“Wiring” redox-active Polyoxometalates to Carbon Nanotubes using a Sonication-driven Periodic Functionalization Strategy

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Table S1. Electrochemical parameters of electrode materials consisting of POMs, nanocarbon materials or POM-nanocarbon-based nanocomposites.
Figure S1. TEM images of different cation-containing PMo$_{11}$V salts combination of CNTs: a) TBA-PMo$_{11}$V/CNTs; b) TOA-PMo$_{11}$V/CNTs; c) DDA-PMo$_{11}$V/CNTs; d) STA-PMo$_{11}$V/CNTs.

Figure S1 showed the Transmission electron microscopy (TEM) images of different cation-containing 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.
As shown in Figure S2a, the presence of chemisorbed TBA-PMo$_{11}$V onto CNTs is evident from FTIR spectrum since the unique bands of both TBA-PMo$_{11}$V 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-PMo$_{11}$V/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-PMo$_{11}$V to 799, 870, 940 and 1053 cm$^{-1}$ in the TBA-PMo$_{11}$V/CNTs nanocomposite, which indicates the interactions between TBA-PMo$_{11}$V and CNTs.

Raman spectra (excited at 633 nm) of pristine CNTs and TBA-PMo$_{11}$V/CNTs have been shown in Figure S2b, 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-PMo$_{11}$V 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 were 1004, 980, 959, 897, 598, and 250 cm$^{-1}$, 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-PMo$_{11}$V/CNTs nanocomposites give both of the characteristic peaks of POM and CNTs. The relatively broad (002) reflection of CNTs is centered at 2θ = 26.5°, which corresponds to a d spacing of 0.36nm (consistent with graphitically spaced CNTs). Another peak (100) of CNTs appear at 44.2°, which is originated from the graphene character of the CNTs. The abundant peaks of TBA-PMo$_{11}$V also appear on the TBA-PMo$_{11}$V/CNTs nanocomposites with a similar intensity and negligible shift. As such, the TBA-PMo$_{11}$V nanocrystals are successfully grafted on the CNTs.

Thermal gravimetric analysis (TGA) of the purified CNTs, TBA-PMo$_{11}$V, and TBA-PMo$_{11}$V/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-PMo$_{11}$V and TBA-PMo$_{11}$V/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-PMo$_{11}$V content in the TBA-PMo$_{11}$V/CNTs nanocomposite to approximately 63.5 wt.-%.

BET analysis (Figure S3) gives the surface areas of pure CNTs (348 m$^2$ g$^{-1}$) TBA-PMo$_{11}$V (9 m$^2$ g$^{-1}$) and TBA-PMo$_{11}$V/CNT nanocomposites (143 m$^2$ 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.
As shown in Figure S4a and b, for the pure TBA-PMo$_{11}$V cluster, Mo(VI) 3d and V(V) 2p signals are detected with binding energies of 233.1 eV, 236.2 eV and 517.4 eV\cite{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 516.9 eV.
Figure S5. Comparison of the specific capacity of the purified CNTs, TBA-PMo$_{11}$V, TBA-PMo$_{11}$V/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-PMo$_{11}$V, and TBA-PMo$_{11}$V/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-PMo$_{11}$V showed a first discharge capacity of 593 mAh g$^{-1}$, which decreased to 245.4 mAh 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-PMo$_{11}$V 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-PMo$_{11}$V/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.
When we do the cell test, the TBA-PMo$_{11}$V/CNTs nanocomposite was mixed with the carbon black and PVDF. Due to the small amount of the content of the TBA-PMo$_{11}$V/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-PMo$_{11}$V/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-PMo$_{11}$V 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-PMo$_{11}$V/CNTs nanocomposites. This result indicates that the structure of the POM in the TBA-PMo$_{11}$V/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-PMo$_{11}$V/CNTs.
<table>
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<th>Type</th>
<th>Electrode Type</th>
<th>Current Density</th>
<th>Residual reversible Capacity (mAh g⁻¹)</th>
<th>Ref.</th>
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<td>Cathode</td>
<td>TBA₃[PMo₁₂O₄₀]⁻⁻-Graphene</td>
<td>1.0 mA cm⁻²</td>
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<td>Anode</td>
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<td>0.5 mA cm⁻²</td>
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<td>Physical mixture TBA-PMo₁₁,V/CNT</td>
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</table>

(The physical mixture of TBA-PMo₁₁,V 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.)

**Reference:**


