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**Electronic Supplementary Information**

# Highly dispersed redox-active polyoxometalates periodic deposition on multi-walled carbon nanotubes for boosting electrocatalytic triiodide reduction in dye-sensitized solar cells

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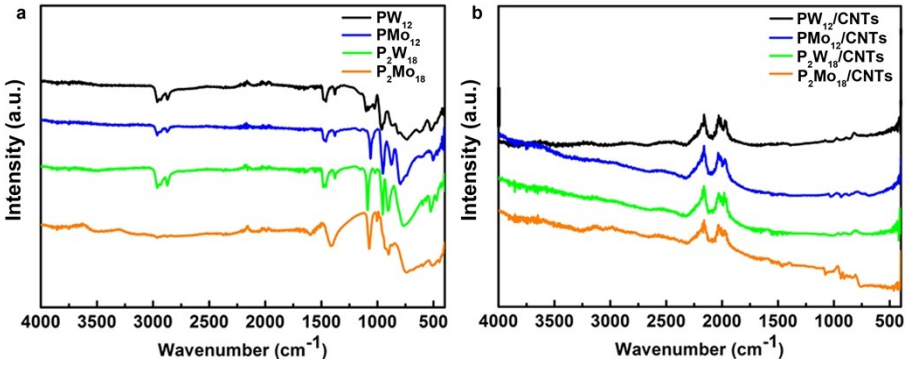


**Fig. S1**. IR spectra of POMs salts, POMs/CNTs nanocomposites employed as the CEs.

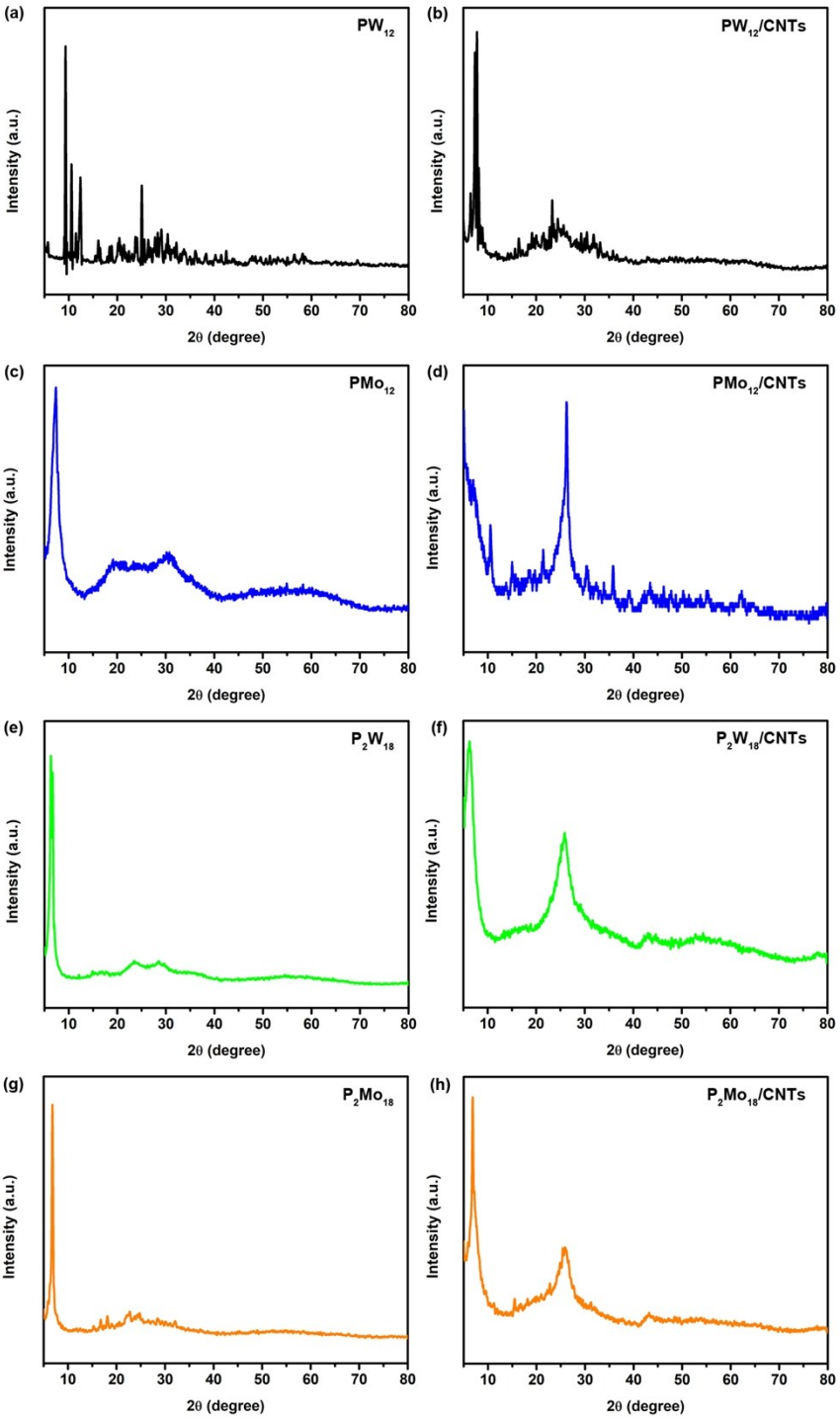


**Fig. S2**. The PXRD patterns of (a, c, e, g) POMs salts; (b, d, f, h) POMs/CNTs nanocomposites employed as the CEs.

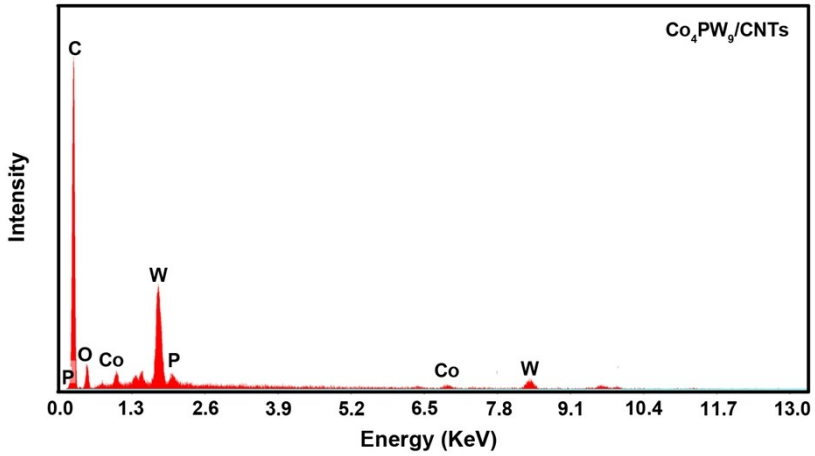


**Fig. S3**. The EDX result of $Co_4PW_9$/CNTs nanocomposites.

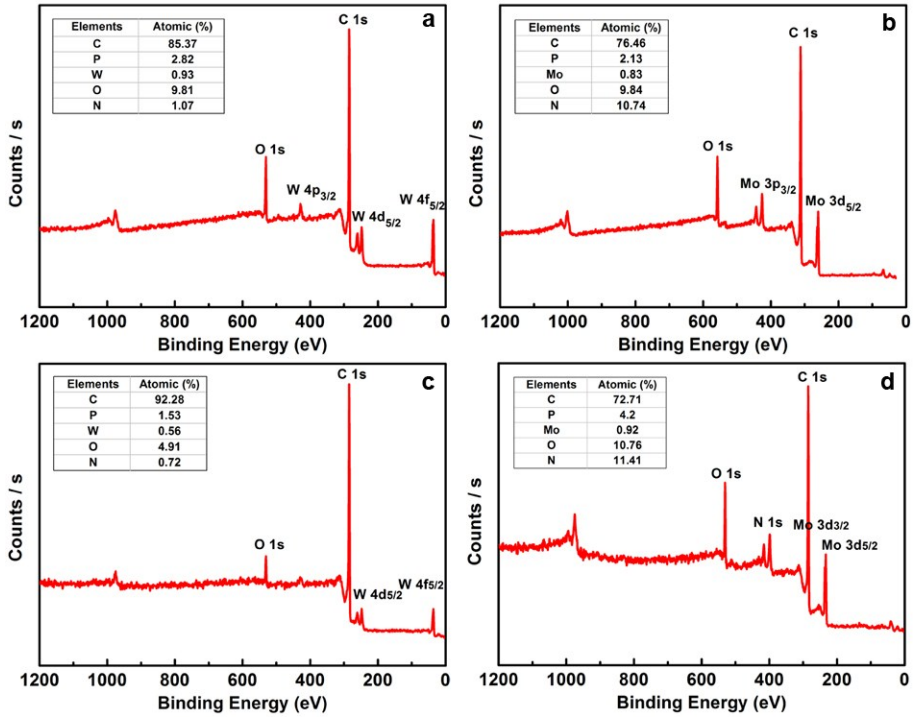


**Fig. S4.** The full XPS spectra of (a) $PW_{12}$/CNTs, (b) $PMo_{12}$/CNTs, (c) $P_2W_{18}$/CNTs and (d) $P_2Mo_{18}$/CNTs nanocomposites.

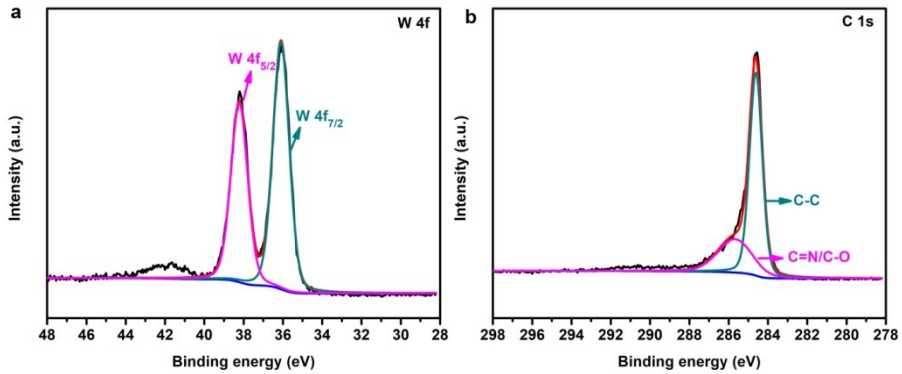


**Fig. S5.** High-resolution XPS spectra of (a) W and (b) C in $PW_{12}$/CNTs nanocomposite.

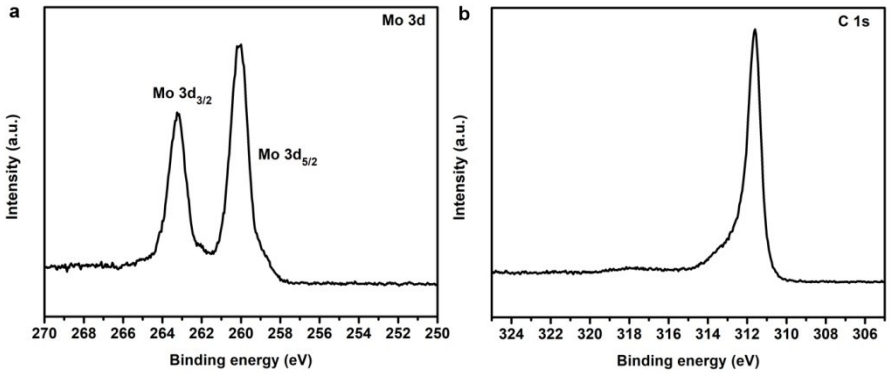


**Fig. S6.** High-resolution XPS spectra of (a) Mo and (b) C in $PMo_{12}$/CNTs nanocomposite.

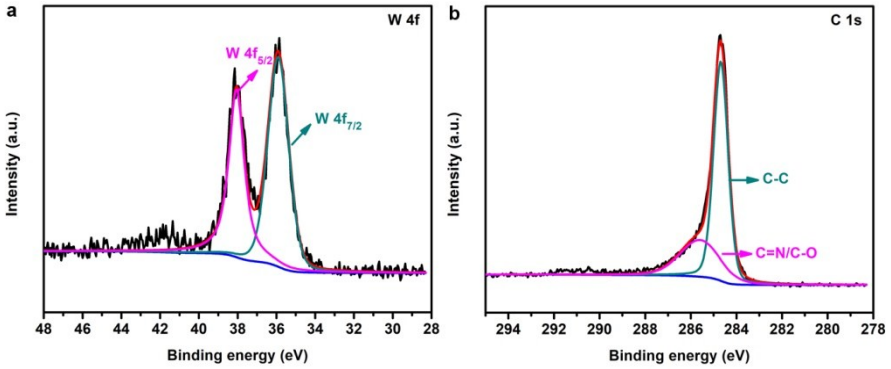


**Fig. S7.** High-resolution XPS spectra of (a) W and (b) C in $P_2W_{18}$/CNTs nanocomposite.

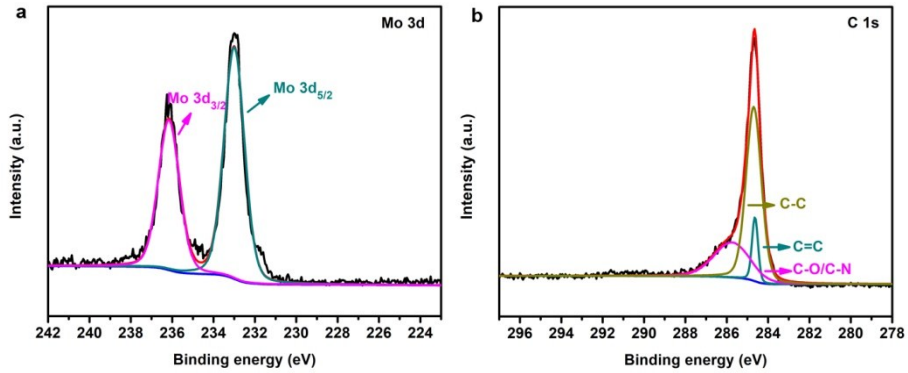


**Fig. S8.** High-resolution XPS spectra of (a) Mo and (b) C in $P_2Mo_{18}$/CNTs nanocomposite.

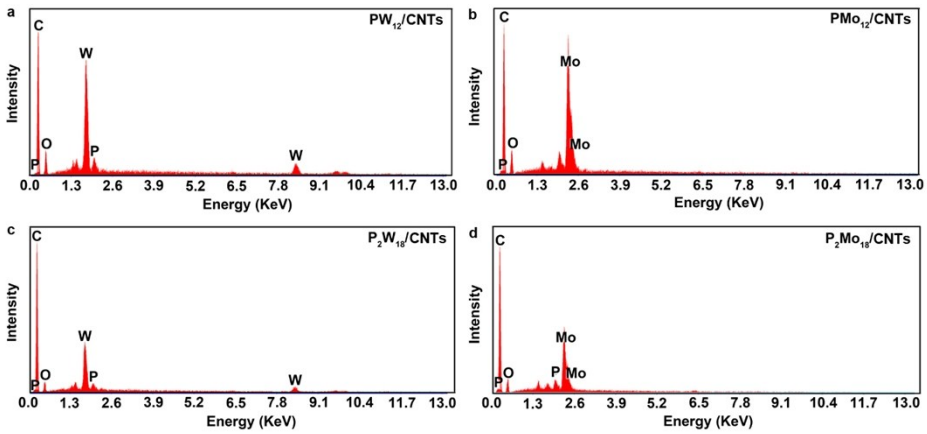


**Fig. S9.** The EDX results of (a) $PW_{12}$/CNTs, (b) $PMo_{12}$/CNTs, (c) $P_2W_{18}$/CNTs and (d) $P_2Mo_{18}$/CNTs nanocomposites.

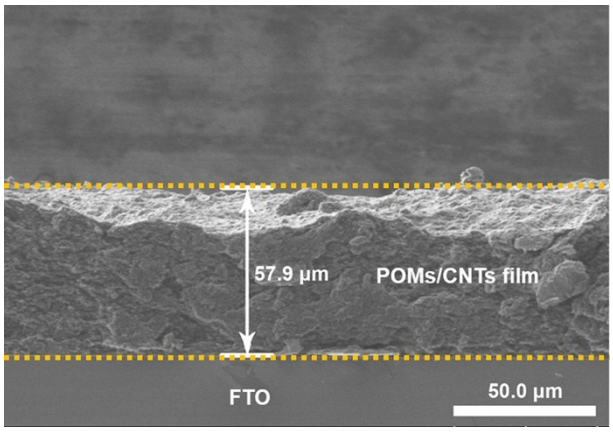


**Fig. S10.** The cross sectional view of the $Co_4PW_9$/CNTs CE.

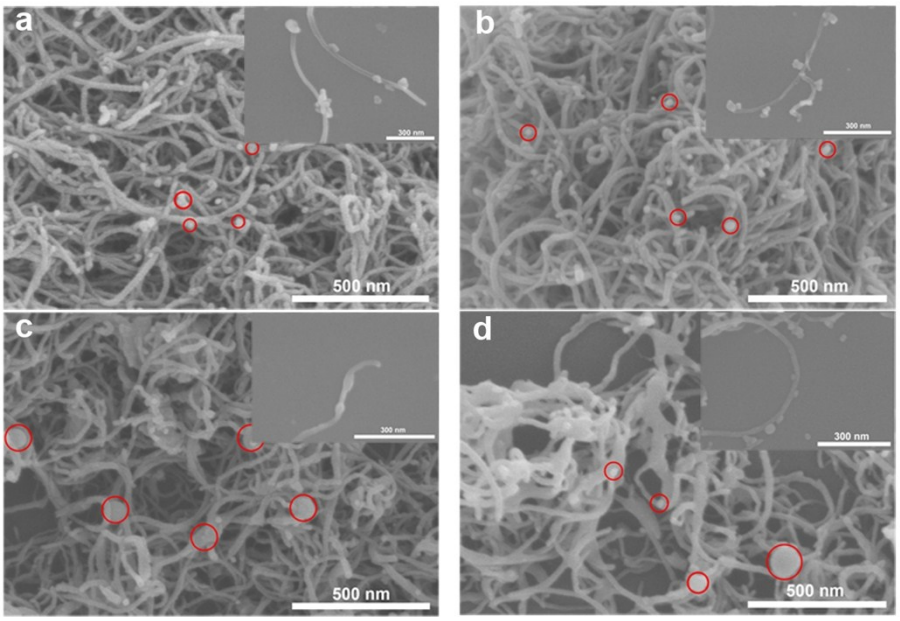


**Fig. S11.** The SEM images of (a) $PW_{12}$/CNTs, (b) $PMo_{12}$/CNTs, (c) $P_2W_{18}$/CNTs and (d) $P_2Mo_{18}$/CNTs nanocomposites.

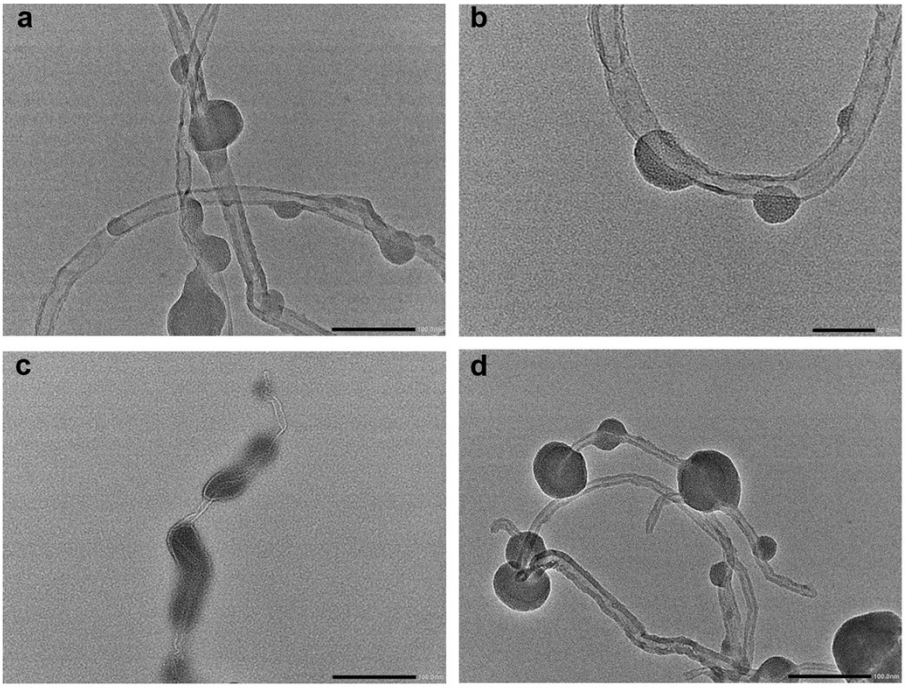


**Fig. S12.** The TEM images of (a) $PW_{12}$/CNTs, (b) $PMo_{12}$/CNTs, (c) $P_2W_{18}$/CNTs and (d) $P_2Mo_{18}$/CNTs nanocomposites.

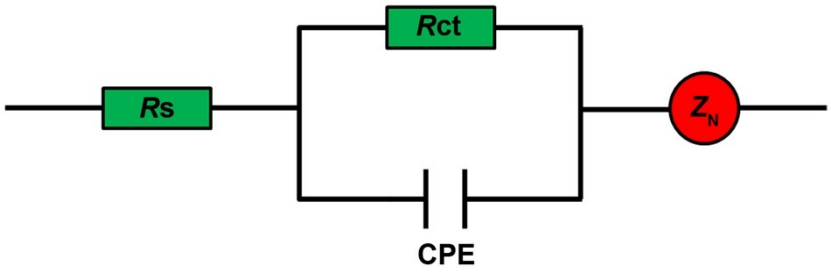


**Fig. S13.** The equivalent circuit for EIS analysis; $R_s$ is the series resistance, CPE represents the electrochemistry double-layer capacitance, the charge transfer resistance related to the IRR process is $R_{ct}$.

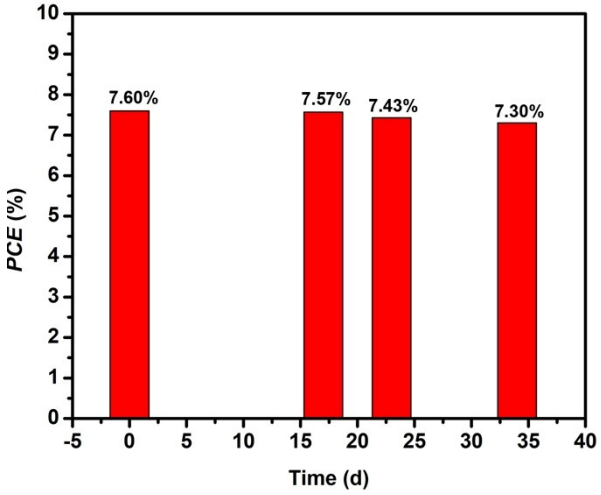


**Fig. S14.** Long-term stability of a DSSC based on $Co_4PW_9$/CNTs CE.

**Supplementary Tables**

**Table S1**. The POMs salts employed as the CEs in this study.

| Entry no | POMs salts | Abbreviation | Ref. |
|---|---|---|---|
| 1 | $TBA_3[PW_{12}O_{40}]$[a] | $PW_{12}$ | [1] |
| 2 | $TBA_3[PMo_{12}O_{40}]$ | $PMo_{12}$ | [2] |
| 3 | $TBA_6[P_2W_{18}]$ | $P_2W_{18}$ | [3] |
| 4 | $TBA_6[P_2Mo_{18}]$ | $P_2Mo_{18}$ | [4] |
| 5 | $Na_{10}[Co_4(H_2O)_2(PW_9O_{34})_2] \cdot 27H_2O$ | $Co_4PW_9$ | [5] |

[a] TBA: tetra-n-butylammonium.

**Table S2**. Electrochemical parameters for different CEs.

| CEs | $R_s$(Ω·cm$^2$) | $R_{ct}$(Ω·cm$^2$) | $J_{Red}$(mA cm$^{-2}$) | *E*pp(mV) | $f_{max}$(Hz) | τ(μs) |
|---|---|---|---|---|---|---|
| Pt | 10.54 | 13.50 | -3.16 | 900 | 2234.36 | 71.27 |
| CNTs | 19.04 | 24.04 | -1.47 | 740 | 19.96 | 7977.66 |
| $PW_{12}$/CNTs | 11.03 | 10.90 | -3.50 | 600 | 5067.43 | 31.42 |
| $PMo_{12}$/CNTs | 11.05 | 15.50 | -6.18 | 280 | 5937.08 | 26.82 |
| $P_2W_{18}$/CNTs | 11.56 | 6.97 | -2.81 | 560 | 1320.82 | 120.56 |
| $P_2Mo_{18}$/CNTs | 10.48 | 10.85 | -3.20 | 690 | 3593.43 | 44.31 |
| $Co_4PW_9$/CNTs | 11.75 | 1.20 | -8.43 | 230 | 7316.63 | 21.76 |

**References**


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