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# Hollow and microporous triphenylamine networks post-modified with TCNE for enhanced organocathode performance

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Hollow microporous triphenylamine networks (H-MTPN) were post-modified with tetracyanoethylene (TCNE) to generate tetracyanobutadiene moieties in H-MTPN-TCNE. The H-MTPN-TCNE showed the improved electrochemical performance of cathode materials for lithium ion batteries, compared to the original H-MTPN.

As energy storage becomes an important issue, extensive studies are underway on new energy storage materials.<sup>1</sup> Among various electrode materials for lithium ion batteries, organic cathode materials have attracted significant attention of scientists due to their sustainability, environmentally benign nature, and promising capacities.<sup>2</sup> In this regard, various organic redox molecules have been applied as cathode materials.<sup>3</sup> However, the molecules can be leached into electrolyte solution during charge/discharge processes, resulting in the decrease of capacities. Thus, the efficient fixation of organic redox molecules is important to overcome the leaching problems.<sup>4</sup> In addition, further exploration is required for the enhancement of storage capacities.

Recently, microporous organic networks (MONs) have been prepared by coupling of various organic building blocks.<sup>5</sup> Conventional MONs are insoluble in solvents and highly porous in nature. The redox active moieties can be incorporated into MON materials through a predesigned building block approach.<sup>6</sup> Moreover, due to the existence of micropores, the redox active moieties in inner MON can be utilized in electrochemical events. Thus, MON materials are promising for the engineering of organic electrode materials for lithium ion batteries. Recently, organic cathode materials based on MON chemistry have been reported,<sup>7</sup> in which most studies used powdery materials with irregular morphologies.

Our research group has reported the shape engineering methods of MON materials.<sup>8</sup> Especially, hollow MON materials have been prepared by template methods.<sup>8</sup> The hollow MON materials with thin shells have an advantage in facile post-modification.<sup>10</sup> Moreover, hollow MON materials provide the short diffusion pathways of guests including electrolytes in the utilization of inner functional species.<sup>11</sup> Thus,

the redox active MONs with hollow structures can be promising as electrode materials.

Triphenylamines showing a reversible one-electron redox reaction<sup>7,12</sup> and tetracyanoalkenes<sup>13</sup> showing a reversible twoelectron redox reaction have been used as redox active moieties in organic cathode materials. (Fig. 1a) In this work, we report the synthesis of hollow MON materials containing triphenylamine moieties (H-MTPN), the post-modification of H-MTPN with tetracyanoethylene (TCNE) to form H-MTPN-TCNE, and the enhanced electrochemical performance of H-MTPN-TCNE as cathode materials in lithium ion batteries.

Fig. 1b shows a synthetic scheme for H-MTPN-TCNE.



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For the preparation of H-MTPN, Zn-based zeolitic imidazolate framework (ZIF-8)<sup>14</sup> was used as a template. Using tri(4-ethynylphenyl)amine and tri(4-iodophenyl)amine as building blocks, microporous organic networks bearing triphenylamines were formed on the surface of ZIF-8 particles by the Sonogashira coupling to form ZIF-8@MTPN. The ZIF-8 in ZIF-8@MTPN was easily removed by the treatment with acetic acid to form orange colored H-MTPN.<sup>13</sup> The heating of H-MTPN with TCNE resulted in H-MTPN-TCNE materials. The materials were investigated by scanning (SEM) and transmission electron microscopy (TEM). (Figs. 2a-e and S1 in the ESI)



Fig. 2 SEM and TEM images of (a) ZIF-8 nanoparticles, (b) ZIF-8@MTPN, (c) H-MTPN, and (d-e) H-MTPN-TCNE. (f) PXRD patterns of ZIF-8, ZIF-8@MTPN, H-MTPN, and H-MTPN-TCNE. (g)  $N_2$  sorption isotherm curves at 77K and pore size distribution diagrams (based on the DFT method) of H-MTPN and H-MTPN-TCNE.

As shown in Figs 2a-b, the ZIF-8 nanoparticles with average size of 128  $\pm$  13 nm were coated homogeneously with MTPN (15  $\pm$  1 nm thickness) through the Sonogashira coupling of building blocks. The hollow structure of H-MTPN was confirmed through the TEM analysis. (Fig. 2c) The hollow morphology was retained after the post-modification of H-MTPN with TCNE. The average size and shell thickness of H-MTPN-TCNE were measured as 157  $\pm$  14 nm and 16  $\pm$  1 nm, respectively. (Figs. 2d-e and S1 in the ESI)

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As shown in Fig. 2f, the structure of ZIF-8 was retained after the coating of ZIF-8 with MTPN. H-MTPN-14Ad/GCMTPNE TCNE showed amorphous characteristics, matching well with the property of MONs in the literature.<sup>15</sup> The analysis of N<sub>2</sub> adsorption-desorption isotherm curves of H-MTPN showed the surface area of 767 m<sup>2</sup>/g and microporosity (V<sub>mic</sub>: 0.18 cm<sup>3</sup>/g). (Fig. 2g) The post-modification of H-MTPN with TCNE resulted in the decrease of the surface area and micropore volume to 589 m<sup>2</sup>/g and 0.13 cm<sup>3</sup>/g, matching well with the common observations in the post-modified MON materials.<sup>16</sup>

One of the interesting observations in the post-modification of H-MTPN with TCNE was a vivid color change from orange ( $\lambda_{abs}\!\!:$  391 nm) to very dark (The  $\lambda_{abs}$  of 500 and 391 nm corresponds to post-modified and intact materials, respectively). (Fig. 3b) To confirm the post-modification, we conducted model studies. As shown in Fig. 3a, first model compound (4,4'-(ethyne-1,2-diyl)bis(*N*,*N*-diphenylaniline), TP) was prepared by the Sonogashira coupling of 4-ethynylphenyl-N,Ndiphenylamine with 4-iodophenyl-N,N-diphenylamine. The treatment of TP with TCNE resulted in second model compound (TP-TCNE) with the vivid color change from yellow ( $\lambda_{abs}$ : 374 nm) to very dark ( $\lambda_{abs}$ : 489 nm). (Fig. 3a) The color change by reaction with TCNE originates from a photo-induced intramolecular charge transfer between electron rich triphenylamine to electron deficient cyano groups, supporting the reaction of an internal alkyne with TCNE. The chemical structures of model compounds were fully characterized. (Fig. S2 and the ESI) The reactions of internal alkynes with TCNE and their color changes have been reported in the literature.<sup>17</sup>



**Fig. 3** (a) Model reaction of H-MTPN with TCNE to form H-MTPN-TCNE: The reaction of TP with TCNE to form TP-TCNE. (b) UV-vis absorption spectra and photographs of TP (pale yellow), TP-TCNE (dark), H-MTPN (orange), and H-MTPN-TCNE (dark). (c) IR spectra of TP, TP-TCNE, H-MTPN, and H-MTPN-TCNE.

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Infrared (IR) absorption spectroscopy of H-MTPN-TCNE showed the appearance of a new peak at 2221 cm<sup>-1</sup>, which is assigned to CN stretching<sup>18</sup> and matches with the trend in the IR spectrum of TP-TCNE. (Fig. 3c) The chemical structures of H-MTPN and H-MTPN-TCNE were further investigated by solid phase <sup>13</sup>C nuclear magnetic resonance spectroscopy (NMR). (Fig. 4) The <sup>13</sup>C peaks of internal alkyne and aromatic carbons adjacent to the nitrogen of H-MTPN were observed at 89 and 146 ppm, respectively, matching with those at 89 and 147 ppm of the model compound, TP. After post-modification, the <sup>13</sup>C NMR of H-MTPN-TCNE changed significantly with a new peak at 165 ppm, resulting from the chemical reaction of internal alkynes with TCNE.<sup>19</sup> The trend of <sup>13</sup>C NMR of H-MTPN-TCNE matched with those of TP-TCNE. The elemental analysis showed the increase of N contents from 4.3 (3.1 mmol N/g) to 10.9w% (7.8 mmol N/g) through the post-modification of H-MTPN with TCNE, indicating that the ~34% of internal alkynes were modified with TCNE (1.3 mmol TCNE/g).<sup>20</sup>



**Fig. 4** Solid and liquid phase <sup>13</sup>C NMR spectra of TP, TP-TCNE, H-MTPN, and H-MTPN-TCNE.

Next, we studied the electrochemical performance of H-MTPN and H-MTPN-TCNE for lithium ion batteries. Fig. 5 summarizes the results. Coin cells were fabricated<sup>21</sup> using H-MTPN and H-MTPN-TCNE as cathode materials and lithium metal as anode materials. The charge-discharge processes were cycled in a range of  $1.5 \sim 4.2$  V (vs Li/Li<sup>+</sup>). As shown in Fig. 5a, the discharge capacities of H-MTPN-TCNE (current density: 50 mA/g) decreased gradually from 159 mAh/g to 133 mAh/g during the first 20 cycles. The discharge capacities maintained 123 mAh/g (92% of that of 20 cycle) after 100 cycles. The extended cycle tests (current density: 100 mA/g) showed that the H-MTPN-TCNE maintained 91% (106 mAh/g) of the discharge capacity (117 mAh/g) of the first cycle after 500 cycles. (Fig. S3 in the ESI) In the case of H-MTPN, discharge capacities decreased from 103 mAh/g to 80 mAh/g during the first 20 cycles and were maintained at 72 mAh/g (90% of that of 20 cycle) after 100 cycles. The enhanced storage capacity of H-MTPN-TCNE, compared to that of H-MTPN, resulted from

the additional tetracyanobutadiene moieties. Considering the amount of triphenylamine (3.1 and 2.6 minil/goffer H-WFPPN and H-MTPN-TCNE, respectively) and tetracyanobutadiene (1.3 mmol/g for H-MTPN-TCNE) based on elemental analysis, theoretical capacities were calculated as 82 mAh/g and 139 mAh/g for H-MTPN and H-MTPN-TCNE.<sup>22</sup> The observed discharge capacities of H-MTPN (72 mAh/g after 100 cycles) and H-MTPN-TCNE (123 mAh/g after 100 cycles) matched well with the expected values. It is noteworthy that cathode MONs containing triphenylamines have shown the discharge capacities in a range of 50 $\sim$  100 mAh/g in the literature.<sup>7</sup> At the current densities of 0.1, 0.2, 0.5, 1, and 2 A/g, H-MTPN-TCNE showed the discharge capacities of 120, 107, 92, 80, and 72 mAh/g, respectively. (Fig. 5b) The coulombic efficiency of H-MTPN increased from 76 to 97 % during the first 5 cycles and maintained values above 97% in next cycles. In the case of H-MTPN, coulombic efficiency increased from 74 to 94 during the first 70 cycles and maintained values above 97%. (Fig. 5c)

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**Fig. 5** (a) Cycle tests with a 50 mA/g current density and a 0.22  $mg/cm^2$  loading<sup>21</sup>, (b) rate performance, (c) coulombic efficiency, (d) charge-discharge profiles, and (e) impedance of H-MTPN and H-MTPN-TCNE.

Compared to those of H-MTPN, the charge-discharge profiles of H-MTPN-TCNE showed additional redox activities in a range of  $1.5 \sim 3.5$  V (vs Li/Li<sup>+</sup>), which is attributable to the redox reaction of tetracyanobutadiene moieties.<sup>13</sup> (Figs. 5d and S4-7 in the ESI) The Nyquist plots through impedance measurement of H-MTPN-TCNE and H-MTPN showed the

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charge transfer resistances of 93 and 165  $\Omega$ , respectively. (Fig. 5e) The enhanced charge transfer ability of H-MTPN-TCNE, compared with H-MTPN can be attributed to the incorporation of additional redox active moieties to H-MTPN. The microscopic analysis on the H-MTPN-TCNE recovered after cycles showed the complete maintenance of original hollow morphologies, indicating the robustness of MON materials. (Refer to SEM and TEM images in Figs. S8-9 in the ESI)

In conclusion, this work shows that the hollow and redox active MON materials can be applied as electrode materials for lithium ion batteries. Moreover, the post-modification of MONs with redox active species can further enhance the electrochemical performance. The post-synthetic strategy in this work can be applied to various MON materials<sup>15</sup> which have been prepared by the Sonogashira coupling. Thus, we believe that electrochemical performance can be further improved through the screening of building blocks.

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## Notes and references

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<sup>+</sup> Electronic Supplementary Information (ESI) available: Synthetic procedure, characterization of new compounds, cyclovoltammograms, and SEM images of H-MTPN-TCNE recovered after cycles. See DOI: 10.1039/x0xx00000x

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