

Electronic Supplementary Information

Tungsten addenda mixed heteropolymolybdates supported on functionalized graphene for high-performance aqueous supercapacitors

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PMo_{12-x}W_x

To verify the successful combination of PMo₁₂ and PW₁₂ aqueous mixtures into PMo_{12-x}W_x (PMoW), a series of measurements were analyzed and a dry mixture was prepared by physical grinding for comparison.

Fig. S1a shows the FT-IR spectra of the products. The characteristic vibrational modes of pure PMo₁₂ are P–O: 1064.17 cm⁻¹, Mo=O: 960.46 cm⁻¹, Mo–O–Mo :870.56, 782.27 cm⁻¹ and pure PW₁₂ are corresponding to P–O: 1080.36 cm⁻¹, W=O: 982.21 cm⁻¹, W–O–W :891.30, 796.27 cm⁻¹. Obviously, the solution-mixed PMoW retains the Keggin structure with peaks at P–O: 1067.97 cm⁻¹,

M=O (M=Mo/W): 968.01 cm^{-1} , M–O–M (M=Mo/W): 875.31, 790.94 cm^{-1} .

This is very different from the physical-grinded mixture which the peaks are the simple superposition of PMo_{12} and PW_{12} . It indicates that the solution-mixed product is not just a simple physical combination of PMo and PW.

The X-ray diffraction (XRD) analysis further explains the chemical change and formation of mixed addenda molecules (Fig. S1b). The typical Keggin structure is retained in both mixtures, but several peaks (marked in the figure) are absent from the solution-prepared PMoW compared to the physical-grinded products, suggesting new chemicals with a Keggin structure are formed.¹

The ^{31}P liquid nuclear magnetic resonance (NMR) is an effective approach to confirm the formation of mixed addenda $\text{PMo}_{12-x}\text{W}_x$. As shown in Fig. S1c, the sharp peak signals at -4.14 ppm and -15.10 ppm correspond to pure PMo and pure PW, respectively.² Obvious chemical shift changes appear in the $\text{PMo}_{12-x}\text{W}_x$ mixed chemicals (Fig. S1d). No PW_{12} signal peak is observed and the PMo_{12} signal fades off sharply, indicating the formation of new mixed addenda chemicals with tungsten substitution, which is in accord with the reported literature.³ The strongest peak signals appeared at -7.23 and -8.24 ppm are corresponding to W-substituted chemicals PMo_9W_3 and PMo_8W_4 molecules.⁴ There are also several other peaks located at -5.24, -6.29, -9.13, and -10.21 ppm,

corresponding to PMo_{11}W , $\text{PMo}_{10}\text{W}_2$, PMo_7W_5 and PMo_6W_6 , respectively.^{3, 4}

The mixed addenda POMs can be reproducibly obtained and are promising pseudocapacitive electrode materials for energy storage.

Fig. S1

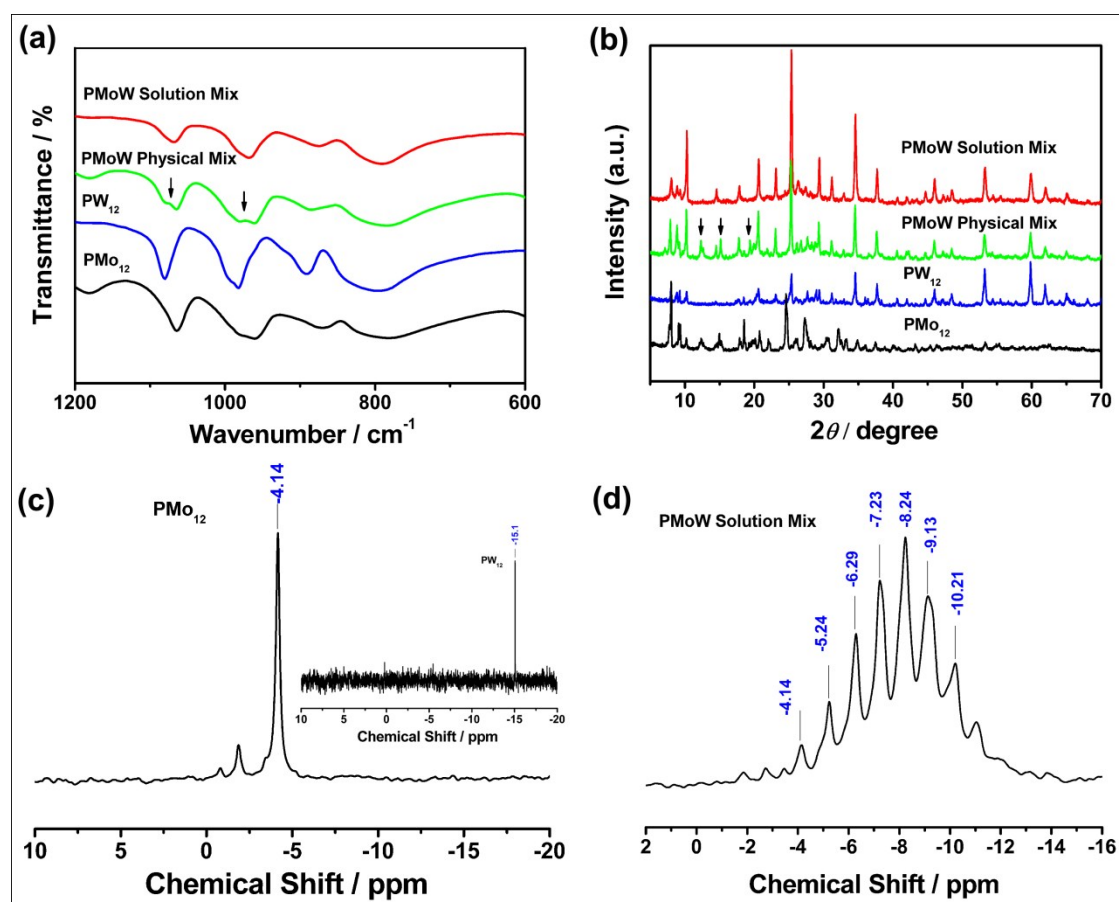


Fig. S1 (a) The FT-IR spectra of pure PMo_{12} , PW_{12} , PMoW physical mix and PMoW solution mix. (b) The XRD patterns of pure PMo_{12} , PW_{12} , PMoW physical mix and PMoW solution mix. (c) ^{31}P NMR spectra of pure PMo and pure PW. (d) ^{31}P NMR spectra of the PMoW solution mix.

Fig. S2

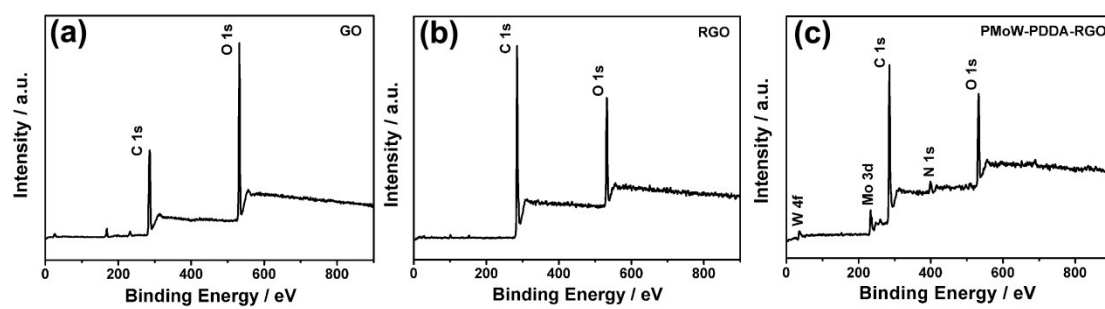


Fig. S2 (a-c) XPS of GO, RGO, and the PMoW-PDDA-RGO composite.

Fig. S3

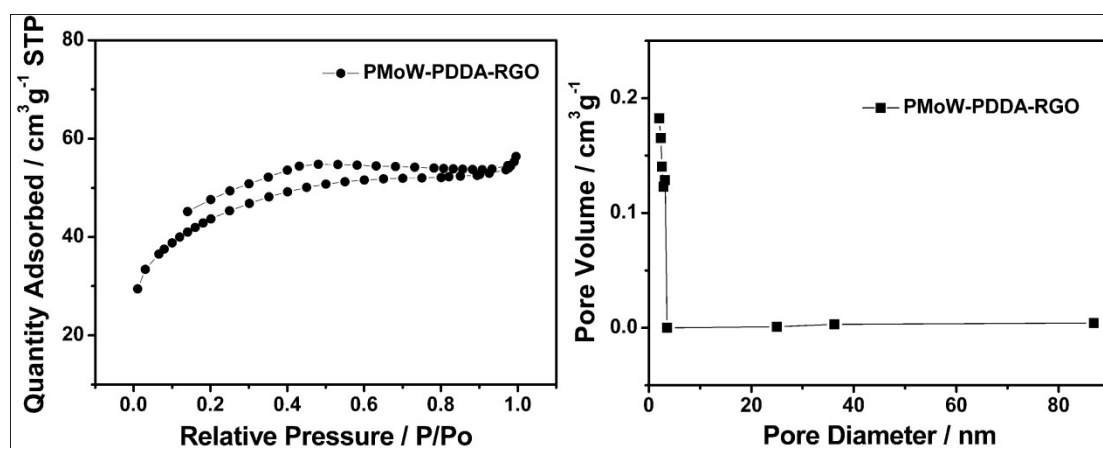


Fig. S3 (a) N₂ adsorption –desorption isotherm and (b) pore size distribution of the PMoW-PDDA-RGO composite.

Fig. S4

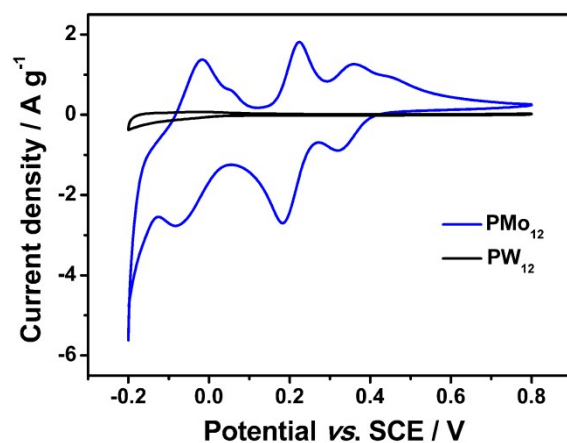


Fig. S4 CV curves of PMo₁₂ and PW₁₂ at 10 mV s⁻¹.

1. M. Genovese, Y. W. Foong and K. Lian, *Journal of the Electrochemical Society*, 2015, **162**, A5041-A5046.
2. R. Massart, R. Contant, J. M. Fruchart, J. P. Ciabrini and M. Fournier, *Inorganic Chemistry*, 1977, **16**, 2916-2921.
3. M. Genovese, Y. W. Foong and K. Lian, *Electrochimica Acta*, 2016, **199**, 261-269.
4. T. Ueda, T. Toya and M. Hojo, *Inorganica Chimica Acta*, 2004, **357**, 59-65.