CO_2$ adsorption value of Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TB-Br<sup>-</sup> and Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TM-Br<sup>-</sup> surpassed that of most reported bifunctional MOF catalysts, such as UiO-67-IL,<sup>11b</sup> MIL-IMAc-Br<sup>-,12c</sup> and polyILs@MIL-101,<sup>13</sup> which are also used for catalyzing the CO<sub>2</sub> cycloaddition reaction.

Considering the co-existence of Lewis acid active sites (CUSs) and nucleophile sites (Br<sup>-</sup> anions) in Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TB-Br<sup>-</sup> and Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TM-Br<sup>-</sup> core-shell hybrid materials, we examined their catalytic performance towards the cycloaddition reaction of CO<sub>2</sub> and propylene oxide (PO) under 60 °C, 0.5 MPa CO<sub>2</sub>, 24 h and co-catalyst free conditions (Fig. 5A). To our delight, Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TB-Br<sup>-</sup> and Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TM-Br<sup>-</sup> exhibit a highly efficient catalytic performance and achieve 82.7% and 96.5% yield with 0.5 MPa CO2 at 60 °C. Control experiments using pure Cu<sub>3</sub>(BTC)<sub>2</sub> or ionic POFs were also conducted under the same conditions. However, only a small amount of propylene carbonate (PC) was formed (yield < 10%, selectivity > 99%), which demonstrates that both Lewis acid sites from Cu<sub>3</sub>(BTC)<sub>2</sub> cores and nucleophile sites from ionic POF shells work synergistically to enhance the catalytic activity. Control experiments were also performed on a mixture of Cu<sub>3</sub>(BTC)<sub>2</sub> and ionic POFs, whose catalytic performance were also lower than that of MOF@iPOF core-shell bifunctional catalysts. These results further suggest that MOF@iPOF can more effectively catalyze the cycloaddition reaction of CO<sub>2</sub> compared



Fig. 5 (A) Catalytic conversion of CO<sub>2</sub> cycloaddition with PO over different catalysts. (B) Recycling performance of Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TB-Br<sup>-</sup> (green) and Cu<sub>3</sub>(BTC)<sub>2</sub>@iPOF-TM-Br<sup>-</sup> (blue) in three consecutive runs of CO<sub>2</sub> cycloaddition.

with the respective parent materials. In addition, we found that  $Cu_3(BTC)_2$ @iPOF-TB-Br<sup>-</sup> exhibited a slightly lower activity than  $Cu_3(BTC)_2$ @iPOF-TM-Br<sup>-</sup> under the same conditions. In response to this difference, we reason that the higher activity of  $Cu_3(BTC)_2$ @iPOF-TM-Br<sup>-</sup> should be attributed to the -CH<sub>3</sub> substituent in the skeleton, which acts as the electron-donating group and increases the electron density on the imidazolium moiety. Therefore, the ionic character of the catalytic system was increased, and the separation of Br<sup>-</sup> anions from positive frameworks became more viable, which is beneficial for the catalytic reaction.<sup>18</sup>

In order to confirm the heterogeneous nature of these MOF@iPOF core-shell bifunctional catalysts, their recyclability and reusability were investigated in the cycloaddition reaction of CO2 and PO. The PC yields showed no obvious decrease after three runs (Fig. 5B), and they could be separated from the reaction mixture by simple centrifugation or filtration. Compared with fresh MOF@iPOF core-shell bifunctional catalysts, no clear changes could be found in the PXRD, FT-IR, or XPS (Fig. S7-S12<sup>†</sup>), which indicates the excellent recyclability and stability of these MOF@iPOF core-shell bifunctional catalysts. In addition, to further verify the catalytic advantage of MOF@iPOF core-shell bifunctional catalysts, the catalytic performance of  $Cu_3(BTC)_2$  was further investigated in the presence of a co-catalyst TBAB. Although the mixture of catalysts exhibits high catalytic activity (96.8% yield), similar to these MOF@iPOF core-shell bifunctional catalysts, such mixed catalysts show a dramatic decrease in catalytic activity in the second cycle and only a small amount of PC was formed after three runs (yield < 10%). In order to explain this phenomenon, the <sup>1</sup>H NMR spectrum of the reaction product is investigated after the first catalytic cycle. As shown in Fig. S13,<sup>†</sup> along with the objective product, TBAB was also detected in the solution. This is because TBAB is a kind of soluble homogeneous catalyst, which can dissolve in PC. With the dissolution and decrease of TBAB, the recyclability of the mixture catalysts will get worse inevitably. Hence, compared with some MOF or POF

Table 1 Cycloaddition of CO2 with various epoxides over Cu3(BTC)2@iPOF-TM-Br^a  $\,$ 



<sup>*a*</sup> Reaction conditions: Epoxide (30 mmol),  $Cu_3(BTC)_2$ @iPOF-TM-Br<sup>-</sup> (0.27 mmol),  $CO_2$  pressure (0.5 MPa), 60 °C, 24 h. <sup>*b*</sup> The yields were determined by <sup>1</sup>H NMR. <sup>*c*</sup> 48 h.

heterogeneous catalysts with TBAB as the co-catalyst,<sup>19</sup> MOF@iPOF core–shell bifunctional catalysts are more environmentally and economically friendly, because of mild reaction conditions (60 °C, 0.5 MPa  $CO_2$ , 24 h) and no requirement of a co-catalyst.

Encouraged by the excellent catalytic performance of these MOF@iPOF core–shell bifunctional catalysts in the cycloaddition reaction of  $CO_2$  and PO, we further investigated the catalytic capacity of  $Cu_3(BTC)_2$ @iPOF-TM-Br<sup>-</sup> using various epoxides. As shown in Table 1, satisfactory catalytic activity was also achieved in almost all the reactions, including epichlorohydrin, 1,2-epoxybutane, epoxide allyl glycidyl ether and *n*-butyl glycidyl ether (Table 1, entries 1–4), indicating the great substrate tolerance of  $Cu_3(BTC)_2$ @iPOF-TM-Br<sup>-</sup> for this reaction. A longer reaction time is required for the epoxides containing phenyl groups to afford good yields (Table 1, entries 5 and 6) under the mild conditions (60 °C, 0.5 MPa  $CO_2$ ), either because of the larger steric hindrance of the substrates or because of a slower diffusion rate through the micropores of the  $Cu_3(BTC)_2$  core.

On the basis of some previous reports,<sup>20</sup> a tentative mechanism for catalyzing  $CO_2$  cycloaddition by the MOF@iPOF coreshell bifunctional catalysts can be proposed (Scheme S2†). First, the coordinatively unsaturated  $Cu(\pi)$  sites in the MOF core, as a Lewis acid, can bind the oxygen atom of epoxide by forming a Cu–O coordination bond and activate the epoxy ring. Simultaneously, the nucleophilic Br<sup>-</sup> anion of the ionic POF shell attacks the least sterically hindered carbon atom of the activated epoxide to promote the ring-opening step of the epoxide. Then,  $CO_2$  inserts into the intermediate to give an acyclic ester. Finally, the intramolecular cyclization results in the formation of the catalyst.

#### Conclusions

In summary, we proposed herein a new strategy to construct a bifunctional catalyst for  $CO_2$  cycloaddition through hybridization of CUS-based MOFs and ionic POFs. The core-shell  $Cu_3(BTC)_2$ @iPOF-TB-Br<sup>-</sup> and  $Cu_3(BTC)_2$ @iPOF-TM-Br<sup>-</sup> hybrid materials contain both CUS as a Lewis acid and the Br<sup>-</sup> anion as the nucleophile and hence exhibit extra high synergic catalytic activity for efficient  $CO_2$  cycloaddition under mild and cocatalyst free conditions (60 °C, 0.5 MPa  $CO_2$ , 24 h). Our results not only provide a new strategy for the development of novel bifunctional catalysts for  $CO_2$  conversion, but also highlight the advantage of MOF@POF core-shell hybrid materials as high performance heterogeneous catalysts.

#### **Experimental section**

Experimental details and characterization methods are described in the ESI.†

### Conflicts of interest

There are no conflicts to declare.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21601103 and 21701097) and the Natural Science Foundation of Shandong Province, China (No. ZR2020QB035).

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