Supporting information

"Wiring" redox-active Polyoxometalates to Carbon Nanotubes using a

Sonication-driven Periodic Functionalization Strategy

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Figure S1. TEM images of different cation-containing PMo₁₁V salts combination of CNTs: a) TBA-PMo₁₁V/CNTs; b) TOA-PMo₁₁V/CNTs; c) DDA- PMo₁₁V/CNTs; d) STA-PMo₁₁V/CNTs.

Figure S1 showed the Transmission electron microscopy (TEM) images of different cationcontaining $PMo_{11}V$ salts combination of CNTs. It can be seen that the shape of the nanocomposites are well controlled by turning the cations of $PMo_{11}V$ salts, which is corresponding to the SEM results. The controllable assembling of POMs and CNTs reveals the specific function of ultrasonic synthesis.



Figure S2. FT-IR, Raman, XRD spectra and TGA analysis of the purified CNTs, TBA-PMo₁₁V, and TBA-PMo₁₁V/CNTs nanocomposite.

As shown in **Figure S 2a**, the presence of chemisorbed TBA-PMo₁₁V onto CNTs is evident from FTIR spectrum since the unique bands of both TBA-PMo₁₁V and CNTs can be observed in the nanocomposite material. For example, FTIR spectrum of pristine CNTs displays two weak C-H stretching bands at 2920 and 2846 cm⁻¹, and the aromatic C=C vibration bands at 1655, 1440 cm⁻¹.^[S1] In contrast, the C-H stretching bands at 2927 and 2869 cm⁻¹, and the C=C vibration at 1629 and 1450 cm⁻¹, respectively, could be observed in the corresponding TBA-PMo₁₁V/CNTs nanocomposite. Furthermore, the Mo-O-Mo、Mo-O-V、V=O and P=O vibration bands shift from 801,873, 944 and 1057 cm⁻¹ in the TBA-PMo₁₁V ^[S2]to 799, 870,940 and 1053 cm⁻¹ in the **TBA-PMo₁₁V/CNTs** nanocomposite, which indicates the interactions between TBA-PMo₁₁V and CNTs.

Raman spectra (excited at 633 nm) of pristine CNTs and **TBA-PMo**₁₁**V/CNTs** have been shown in **Figure S2 b**, the tangential vibration mode (G band) at 1590 cm⁻¹ is clearly observed for both CNTs and **TBA-PMo**₁₁**V/CNTs**. Meanwhile, the disorder-induced D band shifts slightly from 1351 in CNTs to 1355 cm⁻¹ in **TBA-PMo**₁₁**V/CNTs**. Moreover, it should be noted that Raman spectra of TBA-PMo₁₁V exhibit main bands characteristic of heteropoly anion with Keggin structure, which are observed at 1006 cm⁻¹ with a shoulders at 988, 962, 899, 601, and 254 cm⁻¹, which can be respectively assigned to stretching frequencies as v_s(Mo–O_t), v_{as}(Mo–O_t), v_s(Mo–O_b–Mo), v_s(Mo– O_c–Mo), and v_s(Mo–O_a) in the nano composite where in the pure POMs were1004, 980, 959, 897, 598, and 250 cm⁻¹ ^[53], which indicate that the big POMs crystals on the CNTs. On the other hand, the ratio of D/G of the nanocomposites changes a little than the purified CNTs, which indicate that the nanocomposite maintain the integrity of CNTs. Such result could be explained that the POMs crystal grafted on the CNTs under the experimental conditions.

Powder XRD provides a strong evidence of POM crystals on the CNTs. As shown in Figure S2 c, the TBA-PMo₁₁V/CNTs nanocomposites give both of the characteristic peaks of POM and CNTs. The relatively broad (002) reflection of CNTs is centered at $2\theta = 26.5^{\circ}$, which corresponds to a d spacing of 0.36nm (consistent with graphitically spaced CNTs).^[54] Another peak(100) of CNTs appear at 44.2°, which is originated from the graphene character of the CNTs. The abundant peaks of TBA-PMo₁₁V also appear on the TBA-PMo₁₁V/CNTs nanocomposites with a similar intensity and negligible shift. As such, the TBA-PMo₁₁V nanocrystals are successfully grafted on the CNTs.

Thermal gravimetric analysis (TGA) of the purified CNTs, TBA-PMo₁₁V, and **TBA-PMo₁₁V/CNTs** nanocomposite is presented in **Figure S2 d**. It can be seen that the pure CNTs do not exhibit any decomposition before 450 °C. For

TBA-PMo₁₁V and **TBA-PMo₁₁V/CNTs** nanocomposite, weight losses of of 36.01 and 22.88 wt.-%, respectively are observed between 200 – 450 °C. This weight loss is associated with oxidative loss of the organic TBA⁺ counter ions and allows us to estimate the TBA-PMo₁₁V content in the **TBA-PMo₁₁V/CNTs** nanocomposite to approximately 63.5 wt.-%.



Figure S3. BET graphs of the purified CNTs, TBA-PMo₁₁V, and TBA-PMo₁₁V/CNTs nanocomposite.

BET analysis (**Figure S3**) gives the surface areas of pure CNTs (348 m² g⁻¹) TBA-PMo₁₁V ((9 m² g⁻¹) and TBA-PMo₁₁V/CNT nanocomposites (143 m² g⁻¹), showing that deposition of the POMs on CNTs results in a high-surface area electroactive material, thereby increasing the interfacial area for contact with the electrolyte within the electrochemical cell.



Figure S4. XPS spectra of a), b) TBA-PMo₁₁V/CNTs; c), d) TBA-PMo₁₁V.

As shown in **Figure S4a** and **b**, for the pure TBA-PMo₁₁V cluster, Mo(VI) 3d and V(V)2p signals are detected with binding energies of 233.1 eV, 236.2 eV and 517.4eV^[S5], respectively. For the POM-CNT-nanocomposites, only minor changes in the binding energies are observed, suggesting that the structural integrity of the clusters is retained. Binding energies of the POM-CNT-nanocomposites: 232.7 eV, 235.8 eV and 516.9eV



Figure S5. Comparison of the specific capacity of the purified CNTs, TBA-PMo₁₁V, TBA-PMo₁₁V/ CNTs nanocomposites and physical mixture of the CNTs and POM at the same current density (0.5 mA cm^{-2}).

Figure S5 shows the specific capacity of the purified CNTs, TBA-PMo₁₁V, and TBA-PMo₁₁V/CNTs nanocomposites at a current density of 0.5 mA cm⁻². For **pristine CNTs**, the first discharge capacity is 827 mAh g⁻¹, which decreases to 397 mAh g⁻¹ in the second run and stabilizes at approximately 324 mAh g⁻¹ after 10 cycles; the capacity retention was 39.2%. This level was maintained over 100 cycles. The **pure TBA-PMo₁₁V** showed a first discharge capacity of 593 mAh g⁻¹, which decreased to 245.4mAh g⁻¹ in the second run and decreased further to approximately 107 mAh g⁻¹ after 100 cycles, giving a capacity retention of 18.1%. The **physically mixed composite of CNTs and TBA-PMo₁₁V** showed a first discharge capacity of 1406.5 mAh g⁻¹, which decreased to 684.5 mAh g⁻¹ in the second run. The discharge capacity stabilized at *ca*. 460 mAh g⁻¹ after 20 cycles, giving a capacity retention of 32.6%. The **TBA-PMo₁₁V/CNTs nanocomposite** show a first discharge capacity of 3014.1 mAh g⁻¹ which decreased to 1052.6 mAh g⁻¹ in the second run. Over the following runs, a slight increase of capacity was observed reaching values of ca. 850 mAh g⁻¹ after 100 cycles. The capacity retention was 28.2%.

The results demonstrate that the "wiring" of POMs to CNTs indeed significantly enhances the electrochemical charge storage performance of the nanocomposite materials.



Figure S6. FT-IR of a) TBA-PMO₁₁V after 100 cycle test; b) pristine TBA-PMO₁₁V/CNTs.

When we do the cell test, the TBA-PMo₁₁V/CNTs nanocomposite was mixed with the carbon black and PVDF. Due to the small amount of the content of the TBA-PMo₁₁V/CNTs, it is hard to detect the structure stability directly from the mixture. As an alternative, we try to gather the POMs from the electrodes after the electrochemical test by using MeCN to wash the POMs out in order to check the stability.

Work-up procedure: To confirm the POMs structure remain stable in the LIBs after 100 cycles, we use 10 mL x 4 (40 mL) MeCN to wash 10 pieces of TBA-PMo₁₁V/CNTs electrodes to enrich the POMs. After that, the MeCN solution is left for evaporation, and the crystallized solid sample is collected for FT-IR measurement. As shown in Figure S6, FT-IR spectrum of the recycled TBA-PMo₁₁V after 100 cycles shows the vibration bands at 805, 877, 942 and 1059 cm⁻¹, respectively, which slightly shift from the corresponding Mo-O-Mo, Mo-O-V, V=O and P=O stretching bands at 799, 870, 940 and 1053 cm⁻¹ in the TBA-PMo₁₁V/CNTs nanocomposites. This result indicates that the structure of the POM in the TBA-PMo₁₁V/CNTs nanocomposites used for battery measurement remains stable after 100 recycle.



Figure S7. SEM image of the post-cycling samples, measured after 100 charging-discharging cycles.

SEM images of the post-cycling sample shows that the periodic deposition of POM crystals on the surface of CNTs can be observed. Moreover, the crystals with rhombic dodecahedral morphology are not loosely attached to the CNTs, but the CNTs still passes through the POM crystals, highlighting the excellent stability of the TBA-PMo₁₁V/CNTs.

| Туре | Electrode Type | Current Density | Residual | Ref. |
|---------|--|--------------------------|------------------------------|-----------|
| | | | reversible | |
| | | | Capacity (mAh g ⁻ | |
| | | | ¹) | |
| Cathode | TBA ₃ [PMo ₁₂ O ₄₀]-Graphene | 1.0 mA cm ⁻² | 140 | S6 |
| | TBA ₃ [PMo ₁₂ O ₄₀]-SWNT | 1.0 mA cm ⁻² | 320 | 30 |
| | K ₃ [PMo ₁₂ O ₄₀] | 0.05 mA cm ⁻² | 160 | 41 |
| Anode | TBA ₄ [Py-SiW ₁₁]-SWNTs | 0.5 mA cm ⁻² | 580 | 8 |
| | CNTs-SiW ₁₁ | 0.5 mA cm ⁻² | 650 | 6 |
| | CNT nanoarray | 1 mA cm ⁻² | 490 | 43 |
| | TBA-PMo ₁₁ V/CNTs | 0.5 mA cm ⁻² | 850 | This work |
| | Pure CNTs | 0.5 mA cm ⁻² | 324 | This work |
| | Pure TBA-PMo ₁₁ V | 0.5 mA cm ⁻² | 107 | This work |
| | Physical mixture TBA- | 0.5 mA cm ⁻² | 460 | This work |
| | PMo ₁₁ V/CNT | | | |

Table S1. Electrochemical parameters of electrode materials consisting of POMs, nanocarbon materials or POM-nanocarbon-based nanocomposites

(The physical mixture of TBA-PMo₁₁V and CNTs was prepared according to the TG data: the POMs and CNTs was mixed with the weight ratio of 63.5%, and was put into a mortar, followed a full mix procedure for 1h.)

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