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Nitrogen-doped mesoporous carbon/poly-o-phenylenediamine composites for high-performance hybrid supercapacitor electrodes

Hao Xu, Xiang-Hui Yan, Ziwei Meng, Tong Xue, Dong Li, Guoli Fang and Hongfang Shen
School of Materials Science and Engineering, North Minzu University, Yinchuan 750021, People’s Republic of China
E-mail: yanxianghui@tsinghua.org.cn

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Abstract
Nitrogen-doped mesoporous carbon/poly-o-phenylenediamine composites (denoted as N-MC/PoPD) were successfully synthesized by sacrificial hard template method followed by in situ oxidation polymerization initiated by FeCl₃. It is revealed that the resultant N-MC/PoPD composites still remained original graphitization structure and narrow pore size distributions (centered at ~3.8 nm) but suffered visibly monotonical decrease in specific surface area after oPD was increasingly polymerized onto N-MC with an increase of the mass ratio of PoPD to N-MC from 1:1 to 5:1. As supercapacitor electrode measured by galvanostatic charge-discharge in 6 mol L⁻¹ KOH, a volcano curve was found when plotting specific capacitance of the N-MC/PoPD versus the mass ratio of N-MC to oPD; the N-MC/PoPD(2:1) with moderate surface area and the highest electrochemical conductivity delivered the highest specific capacitance of 229 F g⁻¹ at a current density of 1 A g⁻¹, which is twice of that obtained on the single N-MC with the maximum surface area. The remarkable enhancement in specific capacitance could be ascribed to the synergistic effect between two components of N-MC and PoPD.

1. Introduction

Driven by the increasing demand for clean and sustainable energy, supercapacitors or electrochemical capacitors, which offer higher specific energy, long cycling life than conventional capacitors, have been developed as one of the most promising energy storage devices [1–6]. According to charge storage mechanism, supercapacitors are divided into two major categories [2, 7], including electrochemical double-layer capacitors (EDLCs) and electrochemical pseudo-capacitors (EPCs). EDLCs using carbon-based materials such as activated carbon [8], carbon nanotubes [9], graphene [10, 11] and mesoporous carbon [2] as electrode materials are featured with excellent electrical conductivity, high power capabilities but low specific capacitance and energy density due to their capacitance deriving from separation of charges at electrode/electrolyte interface. EPCs using redox-active materials such as transition metal oxides [12, 13] or conductive polymers (CPs) [14, 15] as electrode materials are characterized by high energy density but unsatisfactory power density and cycling stability because of their capacitance arising from reversible redox reactions with slow diffusion of ions [16]. In view of these trade-offs, recent researchers are keen on developing hybrid supercapacitors with electric double-layer capacitance and pseudo-capacitance performance by coupling redox-active materials to carbon-based materials.

Recently, nitrogen-doped mesoporous carbon materials (NMCMs) have attracted intense attention as electrode of supercapacitors because doped N functional groups can significantly enhance the interface wettability, electrical conductivity, and electron–donor affinity of carbon frameworks and have no effect on initial advantages of the mesoporous carbon materials such as their tunable pore size, high surface area, fast mass transfer, and excellent durability [17–19]. However, there is a limited room for improvement in specific capacitance and energy density only by N-doping. The CPs having faradaic-type charge transfer such as polyaniline (PANI) and polypyrrole have been widely explored to combine with the carbon-based materials [20–23]. Shi et al [20] synthesized polypyrrole (PPy)-bonded plasma activated carbon nanotube composites (P-
CNT-PPy) via in situ chemical oxidative polymerization. The P-CNT-PPy as supercapacitor electrode delivered greater specific capacitance (264 F g\(^{-1}\)) than pure PPy (185 F g\(^{-1}\)) in a 1 M H\(_2\)SO\(_4\) aqueous solution. It is believed that the synergistic effect between the components are responsible for the dramatic enhancements in their electrochemical properties. Zhang et al.\(^{21}\) prepared yeast-derived N-doped hollow carbon microsphere/polyaniline (YC/PANI) composites by an in situ polymerization method. As a supercapacitor electrode, the YC/PANI composite exhibited good rate capability and a high specific capacitance (500 F g\(^{-1}\) at a current density of 1 A g\(^{-1}\)), which are higher than those of single YC (234.5 F g\(^{-1}\)) and PANI (257 F g\(^{-1}\)).

The o-phenylenediamine (oPD), a typical member of the aromatic diamine family, is closely related to the aniline (ANI) monomer of PANI in structure but has higher N content and water solubility than ANI. To the best of our knowledge, research works has seldom focused on combining the carbon-based materials with polyo-phenylenediamine (PoPD) as hybrid supercapacitor electrode. Here, we reported inorganic-organic composites (denoted as N-MC/PoPD) consisting of nitrogen-doped mesoporous carbon (N-MC) and poly-o-phenylenediamine (PoPD), which were prepared by sacrificial hard template method followed by noncovalent mixing/adsorption of oPD monomer on the host N-MC, in situ oxidation initiated by FeCl\(_3\) and then self-assembly. The obtained N-MC/PoPD composites were subsequently assessed as hybrid supercapacitor electrodes in aqueous 6 M KOH electrolyte and exhibited specific capacitance as high as 229 F g\(^{-1}\) at a current density of 1 A g\(^{-1}\), which is twice of that attained on the single N-MC.

2. Experimental

2.1. Materials and chemicals

Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (EO\(_{20}\)PO\(_{70}\)EO\(_{20}\), MW = 5800; P123) were purchased from Sigma Aldrich. Ethyl orthosilicate (TEOS), ammonium persulfate ((NH\(_4\))\(_2\)S\(_2\)O\(_8\)), aniline (C\(_6\)H\(_4\)N), sodium hydroxide (NaOH), ethanol (C\(_2\)H\(_5\)OH), hydrochloric acid (HCl) (37%) and ferric chloride (FeCl\(_3\)) were procured from China Sinopharm Group Co. o-phenylenediamine (PoPD) was obtained from Shanghai Aladdin Biochemical Technology co. Poly tetra fluoro ethylene (PTFE) and carbon black were bought from Shen Zhen Kejing Star technology Co. All the chemicals were of analytical grade and used as received without further purification.

2.2. Synthesis of N-MC

The nitrogen-doped mesoporous carbon (N-MC) was prepared according to the procedure reported in our previous work.\(^{24}\) Briefly, 0.4 g self-made SBA-15 was impregnated in 45 ml of 0.5 M HCl solution containing 2.0 ml of aniline. The suspension was stirred for 2 h below 10 °C followed by addition of 1 M ammonium peroxysulfate (APS). After continuous stirring for 24 h, the mixture was dried at 100 °C for overnight. The resultant solid composite was ground into a fine powder and carbonized in dynamic nitrogen atmosphere (20 ml min\(^{-1}\)) with a heating rate of 5.0 °C min\(^{-1}\) from ambient temperature to 900 °C and then kept for one hour and finally cooled to ambient temperature. The carbonized sample was further etched in 2 M NaOH at 60 °C for 24 h to remove the silica template SBA-15, rinsed with de-ionized water and ethanol, and then dried at 100 °C for overnight. The obtained sample was designated as N-MC.

2.3. Preparation of N-MC/PoPD

The N-MC/PoPD composites were prepared by a modified method reported in literature.\(^{25}\) 0.1 g of N-MC as host was dispersed in 0.02 M o-phenylenediamine (oPD) solution and then 0.08 M FeCl\(_3\) solution was added by dropwise. After stirring for 5 h at ambient temperature, the suspension was filtered, washed and dried. To keep other conditions unchanged, the amount of o-phenylenediamine was also investigated for screening inorganic-organic composite with high electrochemical performance. The as-prepared sample was denoted as N-MC/PoPD(x:y), where x:y is the mass ratio of N-MC to PoPD.

2.4. Characterization

Scanning electron microscopy (SEM) images for morphology were recorded on a Zeiss G300 microscope at 30 kV. The x-ray powder diffraction patterns for crystal structure were taken using a D-Max-2200PC X-ray powder diffractometer with Cu K\(_\alpha\) radiation (\(\lambda = 1.5418\) Å) at 40 kV and 30 mA at a scan rate of 0.5° min\(^{-1}\) and 5° min\(^{-1}\) for small angle and wide angle, respectively. The N\(_2\) adsorption-desorption analyses for porous structure were determined at 77 K using a 3H-2000PS2 physisorption apparatus. Prior to the measurement, all the materials were outgassed at 473 K under vacuum for 2 h. BET and BJH analyses were utilized to calculate the surface area, pore size distribution and pore volume. The FT-IR spectra for functional groups were measured by a WQF-520A FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) for surface elementary composition was performed on ESCALAB220-IXL. Thermogravimetric-differential scanning calorimetry (TG-DSC) analysis
for thermal stability were implemented on the NETZSCH STA449F3 thermal analyzer from room temperature to 800 °C in air.

2.5. Electrochemical measurements
The cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), electrochemical impedance spectroscopy (EIS) and cycling stability measurements were performed at room temperature in a three-electrode cell using an electrochemical workstation (CHI630). Pt wire and Hg/HgO electrode were used as the counter and reference electrodes, respectively. A foam nickel (1 cm²) with loading was adopted as working electrode, which was prepared by mixing 80 wt% N-MC/PoPD (x:y), 10 wt% carbon black and 10 wt% polytetrafluoroethylene (PTFE), dispersing them in ethyl alcohol and then pressing the slurry onto the foam nickel at 10 MPa in order to ensure a good electrical contact. After drying in vacuum oven at 80 °C for 12 h, the working electrode with active material loading of ~5 mg could be assessed in 6 M KOH. CV experiments were carried out by scanning the potential in the range of −1 to 0 V with different sweep rates. GCD measurements were implemented at different current densities within a potential range of −1 to 0 V. The specific capacitance (C) was calculated according to the following equation [26].

\[ C = \frac{I \Delta t}{m \Delta V} \]

where C is the specific capacitance, I the charge/discharge currents, \( \Delta t \) the time of discharge, \( \Delta V \) the voltage difference between the upper and lower potential limits, and m the mass of active materials (N-MC/PoPD).

3. Results and discussion

From the small angle XRD diffraction patterns (figure 1(a)), in spite of absence of the secondary (110) and (200) diffractions for an ordered 2D hexagonal mesostructure, one broad peak assignable to the characteristic (100) diffraction at 2θ = 0.81° is observed for the N-MC, suggesting that ordered mesoporosity of the N-MC could be inversely replicated from the hard template SBA-15 to some extent [24, 27]. The (100) diffraction has not disappeared until the mass ratio of N-MC to oPD reaches to 2:1, demonstrating that the regular mesoporous structure has be sheltered or broken by the polymerization of excess oPD in the pores and on the surface of the N-MC. The two broad peaks centered at 2θ = 24.7° and 43.3°, attributing to the (002) and (101) diffractions of graphitic carbon [28], respectively, are found in the patterns for all the samples (figure 1(b)) and their full width at half maximum of (002) diffraction is almost identical, suggesting that the host N-MC prepared by hard template possess graphitic structure, which is not affected by \textit{in situ} polymerization of oPD. It is noting that there is no visible diffraction corresponding to PoPD on these patterns. In the previous report [25], it has been verified that the oPD was first oxidized into individual 2,3-diaminophenazine molecules by rapidly pouring FeCl₃ aqueous solution at room temperature and then self-assembled into nanobelts or bunchy aggregates of one-dimensional structures (refer to as PoPD). Thus, it could be explained by that formed PoPD through self-assembly of the 2,3-diaminophenazine is amorphous.
To further study porosity of all the samples, the nitrogen adsorption–desorption analysis was implemented to determine pore structure and BET surface area. From figure 2(a), the isotherm of the N-MC exhibits type II with H3 hysteresis loop at the intermediate-high relative pressure, which indicates that the porous structure of the N-MC lacks long-range order and is composed of some inhomogeneous pores and slit pores from stack of aggregated particles [29]. In contrast, the isotherms for all composite N-MC/PoPD show type III and H3 hysteresis loop gradually disappears, as are indicative of weak interaction between the surface of these composites and N2 molecules. It is rational to infer that internal and external surfaces of the N-MC have been largely covered by one-dimensional self-assemble structure of the 2,3-diaminophenazine.

From the PSD curves (figure 2(b)), the pore sizes fall in a narrow range of 3.0–4.5 nm. Table 1 lists a clear comparison of the textural data for all the samples. As can be seen, once the oPD is introduced to N-MC, the as-prepared composite N-MC/PoPD (5:1) is subjected to a noticeable decrease in surface area, which accounts for blockage to the pores of the host N-MC to a great extent owing to the oxidation of oPD followed by self-assembly [30]. To further increase the mass ratio of N-MC to oPD, the pore size still remains nearly unchanged while the pore volume and surface area have a gradual decline, which is attributed to that an increasing number of pores is blocked by the PoPD.

Figure 3 shows the SEM images of (a) single N-MC and (b)–(e) composite N-MC/PoPD. The host N-MC appears to be lump aggregates composed of irregular particles. When the loading of oPD is the lowest, the obtained composite N-MC/PoPD(5:1) exhibits the similar morphology to the host N-MC, in retrospect of the dramatic decrease in specific surface area from the single N-MC to the composite N-MC/PoPD(5:1), implying that the oPD is supposed to be filled or polymerized preferentially in some inner mesopores rather than on the outer surface of the N-MC [30]. With the increase of mass ratio (c and d), it is obviously observed that the surface of the composite N-MC/PoPD(3:1 and 2:1) has been entirely covered by untight PoPD agglomerates, indicating that the polymerization of excess monomer dominates on the outer surface of the N-MC or separately occurs in solution. Aside from partial coverage of PoPD on the surface of the N-MC, some separate nanobelts are clearly visible near to aggregates of the N-MC as further increasing the mass ratio (e).

Some featured absorption peaks at 748, 833, 1149, 1240, 1369, 1523, 1628, 3196 and 3313 cm⁻¹ on the spectrum of self-made PoPD (figure 4(a)) disclose the formation of the 2,3-diaminophenazine, which is in accordance with the previous report [25, 31]. As for the host N-MC, presence of the band at 1628 cm⁻¹ due to C=N bonds reveals that nitrogen-doped mesoporous carbon could be obtained by using aniline and SBA-15 as.

Table 1. Textural properties of the N-MC and N-MC/PoPD composites.

| Sample                  | Pore diameter (nm) | Pore volume (cm³ g⁻¹) | S_{BET} (m² g⁻¹) |
|-------------------------|--------------------|-----------------------|-----------------|
| N-MC                    | 3.5                | 0.44                  | 224.5           |
| N-MC/PoPD(5:1)          | 3.5                | 0.25                  | 97.2            |
| N-MC/PoPD(3:1)          | 3.5                | 0.25                  | 81.1            |
| N-MC/PoPD(2:1)          | 3.8                | 0.23                  | 49.8            |
| N-MC/PoPD(1:1)          | 3.8                | 0.16                  | 28.1            |
precursor and hard template, respectively. Unexpectedly, these featured peaks for the 2,3-diaminophenazine are not observed on the spectra of these composite N-MC/PoPD and only weak peaks at 3200 cm\(^{-1}\) corresponding to stretching vibrations of N–H bonds in amino groups are found when the ratio of the N-MC to oPD reaches to 2:1, which is possibly attributed to low content of the 2,3-diaminophenazine and transmittance on the black composite powder. The XPS spectra of the composite N-MC/PoPD (figure 4(b)) show the presence of C1s, N1s and O1s signals and reveal a general trend of gradual increase in N content (from 10.7 to 18.2 at%) with the increase in the ratio of PoPD to N-MC, indicating that PoPD had been coated on the host N-MC. TG-DSC analyses were performed up to 900 °C to provide information on the thermal stability of the prepared N-MC/PoPD composites (figure 5). The obvious weight losses associated with the endothermic and exothermic peaks begin to occur at ~332 and 570 °C on the DSC curves, respectively, which should be attributed to oxidative decomposition of PoPD and combustion of carbon structure in air, indicating good thermal stability of these N-MC/PoPD composites.
CV measurements were conducted to evaluate the electrochemical performance of the N-MC and N-MC/PoPD composites using a three-electrode system in 6 M KOH. It is generally regarded that the quasi-rectangle shape-like CV profile reflects good electrical double layer capacitance (EDLC) of the electrode material [32]. As shown in figure 6(a), the CV curve of the N-MC is a relatively irregular rectangle, suggesting that it has not good EDLC feature, which should be ascribed to its not obvious porous structure. Furthermore, a couple of obvious hump peaks at lower potential indicate that besides EDLC, the pseudo-capacitance due to the nitrogen-doping effect also contributes to the capacitive performance of the N-MC electrode [4, 33]. In contrast, the CV curves of the N-MC/PoPD composites present deteriorated deviation from the rectangle shape due to more noteworthy oxidation peaks appearing in the range of −1.0 to −0.6 V, which is perhaps related to the oxidation of the 2,3-diaminophenazine coated on the N-MC [34–36]; however, the integral areas of the N-MC/PoPD composites are notably superior to the host N-MC, especially the N-MC/PoPD(2:1) has the highest CV area. Therefore, it can be preliminarily judged that the N-MC/PoPD(2:1) electrode exhibits the highest electrochemical capacitance which is mainly from the pseudo-capacitance behavior in all of the composites and a volcano curve is obtained correlating specific capacitance of the N-MC/PoPD composites with the mass ratio of N-MC to oPD. Figure 6(b) shows the CV curves of N-C/PoPD(2:1) electrode at different scanning rates (10 mV s⁻¹ to 200 mV s⁻¹). It can be clearly seen that the CV curve still maintains its original shape even with an increase of the scanning rate to as high as 100 mV s⁻¹, which signifies that the N-C/PoPD(2:1) electrode is qualified for good electrochemical performance.

Figure 5. TG-DSC curves (b) of the N-MC and N-MC/PoPD composites.

Figure 6. CV curves of (a) the N-MC and N-MC/PoPD composites electrodes at a scanning rate of 20 mV s⁻¹ and (b) the N-MC/PoPD(2:1) electrode at various scanning rates in 6 M KOH solution.
The supercapacitor performance of the N-MC and N-MC/PoPD composites electrodes was further investigated by the galvanostatic charge/discharge (GCD) test. As a representative illustrated in figure 7(a), it can be clearly observed that the charge/discharge curves of the N-C/PoPD(2:1) at different current densities (1 A g$^{-1}$, 7–10 A g$^{-1}$) are divided into two parts [37], namely −1.0 V−0.6 V based on fast Faradaic reaction associated with the surface of PoPD, and −0.6 V−0 V which is provided by EDLC. The specific capacitance from the GCD was calculated according to the formula described in section 2.5. Figure 6(b) plots specific capacitance versus the current densities for various electrodes. Although the specific surface area (224.5 m$^2$ g$^{-1}$) of the host N-MC is much less than that of activated carbon materials [8, 38], its specific capacitance still reached as high as 110 F g$^{-1}$, which could be ascribed to the pseudo-capacitance effect provided by the doped pyridinic and pyrrolic N, and enhanced surface wettability [4, 33, 39]. Obviously observed from the inset in figure 7(b), there is volcano curve showing the specific capacitance as a function of the mass ratio of N-MC to opd at the current density of 1 A g$^{-1}$ as a representative and the specific capacitance reaches the maximum value of 229 F g$^{-1}$ when the ratio is 2:1, which is in good agreement with the results from CV tests. The maximum value is twice as high as that obtained on the host N-MC electrode.

The aforementioned characterizations reveal that the pore size and graphitization degree remain nearly unchanged while the surface area suffers a dramatic decrease once introducing opd and then constantly reduces with further increasing the mass ratio of opd to N-MC, especially the N-C/PoPD(2:1) has a low surface area of 49.8 m$^2$ g$^{-1}$, which is only a quarter smaller than that of the host N-MC. Even when the ratio is 1:1, the composite N-C/PoPD(1:1) possesses the lowest surface area (28.1 m$^2$ g$^{-1}$) but still has advantages over the host N-MC in electrochemical behavior. As a result, it is plausible to conclude that the pseudo-capacitance plays dominant role in the total capacitance. As previously reported [40, 41], the bare conducting polymers displayed a very low specific capacitance due to poor electrical conductivity and weak flexibility. Therefore, the synergistic effect between the two components (N-MC and PoPD) could be responsible for the obvious improvement in specific capacitance of the composite N-C/PoPD(2:1). Moreover, the specific capacitance of the N-C/PoPD (2:1) still achieves 147 F g$^{-1}$ at the current density of up to 10 A g$^{-1}$ (figure 7(b)), indicating a good rate capability (64.2% of retention).

To make comparison, the specific capacitance data are also summarized in table 2 for some similar composite electrode materials reported in other research work [20–22, 40, 42, 43]. It can be observed that the HPNC-3 prepared by carbonization and sequential chemical activation of CuPcTs assembled PPy delivered the highest electrochemical performance, which is attributed to better pore connectivity, more efficient electron transfer and higher surface area together with increased non-graphitic N content rendered by hierarchically porous interconnected nanofiber architecture [22]. The specific capacitance obtained on the N-MC/PoPD composites in this work is at the moderate level among the reported data; however, it is predicted that there is still a flexible room for boosting their electrochemical performance because their hierarchically porous structure could be further tailored by controlling structural properties of the host N-MC.

The resistance between electrode and electrolyte, and the internal resistance of electrode can be characterized via EIS. The Nyquist plots of impedance for the composite N-MC/PoPD are presented in figure 8(a). All the Nyquist plots exhibit a small quasi-semicolonircle in the high-frequency region, indicating a low...
charge-transfer resistance. Furthermore, the values of equivalent series resistance (ESR) are 2.92, 1.93, 0.87, 0.86 and 0.74 Ω for N-MC, N-MC/PoPD (1:1), N-MC/PoPD (5:1), N-MC/PoPD (3:1) and N-MC/PoPD (2:1), respectively, according to the real axis intercept. As reported \[2, 4, 23\], the smaller the ESR value, the higher the electrochemical conductivity, as basically reflects the order of specific capacitances for the N-MC and N-MC/PoPD composites. This implies that an appropriate N content, namely the ratio of N-MC to PoPD, can result in a low charge-transfer resistance and high electrochemical conductivity, and thus improving the specific capacitance of the composite materials. Lastly, a cycling stability test of 1000 cycles at 2 A g\(^{-1}\) shows ∼9% of drop for both the composite N-C/PoPD, which indicates that they have good cycling stability (figure 8(b)).

### Table 2. Specific capacitance of the N-MC/PoPD composites in 6 M KOH and comparison with that of various composite electrode materials reported in literature.

| Electrode materials | Specific capacitance \((\text{F g}^{-1})\) | References | Electrode materials | Specific capacitance \((\text{F g}^{-1})\) | References |
|---------------------|-----------------------------------------|------------|---------------------|-----------------------------------------|------------|
| P-CNT-PPy           | 188, 148                                | [20]       | GN-PPy              | 165, —                                | [42]       |
| YC/PANI             | 100, 75.6                               | [21]       | PANI/CMK-3          | 191, —                                | [43]       |
| HPNC-3              | 420\(^a\), 344                          | [22]       | N-MC/PoPD(3:1)      | 180, 109                              | This work |
| PG12                | 248\(^b\), 200                          | [40]       | N-MC/PoPD(2:1)      | 229, 147                              |            |

\(^a\) Estimated according the GCD curve described in literature [22] and corresponding equation;  
\(^b\) Specific capacitance at 2 A g\(^{-1}\);  
\(^c\) Not given in literature [42, 43] and also not estimated.

### 4. Conclusions

A sacrificial hard template method together with \textit{in situ} oxidation polymerization of o-phenylenediamine (oPD) was employed to successfully prepare nitrogen-doped mesoporous carbon/poly-o-phenylenediamine composites (designated as N-MC/PoPD). The specific surface area suffered a remarkable decline while the mesopore size and graphitization degree were nearly not influenced by introduction of the oPD and kept on decreasing with further increasing the ratio of oPD to N-MC. However, a volcano curve was observed when plotting the specific capacitance as a function of the mass ratio of N-MC to oPD; the maximum specific capacitance (229 F g\(^{-1}\) at the current density of 1 A g\(^{-1}\)) was obtained for the composite N-MC/PoPD(2:1) with a low surface area of 49.8 m\(^2\) g\(^{-1}\) and the highest electrochemical conductivity. It is maybe reasonable that a combination of nitrogen-doping, surface wettability, mesoporous structure and connectivity or interaction between N-MC and PoPD contribute to the conspicuous enhancement in specific capacitance and a good rate capability of the composite N-MC/PoPD(2:1).
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ORCID iDs
Xiang-Hui Yan  https://orcid.org/0000-0002-6390-3181
Tong Xue  https://orcid.org/0000-0002-9742-4656

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