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Sodium birnessite@graphene hierarchical structures for ultrafast sodium ion storage



Jianwei Ben^{a,b}, Yuping Jia^c, Tong Wu^c, Xinke Liu^{a,*}, Xiaohua Li^a

^a College of Materials Science and Engineering, College of Electronics and Information Engineering, Guangdong Research Center for Interfacial Engineering of Functional Materials, Shenzhen University – Hanshan Normal University Postdoctoral Workstation, Shenzhen University, 518060, China

^b College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China

^c State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888 Dong Nan Hu Road, Chang Chun 130033, China

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ABSTRACT

The sodium ion batteries have received great attention in recent years. However, the radius of sodium ion is larger than that of lithium ion, which results in the limited performance of sodium ion battery. In this work, to decrease the the diffusion time of sodium ions and improve the cyclic stability of sodium ion battery, the stack of manganese layered transition metal oxides and reduced graphene oxide (rGO) sheets has been fabricated as the cathode material. The layered MnO₂@rGO composites were synthesized via the flocculation of the delaminated MnO₂ nanosheets and rGO nanosheets with Na⁺ ions. By the synergistic effect of the two-dimensional MnO₂ nanosheets and rGO, the sodium ion diffusion distance was decreased efficiently and abundant active sites were provided. By adopting the MnO₂@rGO cathode, the sodium ion battery delivered specific capacity up to 167 mAh g⁻¹ at 0.5C, and exhibited excellent cycling stability (100 mAh g⁻¹after 200 cycles). This work provides an efficient way to improve performance of sodium ion batteries.

1. Introduction

The sodium ion batteries (SIBs) have attracted much attention in recent years because the sodium is abundant in nature and the energy density of SIB can be greater than 100 mAh g^{-1} , which makes the SIBs ideal for large-scale and low-cost electrical energy storage field. [1,2] However, the performance of the SIBs are still limited due to the reduced mass transport caused by the heaviness and large size of sodium ion.[3] As a result, to optimize the design of cathode is essential to increase the performance of the SIBs. In recent years, the layered manganese-based oxides have received extensive attention because of the low cost and high specific capacity, which are promising to fabricate the cathodes of SIBs.[4-7] However, the radius of sodium ion (1.02 Å) is 30% larger than that of lithium ion (0.76 Å), which will lead to the fact that the volume of electrode material will change violently during the process of charging and discharging and thus causing poor cyclic stability.[8,9] Therefore, to study the crystal structure stability in the process of charging and discharging is one of the research emphases in the field of SIBs.

Layered manganese oxide is important for electrochemical energy storage to fabricate electrodes, which can be used as the host for sodium ion intercalation/deintercalation. When the total mass of the electrode material remains unchanged, the thinner two-dimensional (2D) layered electrode material will decrease the diffusion distance of Na⁺, and the redox sites on the surface will be increased because of the higher specific surface area. The electrochemical performance of SIBs will be enhanced theoretically because the increased redox sites and the short ion diffusion time, which is proportional to the square of the diffusion length.[10] Based on the above mechanism, a series of 2D nanosheets have been synthesized and demonstrated to improve electrochemical properties of SIBs such as graphene,[11] hydroxide, [12] and transition metal carbides (Mxenes) [13]. However, the 2D nanosheets will be recombined when preparing the electrode materials, which will result in a large loss of active sites, slow diffusion kinetics and significant capacity attenuation. To ensure the active sites are enough after recombination, different kinds of nanosheets are composited by exfoliation and restack. For example, Tang et al.[14] have stacked two-dimensional manganese and cobalt nanosheets randomly by controlling the pH of the solvent, and the synergistic effect of the materials improved the electrochemical performance. The similar effect can be achieved by assembling the layered electrode materials and nanoparticles. Yang et al. [15] have greatly accelerated the diffu-

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^{*} Corresponding author. *E-mail address*: xkliu@szu.edu.cn (X. Liu).

sion of Na⁺/Li⁺ and improved the electrochemical properties of the electrode materials by assembling two-dimensional molybdenum disulfide nanosheets and stannous sulfide nanoparticles. Therefore, to restack the layered electrode materials with low-dimensional materials is one of the important means to construct stable crystal structure and good electrochemical performance.[16–20]

Although there have been some researches on the restack of layered electrode materilas and low-dimensional materials, the electrochemical performance should be further improved. To accelerate the transport of sodium ions and improve the stability of the sodium ion battery, the intercalated cathode material was designed by the restack of reduced graphene oxide (rGO) and 2D MnO₂ nanosheets in this work. Based on the preparation of tetramethylammonium ions (TMA⁺) intercalated Na_{0.55}Mn₂O₄·1.5H₂O (Bir-TMA), 18 tetrabutylammonium hydroxide solution is added to exfoliate Bir-TMA into 2D-MnO₂ nanosheets. By adding Na⁺, 2D-MnO₂ and 2D-GO with negative charge were randomly flocculated and restacked, and thermal reduction improved their electrical conductivity. The schematic is shown in Fig. 1. Both the rGO and the TMA⁺ work as the pillars to stabilize the volume expansion during charging and discharging, while suppressing the Jahn-Teller effect. Furthermore, the rGO can increase the power density of the material while improving the stability of the crystal structure of the material, providing electric double layers to accelerate the transmission of electrons and ions. This work provides a possible method to further improve the electrochemical performance and cycling stability of sodium ion battery.

2. Experimental methods

2.1. Material synthesis

Bir-TMA was prepared by inserting TMA⁺ into $Na_{0.55}Mn_2O_4$ ·1.5H₂-O and the detailed preparation process was the same as the preparation of Bir-TMA in reference [21]. The GO suspension was prepared by a modified Hummers way.[22,23]

Preparation of 2D-MnO₂: 0.5 g Bir-TMA was dispersed in 200 mL tetrabutylammonium hydroxide solution and the mixed solution was sonicated for 10 h and then stirred for 10 days. The tetrabutylammonium hydroxide conducts further ion exchange on the Bir-TMA, and exfoliates it into 2D-MnO₂. The resulted production was collected, washed and dried overnight at 60 °C. The product was marked as 2D-MnO₂.

Preparation of $MnO_2@rGO$: The mixed solutions of manganese oxide and graphene with mass ratios of 2:1, 1:1, and 1:2 were prepared and marked as solution A. 1 M sodium hydroxide solution were prepared and marked as solution B. Then B was added to A under rapidly stirring for 2 h, which was followed by hydrothermal reduction at $180^{\circ}C$ for 6 h. Finally, the resulted production was collected, washed and dried at 60 °C, and the final products were marked as 2:1 MnO_2/rGO , 1:1 MnO_2/rGO , 1:2 MnO_2/rGO , respectively.

2.2. Materials characterization and electrochemical measurements

Field emission scanning electron microscopy (FESEM, JEOL JSM-6700F) and X-ray diffraction spectroscopy (XRD, Rigaku D/max 2500 pc X-ray diffractometer) were used to characterize the morphology and structure of materials. Ultraviolet-visible spectroscopy (UV-vis, Cary 5000) and Raman (Renishaw, 514 nm excitation lines, 1000 spectrometer) were taken to characterize the composition of materials. The high-resolution TEM (HRTEM) was used to characterize the lattice structure of materials the and the X-ray photoelectron spectroscopy (XPS) was used to characterize the elemental composition and chemical states. CR2032 coin half-cells were used for electrochemical measurement. In order to synthesis the working electrode, the obtained cathode material together with carbon black, polyvinylidenefluoride (weight ratio 80:10:10) were mixed in 1-methl-2-pyrrolidinone (NMP) and coated on aluminum foil. Galvanostatic charge/ discharge (GCD), Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were tested on a CHI600E electrochemical workstation.

3. Results and discussion

Fig. 2(a) shows the XRD patterns of the the two-dimensional MnO_2 nanosheets (2D-MnO₂), the rGO and the 2:1, 1:1 and 1:2 MnO_2/rGO . The positions of the XRD peaks of the 2D-MnO₂ and rGO are compared with the Powder Diffraction File (PDF#42–1169) and the reference [24], respentively. It can be found that the layer spacing of 2D-MnO₂ does not increase significantly because the positions of the XRD peaks of the 2D-MnO₂ are basically consistent with the PDF, which is attributed to the re-aggregation of the wet nanosheets during the drying process.[25,26] Although the interaction between the material layers has been greatly reduced, they will still stack up mechanically. The XRD pattern of different ratios of rGO intercalated sodium



Fig. 1. Schematic of preparation of MnO2@rGO material.



Fig. 2. (a) XRD patterns of different ratios of MnO₂@rGO; (b) Raman of 1:1 MnO₂@rGO; (c) UV absorption spectra of 2D-MnO₂.

birnessite shows that the structure of sodium birnessite is not changed and the layered structure is maintained. However, as the proportion of rGO increases, the peak intensity of sodium birnessite will be weaken because the XRD peak of 2D-MnO₂ gradually turns to amorphization during the exfoliation process,[27] so there is almost no sodium birnessite peak when the proportion of rGO is too large. Moreover, according to the XRD peak of the as-prepared 1:1 MnO₂@rGO as shown in Fig. 2(a), the calulated interplanar spacing is about 1.1 nm, which is attributed to the second-order reflection of the superlattice-like structure, because the calulated interplanar spacing is approximately equal to half the sum of the thicknesses of the MnO₂ (0.8 nm) and rGO (1.5 nm) nanosheets. The peaks at ~ 37° and 65° are attributed to the in-plane M₁₀₀ and M₁₁₀ reflections of the monolayer MnO₂ nanosheets.[27]

The Raman spectra of rGO, 2D-MnO₂ and 1:1 MnO₂/rGO in Fig. 2 (b) all exhibit peaks around 560 cm^{-1} and 641 cm^{-1} , which reflects the in plane along the chemical bond stretching and out of plane stretching of Mn-O in the MnO₆ groups, respectively.[28] The D peak and G peak of the rGO around 1300 cm^{-1} and 1580 cm^{-1} are shown in the Raman spectra of rGO and 1:1 MnO2/rGO.[29] The D peak is attributed to the defects of the carbon atom lattice, and the G peak represents the in-plane stretching of the Sp² hybrid carbon atoms.[30] Therefore, it can be concluded that the 1:1 MnO₂/rGO electrode material retains the respective crystal structures of rGO and 2D-MnO₂, and no new compound is formed. Fig. 2(c) is the ultraviolet absorption spectrum of the colloidal suspension of MnO2 nanosheets exfoliated by tetrabutylammonium hydroxide. There is an absorption peak of Mn at 430 nm.[31,32] The clear Tyndall phenomenon can be observed in the illustration, which can indirectly prove that the Bir-TMA is peeled off into thin and uniform nanosheets.

The flocculation and recombination of 2D-rGO and 2D-MnO₂ nanosheets in different proportions have different morphologies, which are attributed to the different flocculation kinetics of the rGO and the MnO₂ nanosheets. Fig. 3(a) and (b) are the SEM images of the 2:1 MnO₂/rGO. It can be observed that the material is a stack of two-dimensional nanosheets and almost unchanged compared with the previous Bir-TMA surface morphology. Due to the low content of

rGO in this ratio, almost all rGO is restacked with 2D-MnO₂ via Na⁺, and there is no enough rGO to intercalate the 2D-MnO₂ layer. As a result, the 2D-MnO₂ nanosheets restack themselves and the surface morphology are no obvious changes, which causes inevitably losing of the active sites. In the SEM images of the 1:1 MnO2/rGO material as shown in Fig. 3(c) and 3(d), the lamellar structure of rGO can be observed. Combined with XRD analysis, it can be concluded that the rGO and the 2D-MnO2 are randomly restacked and combined on molecular scale to form a loose layered structure, which can provide more active sites. The Fig. 3(e) and 3(f) are the SEM images of the 1:2 MnO2/rGO material. It can be observed that the material is mainly composed of rGO, and the 2D-MnO₂ is completely covered by the rGO. From the SEM results, it can be concluded that the aggregation will occur when the proportion of rGO is small, which will lead to a large loss of active sites, slow diffusion kinetics and significant capacity attenuation.[33]

The HRTEM and the corresponding EDX has been taken to further confirm the lattice and the elemental distribution of the 1:1 MnO_2 @-rGO. From the TEM result as shown in Fig. 4(a), it can be observed that the 1:1 MnO_2/rGO exhibits layered structure. The HRTEM result (as shown in Fig. 4(b)) shows the parallel lattice fringes with two different spacings (about 0.8 nm and 1.4 nm), which may be attributable to the MnO_2 and rGO nanosheets, respectively. The repeating thickness is about 2.2 nm and the average spacing between the MnO_2 sheet and the adjacent graphene sheet is about 1.1 nm, which is consistent with the XRD result. The spacing is much larger than that of the bulk layered MnO_2 (about 0.7 nm).[31] The loose spacing makes it easier to create active sites, which can increase the power density and accelerate the transmission of electron and ion.[34] As shown in Fig. 4(c)-(f), the elements C, Mn, O, and Na were consistently dispersed, indicating that MnO_2 and rGO are uniformly mixed.

As shown in Fig. 5, the XPS measurement has been taken to characterize the elemental composition and chemical states (including Na, C, O, and Mn) of the MnO2/rGO materials. The C 1 s spectrum is exhibited in Fig. 5(a), there are three fitting peaks at 284.9 eV, 286.6 eV, and 288.8 eV, corresponding to C=C, C-O, and O-C=O. [35] The low C-O ratio implies that the successful fabrication of the



Fig. 3. SEM image: 2:1 MnO₂/rGO (a) low magnification and (b) high magnification; 1:1 MnO₂/rGO (c) low magnification and (d) high magnification; 1:2 MnO₂/rGO (e) low magnification and (f) high magnification.

reduced graphene oxide. As shown in Fig. 5(b), the peak of 1071.4 eV

is attributed to Na 1 s, which provides positive charge to promote the



Fig. 4. (a) The transmission electron microscope's bright field image of 1:1 MnO2@rGO. (b) High-magnification TEM image and the insets represent the IFFT. (c-f) The corresponding EDX elemental distribution in 1:1 MnO₂@rGO.



Fig. 5. XPS survey spectrum of 2:1 MnO2/rGO, 1:1 MnO2/rGO and 1:2 MnO2/rGO. HR XPS spectra (a) C 1 s, (b) Na 1 s, (e)Mn 2p and (f) O 1 s, respectively.

recombination of the negatively charged MnO₂ and RGO nanosheets. [36] The Mn 2p XPS peaks around 641.4 and 653.1 eV for the three samples could be confirmed in Fig. 5(c), corresponding to Mn^{4+} and Mn³⁺. The O-related XPS peaks are shown in Fig. 5(d), it can be found that there is a tiny average peak at 530.96 eV in the XPS spectrum of O1s. The OI peak (529.8 eV) is contributed by the lattice oxygen O^{2-} and the OII peak (530.96 eV) is contributed by the surface oxygen O^{2-} , O^{-} , OH groups and oxygen vacancies, while the OIII peak (532.3 eV) is contributed by the water molecules.[29] Combining Fig. 5(c) and 5(d), it can be found that the oxidation state of Mn is increased with the proportion of MnO2@rGO increases from 1:2 to 2:1, because the Mn 2p XPS peaks slightly shifts to high binding energy and the proportion of OI and O2 peak to the whole O1s increases. The oxidation of Mn is advantageous to decrease the amount of Mn³⁺, which is beneficial to decrease the deformation of the octahedron crystal structure with Mn³⁺ as the center that caused by the Jahn-Teller effect during the charge/discharge process.

The CV curves of the reconstructed birnessite-type sodium birnessite electrode material (Re Bir-Na, prepared by adding Na⁺ to the 2D nanosheets after the Bir-TMA peeling), 2:1 MnO₂/rGO, 1:1 MnO₂/rGO and 1:2 MnO₂/rGO cathodes are shown in Fig. 6. The CV curves of Re Bir-Na is shown in Fig. 6(a), which is indistinguishable from the original material Bir-Na, and both have a pair of obvious redox peaks around 2.3 V-2.5 V, which are typical Mn⁴⁺/Mn³⁺ redox.[37,38] Fig. 6(b) is the CV curves of 2:1MnO₂/rGO. Compared with the Fig. 6(a), it is obvious that there is almost no change in the redox peak, indicating that the graphene intercalated sodium birnessite structure only plays a structural support role, which will release the volume expansion during charge and discharge and won't provide capacity. The obvious widening of the CV is mainly caused by the electric double layer capacitance of rGO.[39,40] In the process of charging and discharging, the physical action of electrostatic adsorption is used to accelerate the transmission of sodium ions, which greatly improves the cycle stability of the electrode material. Therefore, the rGO could improve the electrochemical stability of the material. However, it can

also be observed in Fig. 6(c) and 6(d) that as the content of rGO increases, the peak intensity of Mn^{4+}/Mn^{3+} decreases. One of the reasons is that too much rGO induces electric double layer capacitance as the main contribution. The other reason is that the rGO will wrap the 2D-MnO₂, so that Na⁺ needs to overcome a stronger barrier for migration, inhibiting the redox reaction of the material itself, thereby reducing the electron transport capacity.

The galvanostatic discharging-charging curves of Re Bir-Na, 2:1 MnO₂/rGO, 1:1 MnO₂/rGO and 1:2 MnO₂/rGO cathodes are shown in Fig. 7 at a current rate of 1.0C, which are consistent with the CV curves. It can be found that the first-cycle discharge capacity of each material at 1C is 139 mAh g^{-1} , 122 mAh g^{-1} , 107 mAh g^{-1} and 121 mAh g^{-1} , respectively. After 200cycles of charging and discharging, the discharge capacity of each material is 42 mAh g^{-1} , 48 mAh g^{-1} , 81 mAh g^{-1} and 76 mAh g^{-1} , respectively. The conclusion obtained by analyzing the discharging-charging curves is similar to that obtained from the CV measurements, that the rGO acts as pillar between the main MnO2 octahedral layers to release the volume expansion of the material during charging and discharging. Furthermore, the large specific surface area provides more active sites, which can promote the intercalation/deintercalation of Na⁺. However, too much graphene will wrap the the main manganese material, and thus hinder the rapid transfer of charges, causing uneven phase transition and charge distribution, and even severe pulverization, decline in rate capability, and capacity decreasing gradually.

The 1:1 MnO₂/rGO was assembled into a half-cell and the charging and discharging curves at 1.5 ~ 4 V voltage under different current density have been characterized. The specific capacity of 1:1 MnO₂/ rGO electrode in the first cycle of charge and discharge at different rates is 202 mAh g⁻¹, 167 mAh g⁻¹, 107 mAh g⁻¹ and 99 mAh g⁻¹ as shown in Fig. 8(a). Fig. 8(b) exhibits the discharge rate capability of Re Bir-Na and 1:1 MnO₂/rGO at different current densities for 100 cycles. The rate capability gradually decreases with the increase of current density. After 100 cycles, the specific capacity of the 1:1 MnO₂/rGO composite cathode can be recovered to a great extent when



Fig. 6. CV profiles of the (a) Re Bir-Na; (b) 2:1 MnO₂/rGO; (c) 1:1 MnO₂/rGO; (d) 1:2 MnO₂/rGO at the first three cycles in a potential window from 1.5 to 4 V.



Fig. 7. Galvanostatic charge-discharge voltage profiles of 1C between 1.5 and 4.0 V: (a) Re Bir-Na; (b) 2:1 MnO₂/rGO; (c) 1:1 MnO₂/rGO; (d) 1:2 MnO₂/rGO.

the rate is restored to 0.1C, which indicates that the cathode is reversible during the charge and discharge process. The main reason is that the rGO intercalated sodium birnessite increases the specific surface area of the material and provides more active sites for Na⁺ intercalation/deintercalation, and the rGO can release the volume expansion during charging and discharging and improve the structural stability of the material. By increasing the layer spacing to shield the electrostatic interaction between the main layers, the Jahn-Teller deforma-

tion and dissolution of Mn^{3+} are suppressed. Furthermore, as shown in Fig. 8(c), the capacity retention of the 1:1 MnO_2/rGO composite cathode after 200 cycles was 100 mAh g⁻¹ at 0.5C, which indicates exceedingly stable cycling performance for the sodium-ions cells. The results proves that the stability of the material structure has been improved by inserting the rGO.

In order to further verify the internal mechanism of the modification of the sodium birnessite main electrode material by the rGO inter-



Fig. 8. (a) Galvanostatic charge–discharge profiles of various current densities from 0.1, 0.5, 1.0 and 2.0C at the first cycles of 1:1 MnO₂/rGO; (b) Rate capability of 1:1 MnO₂/rGO and Re Bir-Na at various current densities from 0.1, 0.5, 1.0, 2.0 to 0.1C; (c) Cycling performance of Re Bir-Na, 2:1 MnO₂/rGO, 1:1 MnO₂/rGO and 1:2 MnO₂/rGO cathodes for 200cycles at a current density of 0.5C.

calation, the impedance test was carried out to calculate the Na⁺ mobility and the EIS spectra were shown in Fig. 9. All the Nyquist plots are composed of the equivalent series resistance (R_s), the charge-transfer resistance (R_{ct}) in the high-frequency region and the Warburg process (Zw) in the low frequency region.[41] The Rs of Re Bir-Na, 2:1 MnO₂/rGO, 1:1 MnO₂/rGO and 1:2 MnO₂/rGO are 32.66 Ω, 12.64 Ω , 2.43 Ω and 1.71 Ω , respectively. The results indicating that the introduction of rGO reduces the impedance of the electrode material to form the SEI film, and it can be considered that the rGO will alleviate the irreversible phase change when the SEI film is formed. The diffusion coefficients (D) of Na⁺ for the four samples can be calculated from the EIS spectra based on the equation $D_{Na^+}=\frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2}.$ [42,43] In which the R is the gas constant, the T presents the absolute temperature and the A stands for the surface area of the electrode (1 cm² in this work). The n and the F present the number of electrons per reaction species and Faraday constant, respectively. The C is the concentration of Na⁺ and the σ is Warburg factor, which can be obtained by the linear fitting of the inclined lines at low frequency. The calculated D_{Na^+} of the 1:1 MnO_2/rGO electrode material is 5.38 \times $10^{-12}~cm^2~s^{-1}$, which is much higher than that of the Re BirNa (1.08 \times 10⁻¹² cm² s⁻¹), the 2:1 MnO₂/rGO (2.41 \times 10⁻¹² cm² s⁻¹) and the 1:2 MnO₂/rGO (2.2 \times 10⁻¹² cm² s⁻¹). Although the content of rGO in 1:2 MnO₂/rGO electrode material is relatively high, the mobility of sodium ions is reduced. It is because that the excesive rGO will induce agglomeration and the sodium birnessite material will also agglomerate. This hinders the rapid transfer of charges and causes uneven phase transitions and charge distribution. Furthermore, the electric double layer introduced by rGO regenerates electrostatic interactions between the main layers of sodium birnessite to a certain extent, so that the Na⁺ is embedded, and it is necessary to overcome the high migration barrier when de-embedding, thus slowing down the transmission of Na⁺.

4. Conclusion

In summary, the rGO intercalated sodium birnessite composite material was successfully prepared by exfoliation and restacking, which was used as the cathode of sodium ion battery. At a rate of 0.5C, the discharge specific capacity of 1:1 MnO_2/rGO is 167 mAh g⁻¹ in the first cycle, and the capacity remains at 100 mAh g⁻¹ after



Fig. 9. (a) Nyquist plots of Re Bir-Na, 2:1 MnO₂/rGO, 1:1 MnO₂/rGO and 1:2 MnO₂/rGO cathodes, (b) Z' versus $\omega^{-1/2}$ scheme.

200 cycles. The Na⁺ mobility is analyzed by impedance, and sodium ions can be quickly inserted/deintercalated between the layers of the material with the mobility of 5.38×10^{-12} cm² s⁻¹. The insertion of rGO can alleviate the volume expansion during charging and discharging, and provide electric double layer to accelerate sodium ion transmission. This work provides a possible method to prepare high-performance electrode materials for the sodium ion battery in the future.

CRediT authorship contribution statement

Jianwei Ben: Investigation, Methodology, Data curation, Writing – original draft, Writing – review & editing. Yuping Jia: Resources, Project administration. Tong Wu: Formal analysis. Xinke Liu: Conceptualization, Funding acquisition. Xiaohua Li: Resources.

Declaration of Competing Interest

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.

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