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2D organic-inorganic nanosheets *via* selfassembly of a pillar[6]arene and polyoxometalate for enhanced degradation efficiency[†]

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Construction of 2D hybrid nanosheets was realized through a selfassembly strategy using a pillar[6]arene (P_6) and polyoxometalate (POM) in water. More fascinatingly, the macrocyclic cavity of P_6 could impose a restriction effect on the lamellar arrangement and significantly enhance the catalytic ability of nanosheets for dye degradation.

Polyoxometalates (POMs) are a class of early transition metaloxygen anionic nanoclusters, with unique chemical and physical properties.¹ Through cooperative electrostatic interactions, cationic organic molecules can replace the counterions of POMs to facilitate the supramolecular assembly of POMs. Meanwhile the replacement could also exert a remarkable influence on the electronic properties of POMs, because POMs are able to accept electrons while with minimal structural changes as electrons are usually delocalized within mixed-valent cluster anions. Due to the cooperative properties of inorganic and organic components, supramolecular hybrid materials have potential applications in fabricating multifunctional materials, such as in catalysis,² electronics,3 optics,4 sensing5 and biology.6 However, the selfassembly approach usually provides 3D aggregate morphologies that are difficult to control and not suitable for technological applications. One of the most valuable nanoarchitectures is extended 2D nanosheets, which possess highly accessible active sites, homogeneous features, good dispersibility and large surface areas.⁷ However, challenges such as the limited choice of building blocks and synthetic difficulties still remain in practical preparation. In these assemblies, the counterions are usually required to possess structural flexibility so that they could tune their conformation to accommodate the 2D alignment of rigid POMs.8

Macrocycles with shape-persistent cavities are able to encapsulate suitable guests and therefore they are ideal for the construction of hybrid assemblies.⁹ Various macrocycles such as cyclodextrins,¹⁰ calixarenes,¹¹ cucurbiturils,¹² and crown ethers¹³ have been explored recently to construct 1D or 3D hybrid materials with POMs.

Pillar[n]arenes, as a new class of macrocycles, are described as "fascinating cyclophanes with a bright future", their characteristics and applications have been widely explored.14 To the best of our knowledge, there are no previous reports on hybrid assemblies using pillararenes and POMs. Pillararene derivatives possess rigid columnar cavities while bearing peripheral flexible groups on the side.¹⁵ Therefore, it would be possible to produce porous hybrid 2D assemblies on the basis of electrostatic interactions between cationic pillararenes and POM polyanions. Herein, we report a self-assembly strategy to fabricate 2D nanosheets using imidazolium functionalized pillar[6]arene (P_6) as the cationic bridging monomer and phosphotungstic acid (H₃PW₁₂O₄₀, here referred to as POM), a strong Bronsted acid, as the anionic connection node (in Scheme 1). More fascinatingly, in comparison to P_1 which is the building block of P₆, the macrocyclic cavity of P₆ allows H₂O₂ to move toward POM and can significantly enhance the efficacy of 2D nanosheets for dye degradation. This is the first report of P6 induced aggregation of 2D nanosheets and enhanced degradation efficiency of POM, which holds possible practical applications in materials for catalysis.

The water soluble pillar[6]arenes (P₆) in Scheme 1 were synthesized according to ref. 16. The supramolecular assembly was initially prepared by addition of an aqueous solution of P₆ to a solution of $H_3[PW_{12}O_{40}]$ (Scheme 1) in a 1 : 1 charge ratio at room temperature. The mixing resulted in an immediately cloudy suspension with an obvious Tyndall phenomenon (Fig. S1a in the ESI†), implying the formation of an ionic selfassembly.¹⁷ The molar ratio of POM to P₆ in the hybrid material was calculated to be about 3.91 through elemental analysis (C = 9.58%, N = 2.56%), indicating that almost all of the POM used was incorporated in the obtained hybrid material.



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Scheme 1 The illustration of the constructed 2D hybrid nanosheets, the chemical formula and the corresponding cartoon representations of P_{6} , POM, and P_{1} .

The zeta potential of the hybrid material was determined to be -10.5 mV (Fig. S1b, ESI†), indicating the outer surface of the assembly covered by the anionic POMs.¹⁸ The pore size distribution (Fig. S2, ESI†) obtained by the non-localized DFT (NLDFT) method in a N₂-sorption experiment at 77 K showed two main peaks at around 2 and 2.5 nm, demonstrating the porous structure of the hybrid material.

The obtained hybrid materials were imaged using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The TEM image in Fig. 1a shows that the assemblies are micrometer-scale 2D nanosheets, with curled and folded edges. The high-resolution TEM image displays many dark objects approximately 1 nm in size (attributed to single POM clusters) distributed uniformly on the sheet (Fig. S3, ESI†). Energy-dispersive X-ray (EDX) spectroscopy (Fig. 1b) corroborates that the observed films are composed of both P₆ and POM, in the presence of tungsten and carbon elements.¹⁷ The SEM images (Fig. 1c and d) demonstrate that such films consisted of multiple 2D sheets stacking on each other. The morphologies of the hybrid assemblies with other charge ratios (cation : anion = 1 : 6, 1 : 3, 3 : 1, 6 : 1) were also investigated by TEM in Fig. S4 (ESI†). Only wormlike structures were observed at these ratios which demonstrate that the mixed ratio is critical for the construction of 2D nanosheets. The cyclic structure of P_6 is crucial for forming lamellar structures. When an aqueous solution of P_1 , the monomer of P_6 with no methylene linkage (Scheme 1), was mixed with POM with a 1 : 1 charge ratio, 3D nanoparticles were obtained instead of nanosheet structures (Fig. S5, ESI†). This indicates that P_6 with a macrocyclic structure could impose a restriction effect on the lamellar arrangement of POM molecules.

The driving forces for the formation of hybrid nanosheets were supported by the FTIR spectra in Fig. S6 (ESI⁺). Four main characteristic vibration peaks of the POM powder appear at 717 cm⁻¹ (W–O_c–W), 880 cm⁻¹ (W–O_b–W), 955 cm⁻¹ (W–O_d), and 1075 cm^{-1} (P–O_a), consistent with the Keggin structure of $[PW_{12}O_{40}]^{3-.8}$ After complexation with P₆, the ν (W–O_b–W), ν (W–O_d) and ν (W–O_c–W) stretches shift to 890, 972, and 778 cm⁻¹, respectively, demonstrating strong electrostatic interactions between POM and P₆.^{8,17} In addition, a new band at 735 cm⁻¹ branched from 778 cm⁻¹ arises, indicating the presence of a hydrogen bond between the proton on imidazolium and the O atom of W-O_c-W^{VI}.¹⁹ There also exists a notable difference between the POM powder and the P6/POM hybrid material in Raman spectra. The Raman spectrum of POM exhibits three characteristic vibration bands at about 904, 990, and 1006 cm⁻¹, for the stretching modes of W-O-W, W=O, and P-O respectively (Fig. S7, ESI[†]). After complexation with P_6 , the band at around 904 cm⁻¹ moved to 919 cm⁻¹ due to the electrostatic and hydrogen bond interactions.²⁰ These FTIR and Raman spectra demonstrate that POM clusters have been incorporated into the hybrid material while the Keggin structure of POM is preserved.17,20a

In the XRD pattern of the hybrid material in Fig. 2, all of the characteristic Bragg reflections of POM disappear, and three Bragg diffraction peaks emerge at $2\theta = 8.57$, 9.17 and 27.56°. According to the previous reports,²¹ when POMs were homogeneously dispersed within the support at the microscopic level, they did not possess a separate crystal phase, as their crystalline structures were supposed to be rearranged through



Fig. 1 2D hybrid nanosheets self-assembled through a combination of $\rm P_6$ and POM. (a) TEM image, (b) EDX spectrum, and (c and d) SEM images.



Fig. 2 XRD patterns of POM/P₆ hybrid nanosheets and pure POM powder.

electrostatic interactions, hydrogen bonding, and van der Waals forces with large organic cations. Therefore, peaks corresponding to the bulk phase of POM were not detected in the XRD pattern. The three peaks of the hybrid material correspond to the layer spacing of 1.03, 0.47 and 0.34 nm, respectively, which can be well indexed as (001), (002) and (003) reflections of a lamellar structure with a layer spacing of 1.03 nm.²² Considering that the diameter of each POM molecule is around 1 nm,²³ these XRD results inferred a single-layer 2D structure. Based on the observation from SEM in Fig. 1, we speculated that the singlelayer can then be accumulated into multilayered nanosheets through layer by layer stacking, as a result of the hydrophobic and/or π - π interactions of the P₆ units.²⁴ On the basis of the above results, a possible assembling model of the nanosheets is proposed in Scheme 2.

Having demonstrated the successful fabrication of the hybrid 2D materials, we next investigated the catalytic performance of the nanosheets. Methyl orange (MO) and rhodamine-B (RhB) were selected as typical organic pollutants to examine the catalytic activity of the prepared hybrid nanosheets. UV-vis spectra were used to monitor the degradation of MO solution. In the presence of H_2O_2 , the as-prepared POM/P₆ hybrid nanosheets exhibit excellent catalysis for the degradation of MO that was completely degraded within 60 min (Fig. 3a).

It was essential to rule out the possible catalytic mechanism of the 2D nanosheets. As a control experiment, we mixed MO solution with the P_6/POM hybrid materials, POM/H_2O_2 , P_6/H_2O_2 and H_2O_2 , respectively, under the same conditions. Decolorization rates of MO solution with various additives are plotted in Fig. 3b. Negligible degradation yields of MO were observed even after 100 min under these conditions. This also demonstrates that the decrease of MO concentration in the $P_6/POM/H_2O_2$ system is mainly caused by the degradation rather than the adsorption by the P_6/POM hybrid materials. It is thus concluded that hybridization of POM/P_6 and synergy with H_2O_2 offer a promising method to realize the effective degradation of MO.

To further investigate the impact of the macrocyclic structure of P_6 toward the catalytic activity of the hybrid materials, we then performed MO degradation by replacing P_6 with P_1 . The catalytic efficiency of P_1 /POM/H₂O₂ was found to be remarkably



Scheme 2 Illustrations of possible self-assembly models of P₆ and POM.



Fig. 3 (a) UV-vis spectra of MO solution in the presence of $P_6/POM/H_2O_2$ with different degrading times; (b) degradation of MO over time with different substances: $P_6/POM/H_2O_2$, P_6/POM hybrid materials, $POM + H_2O_2$, $P_6 + H_2O_2$, H_2O_2 , and $P_1/POM/H_2O_2$, respectively, from 1 to 6.

decreased (Fig. 3b) and only a small amount of MO (about 19%) was degraded with reaction times of more than 200 min (Fig. S8, ESI†). This indicates that the macrocyclic structure of P_6 could enhance the catalytic activity of POM in the P_6/POM 2D nanosheets with highly accessible active sites and large surface areas compared with the P_1/POM nanoparticles.

Taking together all the above results, a possible mechanism for promoting the catalytic activity is proposed in Fig. S9 (ESI⁺). In the P₆/POM/H₂O₂ system, the POM polyanions were isolated and surrounded by their macrocyclic P₆ counterparts through hydrogen-bonding and electrostatic interactions. H₂O₂ molecules were allowed to pass through the macrocyclic cavity easily and move toward POM catalytic sites.¹² In the catalytic cycle, H₂O₂ would firstly precomplex with POM to create 7-coordinated W-O peroxo radicals (W^V-O-O[•]) with oxygen being transferred to POM. Then due to the reduced molecular distance, the intramolecular transferred electron from imidazolium to POM generates the transition structure WV-O-O···P₆.²⁵ Simultaneously and finally, W^V -O-O···P₆ resumed to W^V -O···P₆ that coexisted with W^{VI}=O in the starting hybrid materials, through reaction with H₂O adsorbed on the surface and as a result •OH is formed.^{21b} The generated •OH was also facilitated to be transported to bulk solution through the macrocyclic P_6 , and as a consequence, dyes were degraded efficiently,²⁶ while for the P1/POM/H2O2 nanoparticle system, the absence of a porous cavity and less accessible POM sites caused a rather slow degradation.

Degradation of RhB using P6/POM/H2O2 was also investigated under similar conditions to that of the MO system. As shown in Fig. S10 (ESI[†]), P₆/POM/H₂O₂ also displayed the effective degradation of RhB, needing 180 min to reach a satisfactory degradation of 91.32%. The degradation processes of MO and RhB could be fitted by the first-order kinetics in Fig. S11 (ESI[†]). The corresponding reaction rate constants (k) were calculated to be 0.039 and 0.018 min⁻¹, and half-life times $(t_{1/2})$ to be 18.2 and 37.5 min for MO and RhB, respectively. The fact that the anionic dyes underwent faster degradation than the cationic dyes suggested that the degradation of dyes in the system took place in bulk solution rather than on the surface of the hybrid material. These results are consistent with the mechanism of degradation mentioned above. As the ζ -potential of the assembly was -10.7 mV, it is easy for the cationic RhB to be absorbed on a negatively charged surface, which prevents H2O2 from approaching

the surface of the material. $^{\rm 27}$ Less activated $\rm H_2O_2$ results in the slower degradation of RhB.

In summary, we have successfully constructed hybrid 2D nanosheets containing a Keggin POM and water soluble pillar[6]arene through a simple ionic self-assembly method. These hybrid 2D nanosheets can be used as efficient catalysts in dye degradations. The macrocyclic cavity of P_6 plays a dominant role in building 2D structures and the enhancement of degradation efficiency. Our findings may open a promising avenue to construct ionic–organic hybrid materials with a synergistic effect between POM and macrocyclic molecules to show more synergistic effects.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

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