

Supporting Information

Sub-millimeter free-suspended sheets formed by polyoxometalates with polyelectrolytes

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Experimental Section

Microscopic observations. The SEM images were obtained by using a Hitachi S-4800. To prevent electric charging, a 2-nm thick platinum layer was deposited on the specimen by using a Hitachi E-1030 ion sputter. For the cross-sectional SEM observation, the free suspended films were cast onto a carbon-coated copper grid, which was carefully ripped off to form the cutting surface, and set on a vertical sample holder. The TEM images were obtained with JEOL 2010HC operating at 200 kV. Optical microscopy images were obtained using an instrument, Lasertec VL2000D.

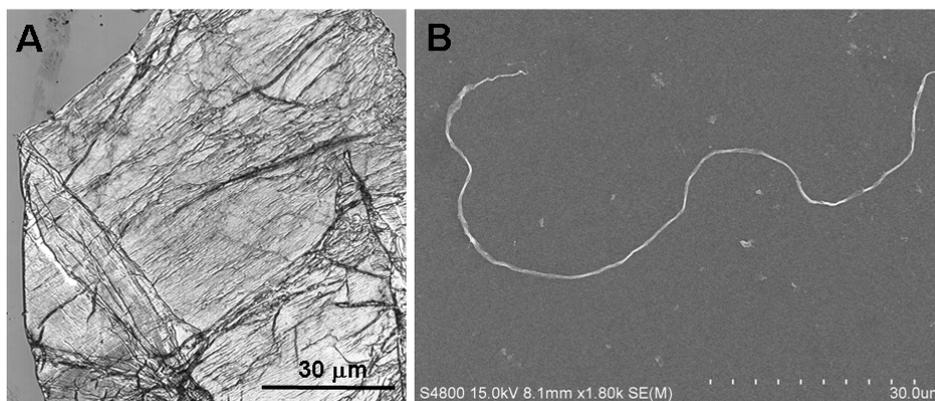


Fig. S1 The folded bilayers in the free-suspended sheets were occasionally observed by Laser optical microscopy (LOM) (A). In several SEM measurements, we sporadically observed nanofibers with a length of a few tens of micrometers and a width of a few tens of nanometers (B).

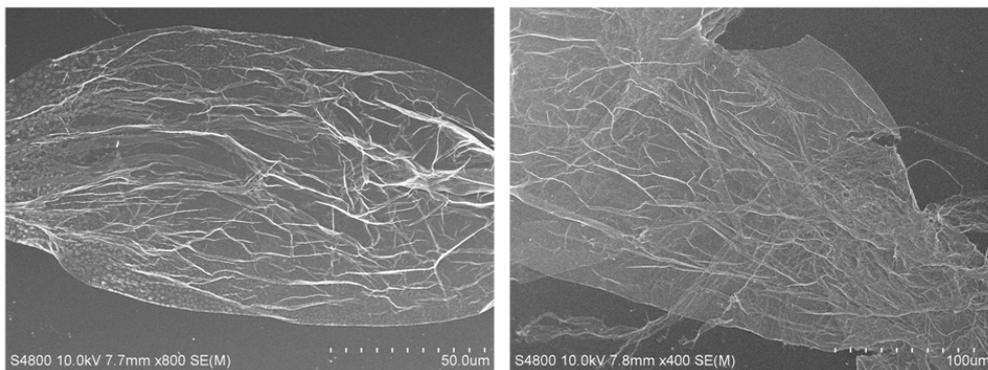


Fig. S2 SEM images of the free suspended sheets formed by TSA with PXTT.

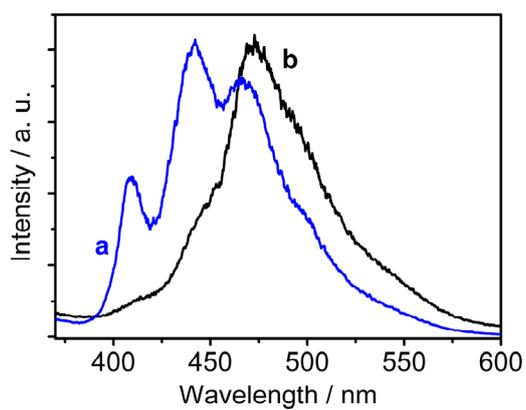


Fig. S3 Fluorescence spectra of PXTT in its dilute solution (a) and the sheet-like nanocomposite (b).

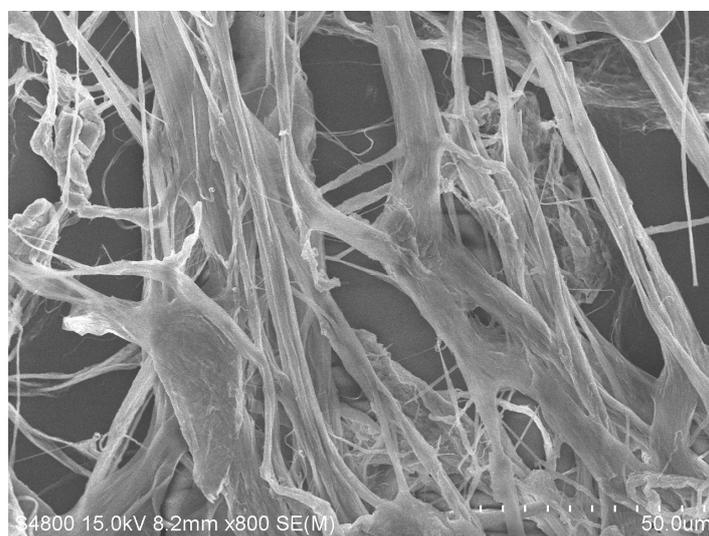


Fig. S4 SEM images showed nanofibers and bundling nanofibers at initial stages of stirring the mixture of TSA with PXTT.

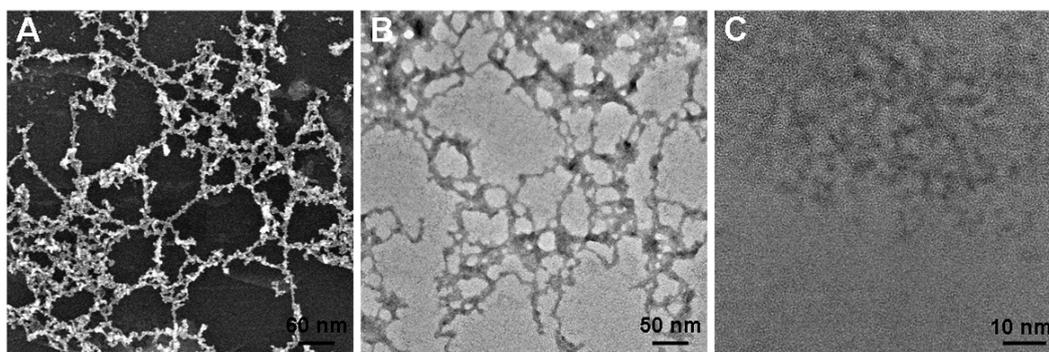


Fig. S5 SEM (A) and TEM (B, C) images of nanocomposite prepared from TSA and PAH at a molar ratio of 1/4 (based on the repeated unit for PAH).

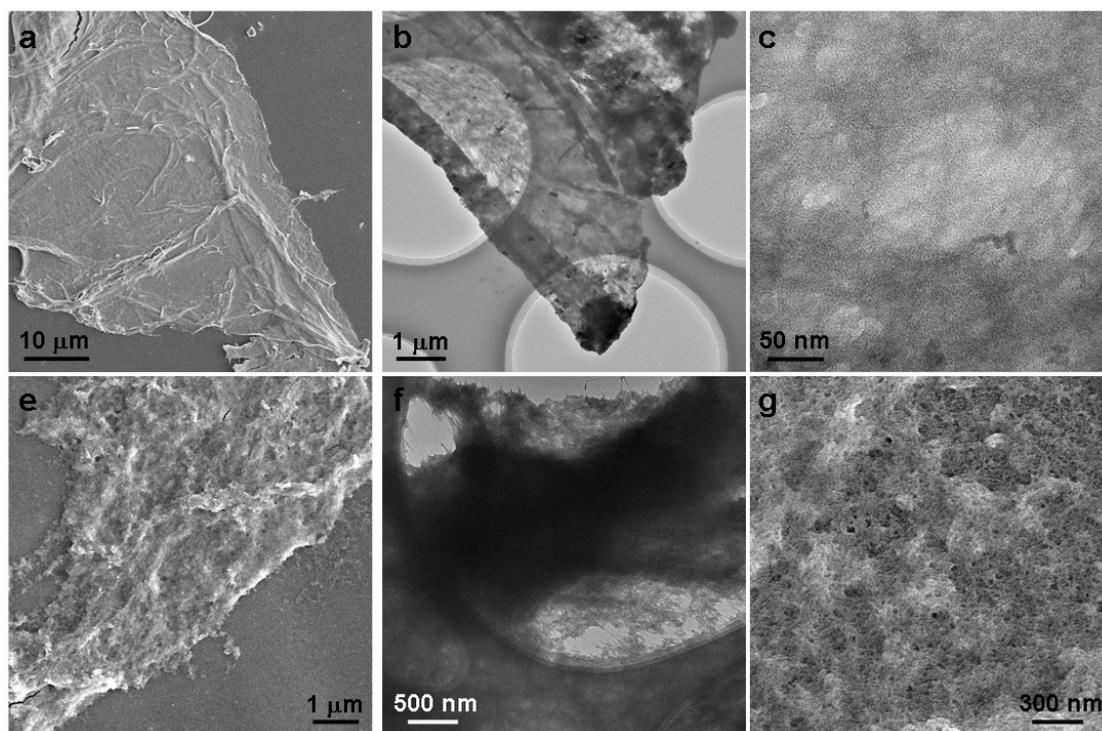


Fig. S6 SEM (a) and TEM (b and c) images of the nanocomposite prepared from TPA and PXTT at a molar ratio of 1/1 (based on the repeated unit for PXTT). SEM (e and g) and TEM (f) images of the nanocomposite prepared from Mo₁₃₂ and PXTT at a molar ratio of 1/1 (based on the repeated unit for PXTT).

Table S1. The assignment of infrared absorption bands of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ and $\text{K}_8[\text{SiW}_{11}\text{O}_{39}]$.

Sample	W-O _d antisym. str.	Si-O _a antisym. str.	W-O _b -W antisym. str.	W-O _c -W antisym. str.
PXTT/ $[\text{SiW}_{12}\text{O}_{40}]^{4-}$	973	922	883	795
$\text{H}_4[\text{SiW}_{12}\text{O}_{40}]^a$	981	928	880	785
$\text{K}_4[\text{SiW}_{12}\text{O}_{40}]^a$	980	925	878	780
$\text{TBA}_4[\text{SiW}_{12}\text{O}_{40}]^a$	967	919	883	799
$\text{DODA}_4[\text{SiW}_{12}\text{O}_{40}]^b$	972	918	883	793
$\text{DDDA}_4[\text{SiW}_{12}\text{O}_{40}]^b$	971	917	882	792
$\text{THAB}_4[\text{SiW}_{12}\text{O}_{40}]^b$	966	919	883	801
$\text{K}_{11}[\text{SiW}_{11}\text{O}_{39}]^c$	952		885, 870	797

^a C. Rocchoccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, *Inorg. Chem.*, 1983, **22**, 207. ^b H. Li, H. Sun, W. Qi, M. Xu, and L. Wu, *Angew. Chem. Int. Ed.*, 2007, **46**, 1300. ^c A. Tézé and G. Hervé, *Inorganic Synthesis*; John Wiley and Sons: New York, 1990.

TBA: tetra-*n*-butylammonium); DODA: dimethyldioctadecylammonium; DDDA: dimethyldidodecylammonium; THAB: tetra-*n*-heptylammonium.

Results and discussion of the infrared spectra:

The infrared bands of the sheet-like hybrid were clearly observed at 973, 922, 883, and 785 cm^{-1} , which showed only slight shifts in comparison with those of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ and $\text{K}_4[\text{SiW}_{12}\text{O}_{40}]$ (981, 928, 880, and 785 cm^{-1}). However, they were almost consistent with those of the encapsulated $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ anions with quaternary ammoniums (Table S1). Such shift means that PXTT cations have a strong interaction with $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ and partly screen the interanionic repulsions. The infrared bands of $\text{K}_8[\text{SiW}_{11}\text{O}_{39}]$ appeared at 952, 885, 875, and 797 cm^{-1} . These values were very different from those of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ anions. It was therefore concluded that the cluster structure of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ was retained when the sheet-like hybrid formed in the aqueous solution.