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General Synthesis of Ordered Mesoporous Carbonaceous Hybrid Nanostructures with Molecularly Dispersed Polyoxometallates

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Abstract: Hybrid nanomaterials with controlled dimensions, intriguing components and ordered structures have attracted significant attention in nanoscience and technology. Herein, we report a facile and green polyoxometallate (POM)-assisted hydrothermal carbonization strategy for synthesis of carbonaceous hybrid nanomaterials with molecularly dispersed POMs and ordered mesopores. By using various polyoxometallates such as ammonium phosphomolybdate, silicotungstic acid, and phosphotungstic acid, our approach can be generalized to synthesize ordered mesoporous hybrid nanostructures with diverse compositions and morphologies (nanosheet-assembled hierarchical architectures, nanospheres, and nanorods). Moreover, the ordered mesoporous nanosheetassembled hierarchical hybrids with molecularly dispersed POMs exhibit remarkable catalytic activity toward the dehydration of tertbutanol with the high isobutene selectivity (100 %) and long-term catalytic durability (80 h).

Introduction

Hybrid nanomaterials with controlled compositions, structures, and dimensionalities have emerged as an important class of functional nanomaterials.^[1-2] The synergistic effect between different components with complementary functionalities in hybrid nanomaterials could endow them with new functionalities, which offers new opportunities in catalysis,^[3] energy conversion and storage,^[4-5] sensor,^[6] etc.^[7] Among different types of hybrid nanomaterials, carbonaceous hybrid nanomaterials are of particular interest owing to their outstanding thermal and chemical stabilities, and high electrical conductivity, which have shown

great potential in heterogeneous catalysis and electrocatalysis.[8-^{10]} Till now, various methods have been developed to prepare carbonaceous hybrid nanomaterials. For example, the direct thermal pyrolysis of biomass or biomass derivatives with metal compounds is a typical route for synthesis of carbonaceous hybrids due to its high efficiency and simplicity.^[11-13] Unfortunately, the aforementioned method suffers from the formation of nonuniform structures^[14-15] and generation of large amount inaccessible pores.^[16-17] Alternatively, hydrothermal carbonization (HTC) of carbohydrates has been recognized as an effective method for the controlled synthesis of functional carbonaceous materials.^[18-19] This straightforward water-based method commonly yields nonporous materials. Considering practical hybrid applications. carbonaceous nanostructures with periodically arranged pore channels and high pore volume are highly desirable and of great potential, in particular for heterogenous catalysis.^[20] The nanocasting method is good for the proof of principles by direct negative replication from hard templates; however, it suffers from inevitably tedious and harsh process.^[21] Generally, soft-templating method is a more prevailing approach for the synthesis of ordered mesopores by using organic surfactants as templates.^[21-22] Yet the direct use of soft templates for the HTC of biomass derivatives severely limits by the difficulty in controlling assembly ability of a soft template and biomass carbon resource at HTC temperatures (160-240 °C), which is found to be critical for the ordered pore formation.^[23-24] Therefore, the HTC strategies for the synthesis of biomassderived ordered mesoporous carbonaceous nanomaterials are still at an early stage of development, and exploring a general and straightforward strategy to improve the HTC of biomass derivatives is of scientific and technological importance.

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Polyoxometallates (POMs), a class of well-defined molecular clusters formed by early transition metal ions (Mo, W, V, U, Nb) and oxo ligands, have been extensively investigated for applications in catalysis,^[25] electronics,^[26] and energy storage^[27] because of their striking chemical and electronic properties. However, these materials generally showed poor application performance owning to their inaccessible active sites induced by the low surface area (3 m² g⁻¹ for commercial phosphomolybdic acid) and small pore volume.^[28] Considering that the POMs are known for their Brønsted acidity and our recent works found that the addition of acid was indispensable to successfully obtain ordered porous materials with HTC,^[23] one has reason to address the thorny problem by combination of HTC and POMs. Moreover, POMs with oxygen-enriched surface have the potential to serve as building blocks for the bottom-up assembly of hybrid materials, allowing a molecularly controlled approach.[29]

Herein, we report a facile and general POM-assisted HTC strategy for the synthesis of ordered mesoporous carbonaceous hybrid nanostructures with molecularly dispersed POMs as well as different compositions and morphologies (nanosheet-assembled hierarchical architectures, nanospheres and nanorods) from ubiquitous, nontoxic, and low-cost natural renewable resources. As a proof-of-concept application, the as made hybrids are used as acid catalyst for the dehydration of tert-butanol (TBA), exhibiting high activity and excellent long-term stability (80 h).

Results and Discussion

Commercially available poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) copolymer Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆) and renewable ribose were used as the soft template and carbon precursor, respectively. Ammonium phosphomolybdate (APMo, (NH₄)₃PO₄(MoO₃)₁₂) with a typical Keggin structure (Figure S1) was chosen as the additive POMs.[30-^{31]} It is widely known that the diethylether and other similar polyethylene glycols can bind to the acidic POMs via the induced dipole interactions between the hydronium cations of POMs and the ether.^[32-33] Here, the strong coordination interaction between APMo and PEO blocks of F127 is confirmed by the formation of porous APMo and UV-Vis analysis (Figure S2).[34] In a typical synthesis, the aqueous mixture containing APMo, F127, and ribose was stirred overnight at room temperature while a color change of the mixture from yellow to green can be explained by interaction between polyoxometallates and the saccharide (Figures S3 and 4). Subsequently, the HTC step was carried out at 140 °C for 8 h to synthesize ordered mesoporous carbonaceous nanohybrids with molecularly dispersed phosphomolybdic (PMo) units (denoted as PMo₁/OMHs).





Figure 1. Characterization of PMo₁/OMHs. a-c, SEM images. d, TEM image. e,f, TEM images viewed along the [001] axis (e) and [110] axis (f).

Scanning electron microscopy (SEM) image (Figure 1a) shows that the as-obtained material has a three-dimensional (3D) hierarchical architecture assembled from nanosheets. The nanosheets for assembling 3D hierarchical architectures have a thickness of about 90 nm and lateral size of up to few micrometers (Figure 1b). Interestingly, the high-magnification SEM image (Figure 1c) clearly shows that the nanosheets possess wellordered cylindrical mesopores on the surface. The lowmagnification transmission electron microscopy (TEM) image (Figure 1d) indicates that these mesopores are uniformly distributed across the entire nanosheet. Furthermore, TEM images viewed along the [001] direction (Figure 1e) and [110] direction (Figure 1f) confirm that these sheets have a highly ordered hexagonal p6m mesoporous pattern. The pore diameter and wall thickness are estimated to be 7 nm and 9 nm, respectively, yielding a cell parameter of 16 nm. The small-angle X-ray scattering (SAXS) pattern of PMo1/OMHs also exhibits a clear broad shoulder, well consistent with the periodic porous structure (Figure S5a).

High-angle annular dark field scanning transmission electron microscope (HAADF-STEM) image and the corresponding energy-dispersive X-ray (EDX) mappings reveal that C, Mo, P, and N elements distribute uniformly throughout the PMo1/OMHs (Figure 2a, b). The molar ratio of Mo to P (Table S1) is close to the theoretical stoichiometry in APMo (i.e. 12), indicating no substantial decomposition of PMo during the HTC process. Moreover, the zoom-in scanning transmission electron microscopy (STEM) image (Figure 2c) shows distinct uniform distributed bright dots (marked with purple arrows), suggesting the uniform distribution of PMo units into the carbon matrix (Figure S6). The diameter of the well-dispersed bright dots is estimated to be ~1.14 nm (inset of Figure 2c), which is consistent with the reported diameter of H₃PMo clusters (~1.1 nm),^[35-36] suggesting the molecular dispersion of the PMo units within the matrix. Powder X-ray diffraction (PXRD) pattern of the PMo₁/OMHs shows no peaks assigned to the parent crystalline APMo, further validating the homogeneous dispersion of the PMo (Figure S5b). The thermogravimetry (TG) curve of the PMo₁/OMHs shows a weight loss of 71 wt% at about 700 °C in air (Figure S5c), and the residuals are confirmed to be MoO₃ by the PXRD pattern (inset of

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Figure 2. Detailed structural characterization. a,b HAADF-STEM image (a) of PMo₁/OMHs and the corresponding EDX mappings (b) as marked by the red square in (a). c, High-magnification STEM image of PMo₁/OMHs. Inset: statistical size distribution histogram of the PMo units. The arrows indicate the molecularly dispersed PMo. d-f, FT-IR (d), XANES (e), and FT-EXAFS (f) spectra of the APMo and PMo₁/OMHs.

Figure S5c). These results indicate that the weight percentage of PMo blocks in PMo₁/OMHs is about 31.5 wt%. Fourier transform infrared spectroscopy (FT-IR) spectrum (Figure 2d) of PMo₁/OMHs shows the characteristic adsorption peaks at 1062, 958, 874, and 805 cm⁻¹, which correspond to v_{as}(P-O_a), v_{as}(Mo-O_d), v_{as}(Mo-O_b-Mo), and v_{as}(Mo-O_c-Mo), respectively (Figure S1).[37] The chemical state of Mo element in the nanostructured framework was explored by X-ray photoelectron spectroscopy (XPS) (Figure S5d). Usually, the Mo 3d core level spectrum of pure APMo consists of a spin-orbit doublet with peaks located at 232.4 and 235.7 eV, associated with Mo atoms in their higher oxidation state (i.e. Mo⁶⁺). As for the PMo₁/OMHs, the Mo 3d core level spectrum is considerably broader, owing to the presence of small amount of lower oxidation state (i.e. Mo5+).[38] The Mo Kedge X-ray absorption near-edge structure (XANES) spectra were also recorded to further investigate the oxidation states and space symmetry of Mo atoms in PMo₁/OMHs at the atomic level. Notably, there is a shoulder peak at around 20006 eV in the preedge region, the intensity of which can reflect the distortion degree of Mo atoms with octahedral coordination.[39] As shown in Figure 2e, the PMo₁/OMHs show similar intensity of the pre-edge compared to the pristine APMo, suggesting the remained Keggin structure. In addition, the absorption threshold position of Mo Kedge has been utilized to confirm the valence state of Mo atom. The slight shift of absorption edge toward lower energy value indicates the partial reduction of Mo in PMo1/OMHs, in agreement with the result from XPS analysis. Extended X-ray absorption fine structure (EXAFS) technique was employed to investigate the

local structure of the molecule. The Fourier transformed EXAFS spectra for the samples are shown in Figure 2f, demonstrating the radial atomic distribution around Mo atoms. The bulk APMo mainly exhibits four characteristic peaks, which can be assigned to the Mo=O double bond, two types of Mo-O distances, and a Mo-Mo distance, respectively.^[40-41] The EXAFS spectrum of asprepared PMo₁/OMHs shows similar peaks as that of APMo, confirming a well-maintained local structure of PMo units (Figure S5).



Figure 3. Characterization of other carbonaceous hybrid nanomaterials. a-c, TEM image (a), STEM image (b), and FT-IR spectrum (c) of POMs/OMHs derived from $H_4SiW_{12}O_{40}$. d-f, TEM image (d), STEM image (e), and FT-IR spectrum (f) of POMs/OMHs derived from $H_3PW_{12}O_{40}$.

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This facile HTC method can be also used for the synthesis of other carbonaceous hybrid nanomaterials with molecularly dispersed POMs with different compositions and morphologies by simply changing the types of used POMs (Figure 3 and Figure S7). Specifically, ordered mesoporous nanospheres and nanorods can be synthesized by using tungstosilicic acid (H₄SiW₁₂O₄₀) and tungstophosphoric acid (H₃PW₁₂O₄₀), respectively. In order to further extend this synthetic protocol to other biomasses, we also chose glucose, xylose and fructose as carbon precursors. All the synthesized hybrid nanomaterials show the typical ordered mesoporous flaky nanoarchitecture (Figures S8), demonstrating the generality of this method. PEO-PPO-PEO surfactants with different compositions (e.g. Pluronic F108 and P123) are also explored as the surfactant, leading to the formation of well-defined ordered mesoporous nanostructures as well (Figures S9 and S10). All these results have proven that this facile HTC method is a versatile strategy for the synthesis of carbonaceous hybrid nanomaterials with molecularly dispersed POMs.

The weak affinity between ribose and soft template, which is confirmed by dynamic light scattering (DLS, Figure S11), can be easily destroyed during HTC process as the low-yield HTC product shows no pores (Figure S12). To unveil whether the protonic acid plays a key role in our strategy, a group of controlled experiments with different pH values (~3.0, ~1.5, ~ 0.4 adjusted by adding sulfuric acid) in F127 and ribose system were carried out since POMs are also a strong Brønsted acid.^[42-43] Little amount of product could be obtained when the experiments were conducted at pH = 3.0 and 1.5. TEM images demonstrate that the products are irregular bulk or solid spheres (Figure S13). Only at pH less than 0.4, ordered mesoporous materials can be fabricated in high yield (Figure S14), which is consistent with our previous results.^[23, 44] These experimental evidences suggest that only the high-concentration acids can work effectively for the synthesis of ordered mesoporous materials. However, the pH values of the PMo₁/OMHs solutions at different reaction time established an equilibrium at about 1.5, a much lower H⁺ concentration (Table

S3). Thus, POM anions also play an important role for the interaction between F127 and ribose. The oxide salt counterparts like ammonium molybdate and ammonium of POMs metatungstate were chosen to replace POMs and a high yield of nanohybrids (~0.4 g) can still be obtained, indicating that the inorganic metal-oxo anions can also facilitate the HTC process. TEM images show that the resultant hybrids possess less ordered pores compared to POM-derived hybrids (Figure S15). Such a periodicity decrease is further certified by SAXS tests (Figures S15c, f). These findings indicate that the inorganic anions, such as molybdate and POM anions, can also promote the carbonization of saccharide and act as enhancer like H⁺ ions to enhance the interaction between the soft template and ribose, partly because the metal-oxo anions can strongly coordinate with both surfactants and carbon precursors (illustration of F127-APMo-Ribose complex, Figure S16). Meanwhile, POM anions with unique phosphates/silicates at the center of their 3D oxide framework behaves better in promoting the formation of longrange periodicity compared with their metal oxide counterparts.

To gain a deeper understanding of the self-assembly during the synthesis process for the PMo1/OMHs, the reaction was quenched at different HTC time. All the hybrids showed ordered mesoporous flaky structures with increasing lateral size along with HTC reaction time from 3 h to 12 h, as confirmed by various characterizations (Figures S18-22). IR tests reveal that the Keggin structures of PMo clusters in the composites are well preserved all the time (Figure S23b). According to TG curves (Figure S24a, b), the PMo content decreases notably from 61 wt% to 42 wt% when the reaction time increases from 2 h to 6 h, suggesting the gradual carbonization of ribose. Strikingly, for a longer reaction time (i.e. from 6 h to 10 h), the as-synthesized hybrids show a similar PMo mass fraction of about 30 wt% while the product yield kept increasing. It is assumed that the building blocks, i.e. cylindrical complex micelles (Figure S24c), consisting of constant mass ratio among F127, PMo, and oligomers, took part in the product assembly during this period.



Figure 4. Schematic illustration of the self-assembly process.

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Based on the aforementioned analysis, the formation mechanism of PMo1/OMHs could be proposed as a POMassisted carbonization process (Figure 4). When the mixture is stirred at room temperature, self-assembly and micellization among F127, APMo, and ribose happen, which is driven by hydrogen bond and coordination interaction. Upon heating, complex structure of the hybrid cylindrical micelles (i.e. F127-POMs-oligomers) can be well maintained with the assistance of both anion and cation of POMs as enhancers to resist the high HTC temperature. These building micelles can further assemble and stack into hexagonal symmetry structures. After that, further cross-linking carbonization of the oligomers, which is facilitated by POMs, can solidify the ordered hybrid structure and simultaneously incorporate the monodispersed POMs in carbonaceous frameworks, resulting in the formation of hybrid nanomaterials.

The triblock copolymer in as-obtained samples could be removed by treatment in hot solvent and the subsequent calcination in N₂ atmosphere (Figure S25). After the removal of the triblock copolymer, the ordered mesoporous architectures can be well reserved (Figure S26a and Figure 5a). To keep the Keggin-patterned POMs, a low pyrolysis temperature (350 °C) was selected due to the relatively low decomposition temperature of APMo (denoted as PMo1/OMHs-350 with 31 wt% content of PMo unit, PMo₁/OMHs-2-350 with 45 wt% content of PMo unit).^[44] Elemental mappings show homogeneous distribution of C. Mo. P. and N elements within the hybrids (Figure S26b-d). XAFS and FT-IR spectra further confirm the Keggin-structure after the treatment (Figure 5b-d). The Brunauer-Emmett-Teller (BET) specific surface area and pore volume of the product with calcination at only 350 were estimated to be 80.4 m² g⁻¹ and 0.12 cm³ g⁻¹, much higher than that of pure APMo (Figure S27).



Figure 5. Structural and composition characterization of catalysts. a, STEM image of PMo₁/OMHs-2-350. b-d, XANES (b), FT-EXAFS (c), and FT-IR (d) spectra of PMo₁/OMHs-2-350 and APMo. e, ³¹P MAS NMR spectra of TMPO-PMo₁/OMHs-350 and TMPO-PMo₁/OMHs-2-350. f, Catalytic performance of TBA dehydration on selected catalysts.

To gain insight into the nature of catalytic sites, acid properties were characterized by ³¹P solid-state magic-angle-spinning (MAS) NMR of adsorbed trimethylphosphine oxide (TMPO).^[37, 46] As shown in Figure 5e and Figure S28a, the main chemical shifts at -5.9 ppm and -8.1 ppm for all samples correspond to phosphorus in the parent PMo. The broad resonance peaks in the range of 70-95 ppm could be attributed to the TMPO bound to Brønsted acid site forming TMPOH⁺ ion complex, whereas the ³¹P

resonance peaks observed in the region of 50-70 ppm may be assigned to TMPO bounded to Lewis acid sites and two TMPO adsorbed on one protonic site. The peak centered at 45 ppm most likely results from the physisorbed TMPO. Ammonia temperatureprogrammed desorption (NH₃-TPD) also indicates a suitable acid property as shown in Figure S28b, which could increase the acid catalytic activity, for example dehydration.^[47] The dehydration of tert-butanol was then chosen as a model reaction using a fix bed reactor to evaluate the catalytic performance of the PMo1/OMHs-350. Except isobutene, no other products were founded in these reactions. Figure 5f shows the conversion of TBA slightly decreased from 100 % to 85 % in an 80 h reaction. In contrast, the composite prepared by wetness impregnation of PMo onto the ordered mesoporous carbons (OMCs-PMo) shows inferior catalytic activity and stability. This may result from carbon deposits catalyzed by the strong acid sites,[48] corresponding to NH₃ desorption peak from 250-350 °C (Figure S28b). HTC-PMo behaves much worse catalytic performance, indicating the importance of mesopores to enhance the activity. These results demonstrate the advantages of the molecularly dispersed POMs and abundant ordered mesopores towards the catalytic applications.

Conclusion

In summary, we have developed a facile and general POMassisted HTC strategy for the synthesis of ordered mesoporous carbonaceous hybrids with molecularly dispersed POMs. To the best of our knowledge, this is the first report on the synthesis of such kind of unique hybrids with molecularly dispersed POMs. The formation mechanism and structure of the novel composites were thoroughly studied. Although the originally designed role of POMs here was only to effectively enhance the reaction kinetics of the HTC process as acidic catalyst, their unexpectedly versatile properties originated from their coordination ability were quickly recognized and enabled the formation of more diverse products. For example, this approach was successfully coupled with different kinds of POMs to directly produce novel ordered mesoporous carbonaceous hybrids with molecularly dispersed POM in matrix for the first time. Impressively, when used as a catalyst, the ordered mesoporous POMs carbonaceous hybrids show excellent catalytic activity and stability toward the dehydration of TBA. We believe these unique hybrid materials may demonstrate new possibilities for the design and construction of well-ordered mesoporous hybrid nanomaterials towards a variety of practical applications, especially for single-molecule heterogeneous catalyst.

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RESEARCH ARTICLE

Entry for the Table of Contents



A facile and green polyoxometallate (POM)-assisted hydrothermal carbonization strategy is developed for synthesis of carbonaceous hybrid nanomaterials with molecularly dispersed POMs and ordered mesopores, which exhibit remarkable catalytic activity toward the dehydration of tert-butanol.