A Polymer-Oriented Self-Assembly Strategy toward Mesoporous Metal Oxides with Ultrahigh Surface Areas

Hailong Xiong, Tunan Gao, Kaiqian Li, Yali Liu, Yali Ma, Jingwei Liu, Zhen-An Qiao,* Shuyan Song, and Sheng Dai

Mesoporous metal oxides (MMOs) have attracted comprehensive attention in many fields, including energy storage, catalysis, and separation. Current synthesis of MMOs mainly involve use of surfactants as templates to generate mesopores and organic reagents as solvents to hinder hydrolysis and condensation of inorganic precursors, which is adverse to adjusting the interactions between surfactants and inorganic precursors. The resulting products have uncontrollable pore structure, crystallinity, and relatively lower surface areas. Here, a facile and general polymer-oriented self-assembly strategy to synthesize a series of MMOs (e.g., TiO$_2$, ZrO$_2$, NbO$_5$, Al$_2$O$_3$, Ta$_2$O$_5$, HfO$_2$, and SnO$_2$) by using cationic polymers as porogens and metal alkoxides as metal oxide precursors in a robust aqueous synthesis system are reported. Nitrogen adsorption analysis and transmission electron microscopy confirm that the obtained MMOs have ultrahigh specific surface areas and large pore volumes (i.e., 733 m$^2$ g$^{-1}$ and 0.485 cm$^3$ g$^{-1}$ for mesoporous TiO$_2$). Moreover, the structural parameters (surface area, pore size, and pore volume) and crystallinity can be readily controlled by tuning the interactions between cationic polymers and precursors. The as-synthesized crystalline mesoporous TiO$_2$ exhibits promising performance in photocatalytic water splitting of hydrogen production and a high hydrogen production rate of 3.68 mol h$^{-1}$ g$^{-1}$.

1. Introduction

Mesoporous metal oxides (MMOs) have been of great interest over the past decades for comprehensive applications including energy storage, selective oxidation, adsorption, and gas sensor.[1–11] Most of these applications are strongly relied on their superior physical, chemical properties, and the combination of their advanced structural properties such as high specific surface areas, large pore volumes, and narrow pore size distributions.[12] Various synthetic methods have been developed to synthesize MMOs. One promising route is nanocasting method,[12–21] which depends on the usage of mesoporous silica, mesoporous carbon, or polymer as hard templates to provide the desired mesoporous structure and subsequent removal of templates by etching or calcination to finally obtain MMOs. However, the application of this method suffers from some limitations, for instance, the mesoporous characteristics of such oxides are completely relied on the framework of hard templates. Moreover, there are only a few templates available for use, and the procedure is tedious, costly as well as not suitable for mass production, which greatly hinders their practical applications.

To overcome these obstacles, a molecular self-assembly method based on cooperative organization of surfactant templates and inorganic precursors has been put forward, called evaporation-induced self-assembly (EISA) method.[22–32] The key issue of EISA method is a controllable and slow hydrolysis–condensation process of metal oxide precursors catalyzed by acid or base in an organic solvent synthesis system.[13] The interactions between surfactants and inorganic precursors are also critical for the formation of mesostructures, including electrostatic interactions ($\text{S}^+\text{I}^-$, $\text{S}^-\text{I}^+$), ligand–metal interactions, coordination type interactions, and so on.[14] In the past of years, Zhao’s group employed traditional triblock copolymer (e.g., Pluronic F127, P123) and diblock copolymer poly (ethylene oxide)-$b$-polystyrenem (PEO-$b$-PS) as the structure-directing agents to successfully prepare a series of highly ordered MMOs (e.g., TiO$_2$, Nb$_2$O$_5$, WO$_3$, In$_2$O$_3$, and Al$_2$O$_3$) by the EISA method.[35,36]
By using acetate groups as a complexing agent to control the hydrolysis and condensation of metal alkoxides, Fan et al. synthesized multicomponent MMOs in a sol–gel solution composed of hydrochloric acid, acetic acid, and ethanol.\[^{37}\] Suib and co-workers reported a sol–gel-based inverse micelle method through hydrogen bonding, which gave direct access to crystalline and thermally stable mesoporous materials by using HNO\(_3\) to prevent the condensation of metal precursors and balance the charge of reaction system.\[^{38}\] Despite the great success of EISA approach, it also has its deficiencies. For example, the synthesis based on complicated sol–gel processes is quite sensitive to experimental conditions, such as temperature, pH, relative humidity, solvent purity, and so forth, which can significantly affect the hydrolysis–condensation process of metal oxide precursors. Introducing plenty of organic solvents plus an acid or an additive agent to hinder hydrolysis and condensation results in the synthesis process laborious, cost-consuming and time-consuming.\[^{39–41}\] Moreover, it is really of hardship to adjust the interactions between surfactants and inorganic precursors in organic solvent synthesis system, which leads to the crystallinity, morphology, and porous structure of products uncontrollable.\[^{39}\] Above all, the resulting MMOs by EISA method have relatively lower surface areas, usually lower than 250 m\(^2\) g\(^{-1}\).

Here, we demonstrate a facile, versatile, yet unexplored method, referred to as a polymer-oriented self-assembly strategy, for the preparation of a series of MMOs (e.g., TiO\(_2\), ZrO\(_2\), NbO\(_5\), Al\(_2\)O\(_3\), Ta\(_2\)O\(_5\), HfO\(_2\), and SnO\(_2\)) with ultrahigh surface areas and monomodal pore sizes by using metal alkoxides as metal oxide precursors in a robust aqueous synthesis system (Scheme 1). In this approach, commercial cationic polymers, polyethylenimine (PEI), or polydimethylallylammonium chloride (PDADMAC) have been employed as porogens on the mesoscale to produce abundant mesopores. Acetic acid (HOAc) not only acts as a pH regulator to dictate the type of interactions between titanium species and polymers, but also as a coordinating agent to modify condensation kinetics of metal alkoxides and balance charge of reaction system. The structural properties (e.g., porous architectures, crystal phases) and morphologies of obtained MMOs can be easily adjusted by tuning the pH of reaction system (pH\(_r\)). When pH\(_r\) > pH\(_{\text{i.e.}}\) (isoelectric point of metal oxides), the positively charged PEI (S\(^+\)) interacts with anionic metal oligomers through an electrostatic interaction (S\(^+\)I\(^-\)) and thus triggers the organic–inorganic assembly into ultrahigh surface area MMOs. The resulting MMOs have ultrahigh surface areas, 733 m\(^2\) g\(^{-1}\) for TiO\(_2\), 422 m\(^2\) g\(^{-1}\) for ZrO\(_2\), 360 m\(^2\) g\(^{-1}\) for NbO\(_5\), 393 m\(^2\) g\(^{-1}\) for Al\(_2\)O\(_3\), 190 m\(^2\) g\(^{-1}\) for Ta\(_2\)O\(_5\), 344 m\(^2\) g\(^{-1}\) for HfO\(_2\), and 174 m\(^2\) g\(^{-1}\) for SnO\(_2\). When pH\(_r\) < pH\(_{\text{i.e.}}\), highly crystallized mesoporous materials can be prepared in the presence of a type of S\(^+\)X\(^-\)I\(^+\) organic–inorganic interaction mode, where X represents acetate ions (CH\(_3\)COO\(^-\)).

The as-synthesized crystalline mesoporous TiO\(_2\) with a relatively high surface area shows properties that are promising application in photocatalytic water splitting of hydrogen production, a high photocatalytic hydrogen generation rate of 3.68 mol h\(^{-1}\) g\(^{-1}\), and exhibits great potential for anticipative applications in gas sensor, energy storage, and catalysis.

2. Results and Discussion

A series of MMOs with ultrahigh surface areas have been synthesized by the polymer-oriented self-assembly strategy in
a robust aqueous synthesis system. Mesoporous TiO$_2$ labeled as MT$x$, $x$ referred to the amount of HOAc, was took as a representative in the following discussion. In this approach, tetrabutyl titanate (TBOT) first hydrolyzed in H$_2$O/PEI/HOAc solution under stirring at room temperature for 2 h to form mesoporous titanium/PEI composites (Figure S1 and Table S1, Supporting Information). Then, the resulting titanium/PEI composites were then hydrothermally treated at 100 °C for cross-linking and condensation of titanium oligomers. Finally, the obtained composites were washed with distilled water and absolute ethanol several times in sequence to remove PEI, giving rise to mesoporous TiO$_2$. When the amount of HOAc ranged from 0 to 1.5 mL, the ultrahigh surface area mesoporous TiO$_2$ could be obtained. When the amount of HOAc was larger than 2.5 mL, we could get mesoporous TiO$_2$ with highly crystallized framework. It was noteworthy that the yield of products was as high as ≈95% and grams of samples could be easily synthesized in one bath.

The effect of HOAc content on the mesostructure and morphology of mesoporous TiO$_2$ was first investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). When HOAc content was less than 1.5 mL, MT0 and MT1.0 were used as representatives, SEM images (Figure S2a,b, Supporting Information) of MT0 and MT1.0 disclosed approximate microscale spheres with partial connections. TEM images (Figure 1a,b) of these two samples exhibited a large number of uniform mesopores with an open pore structure and the pore sizes were estimated to be about 2.6–3.2 nm. High-resolution TEM (HRTEM) image (Figure S2c, Supporting Information) and selected-area electron diffraction (SAED) pattern (inset of Figure 1b) of MT1.0 confirmed the amorphous nature. Besides, there were a few nanosheets coating outside the TiO$_2$ microsphere, which was attributed to further growth and condensation of titanium oligomers during hydrothermal process. To study the element distribution and chemical composition for MT1.0, EDX spectra (Figure S2d, Supporting Information) combined with scanning TEM and EDS mapping images (Figure 1g) were measured, showing the uniform distribution of Ti, O, C, and N. The presence of carbon and nitrogen phases indicated it still had residual PEI molecules in mesoporous TiO$_2$ after washing with water and absolute ethanol, which was beneficial for maintaining the stability of mesostructure. When HOAc content was more than 2.5 mL, the pore structure and morphology were significantly different from MT1.0. MT2.5 and MT3.0 showed similar irregular bulk morphologies with rough surfaces in SEM images (Figure S3a,b, Supporting Information), implying the existence of abundant pores. According to TEM images (Figure S3c, Supporting Information; Figure 1c), MT2.5 and MT3.0 were both consisted of small TiO$_2$ nanocrystals about 8.0 nm and the mesopores about 7.0 nm were interparticle voids. Lattice fringes with a distance of 0.35 nm can be found in HRTEM images.

![Figure 1.](image-url) a–c) TEM images and d) HRTEM image of mesoporous TiO$_2$: MT0 (a), MT1.0 (b), and MT3.0 (c,d). The insets in (b) and (c) are SAED patterns of MT1.0 and MT3.0. e) Nitrogen sorption isotherms and f) pore size distributions of mesoporous TiO$_2$: MT0, MT1.0, MT2.0, and MT3.0. g) Scanning TEM image and the corresponding EDS mapping images of elemental Ti, O, C, and N for MT1.0.
were calculated to be in the range of 226–254 m$^2$ g$^{-1}$, reflecting the presence of large mesopores (6.8–7.2 nm). The $S_{\text{BET}}$ and pore volume of the products were calculated to be in the range of 226–254 m$^2$ g$^{-1}$ and 0.288–0.386 cm$^3$ g$^{-1}$. The small-angle X-ray powder diffraction (XRD) patterns (Figure S6, Supporting Information) of these samples displayed broad diffraction peaks, indicating a homogeneous wormhole-like mesopores, which were consistent with those observed in TEM images.

Wide-angle XRD analysis was employed to confirm the crystal phase and composition of mesoporous TiO$_2$. Figure 2a displayed the transition process from amorphous to crystalline phase with the increase of HOAc content. XRD pattern of MT1.0 showed no obvious diffraction patterns, suggesting its amorphous nature. For MT3.0, all diffraction peaks can be assigned to highly crystalline anatase phase (space group $14I/amd$). The crystal sizes of nanocrystals calculated using the Scherrer equation were about 8.0 nm, which matched well with the observed results from TEM image. Upon further increasing HOAc content, the crystallinity of these products gradually increased (Figure S7, Supporting Information), which further indicated that HOAc indeed played a crucial part in the crystallinity of mesoporous TiO$_2$. Raman test was used to further investigate the crystal phase of mesoporous TiO$_2$. Raman spectra (Figure 2b) of MT1.0 showed some weak peaks ranging from 50 to 800 cm$^{-1}$, indicating that its framework was amorphous. While MT2.0 and MT3.0 displayed four anatase Raman transitions, which could be assigned to $E_g$ (148.8 cm$^{-1}$), $B_g$ (404.3 cm$^{-1}$), $A_1g$ (516.3 cm$^{-1}$), and $E_g$ (648.7 cm$^{-1}$), respectively. The reflected crystallographic microstructures were consistent with HRTEM images and XRD patterns. Above results illustrated that the structural properties (e.g., porous architectures and crystal phases) and morphologies of as-synthesized samples can be easily controlled by tuning HOAc content.

The structural properties of mesoporous TiO$_2$ were elucidated by various spectroscopic measurements. Fourier transform infrared (FT-IR) spectra, solid-state $^{13}$C and $^1$H nuclear magnetic resonance (NMR) spectroscopy were employed to explore the role of HOAc during the synthesis and confirm the presence of PEI in mesoporous TiO$_2$. For MT1.0, the characteristic absorptions of FT-IR spectra (Figure 2c) at 3241 and 1620 cm$^{-1}$ could be assigned to the stretching vibrations of NH groups. The peaks at 1047 cm$^{-1}$ could be attributed to the C–N stretching vibrations of NH groups. The characteristic absorption of FT-IR spectra at 3241 and 1620 cm$^{-1}$ could be assigned to the stretching vibrations of NH groups. The peaks at 1047 cm$^{-1}$ could be attributed to the C–N stretching vibrations of NH groups. The FT-IR spectra (Figure 2d) of MT1.0 showed some weak peaks ranging from 50 to 800 cm$^{-1}$, indicating that its framework was amorphous. While MT2.0 and MT3.0 displayed four anatase Raman transitions, which could be assigned to $E_g$ (148.8 cm$^{-1}$), $B_g$ (404.3 cm$^{-1}$), $A_1g$ (516.3 cm$^{-1}$), and $E_g$ (648.7 cm$^{-1}$), respectively. The reflected crystallographic microstructures were consistent with HRTEM images and XRD patterns. Above results illustrated that the structural properties (e.g., porous architectures and crystal phases) and morphologies of as-synthesized samples can be easily controlled by tuning HOAc content.

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**Table 1.** Structural properties of mesoporous metal oxides.

| Sample | Polymer | $S_{\text{BET}}$/$\alpha$ [m$^2$ g$^{-1}$] | Pore size [nm] | $V_1$/$\beta$ [cm$^3$ g$^{-1}$] |
|--------|---------|-------------------------------------|---------------|-------------------------------|
| M0     | PEI     | 461                                 | 2.6           | 0.296                         |
| MT1.0  | PEI     | 733                                 | 3.2           | 0.485                         |
| MT2.0  | PEI     | 289                                 | 7.0           | 0.577                         |
| MT3.0  | PEI     | 226                                 | 7.0           | 0.384                         |
| ZrO$_2$| PEI     | 422                                 | 3.1           | 0.593                         |
| HfO$_2$| PEI     | 344                                 | 2.6           | 0.195                         |
| Nb$_2$O$_5$| PEI | 360                                 | 2.6           | 0.457                         |
| Ta$_2$O$_5$| PEI | 190                                 | 2.1           | 0.176                         |
| Al$_2$O$_3$| PEI | 360                                 | 7.0           | 0.883                         |
| SnO$_2$| PEI     | 393                                 | 7.0           | 1.044                         |
| TiO$_2$| PDADMAc | 575                                 | 2.6           | 0.335                         |
| ZrO$_2$| PDADMAc | 328                                 | 2.6           | 0.242                         |

$^a$BET surface area; $^\beta$Total pore volume.

(Figure S3d, Supporting Information; Figure 1d), corresponded to d-spacing of the (101) crystal plane of anatase, which verified the crystalline pore walls of MT2.5 and MT3.0. The continuous sharp circled on the SAED (inset of Figure 1c) further confirmed that MT3.0 had a polycrystalline anatase phase with high crystallinity. When HOAc content was in the range of 1.5 to 2.5 mL, it can be observed that MT2.0 was a mixture consisted of amorphous and crystalline phase (Figure S4a,b, Supporting Information), indicating it was an intermediate phase.

The pore structure of mesoporous TiO$_2$ was investigated by nitrogen adsorption–desorption analysis. Figure 1e and Figure S5a (Supporting Information) showed the nitrogen sorption isotherms of all of samples had typical type IV curves, indicating the existence of mesoporous structure. The sorption isotherms of the products with HOAc content below 1.5 mL exhibited an distinct capillary condensation step at a relative pressure of 0.2–0.4, corresponding to a small pore size of 2.6–3.2 nm (Figure 1f). The specific Brunauer–Emmett–Teller (BET) surface areas ($S_{\text{BET}}$) and pore volumes of these samples were as high as 461–733 m$^2$ g$^{-1}$ and 0.296–0.629 cm$^3$ g$^{-1}$, respectively (Figure S5b, Supporting Information, Table 1, and Figure S2), which were higher than those reported for similar materials (Table S3, Supporting Information). For the samples synthesized with HOAc content above 2.5 mL, the isotherms of these samples exhibited a H2 hysteresis loop along with another typical pore condensation step at a higher relative pressure ($P/P_0 = 0.4–0.8$), reflecting the presence of large mesopores (6.8–7.2 nm). The $S_{\text{BET}}$ and pore volume of the products were calculated to be in the range of 226–254 m$^2$ g$^{-1}$ and 0.288–0.386 cm$^3$ g$^{-1}$. The small-angle X-ray powder diffraction (XRD) patterns (Figure S6, Supporting Information) of these samples displayed broad diffraction peaks, indicating a homogeneous wormhole-like mesopores, which were consistent with those observed in TEM images.
The overall composition of mesoporous TiO\textsubscript{2} was characterized by X-ray photoelectron spectroscopy (XPS). XPS survey spectra (Figure S10a, Supporting Information) showed four similar peaks due to species containing Ti, O, C, and N elements in all samples. The Ti 2p spectra (Figure 2e) for MT3.0 presented two peaks at binding energy of 458.5 and 464.1 eV, attributable to Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2}, respectively, of Ti\textsuperscript{4+} in TiO\textsubscript{2}. While the binding energy of Ti 2p for MT1.0 shifted to lower binding energy compared to MT3.0, which may be ascribed to the change of chemical environment for Ti, due to the interaction of PEI with TiO\textsubscript{2}.[50] The O 1s spectra (Figure 2f) for MT1.0 and MT3.0 showed a stronger peak at 529.7 eV with a broader shoulder at 531.7 eV, which were ascribed to lattice oxygen in TiO\textsubscript{2} and bridging hydroxyls, respectively.[51] Furthermore, the C 1s spectra (Figure S10b, Supporting Information) revealed the presence of two types of C bonds. The strong peak at 284.6 eV corresponded to adventitious elemental C, and the other two peaks at 285.8 and 288.4 eV were characteristic of carbonates.[52] The N 1s spectra (Figure S10c, Supporting Information) exhibited three peaks with binding energies of 398.8, 399.4, and 400.8 eV, which matched well the characteristic peaks of primary amino, secondary amino, and tertiary amino groups, respectively.[53]

Based on the above results, we came up with a polymer-oriented self-assembly strategy for the synthesis of mesoporous TiO\textsubscript{2} with ultrahigh surface area. This approach enabled a high degree of control over structural parameters, crystallinity, and morphology. As shown in Scheme 1, at the first stage, TBOT was added into \textit{H\textsubscript{2}O}/PEI/HOAc solution, titanium oligomers hydrolyzed from TBOT could associate with PEI molecules through electrostatic interaction, giving rise to a white colloidal suspension of tiny titanium/PEI composites. When the amount of HOAc was less than 1.5 mL (MT1.0), TiO\textsubscript{2} was negatively charged because the pH\textsubscript{i} (about 7.0) was higher than pH\textsubscript{e} of TiO\textsubscript{2} (about 4.5). PEI was positively charged because portions of amine were protonated. Driven by Coulomb force, the positively charged PEI (S\textsuperscript{+}) molecules captured anionic titanium oligomers (I\textsuperscript{-}) and located in the interstitial space of titanium oligomers to play a role of porogen on mesoscale through electrostatic interaction (S\textsuperscript{+} I\textsuperscript{-}) and thus initiated organic–inorganic assembly into mesoporous TiO\textsubscript{2}/PEI composites. By the subsequent hydrothermal treatment at 100 °C, the cross-linking and condensation of titanium oligomers was further improved. By washing with distilled water and absolute ethanol several times, most of PEI molecules were dissolved, leaving behind a large amount of mesopores. However, there were still many of PEI molecules residues in mesoporous TiO\textsubscript{2}. Owing to strong electrostatic interaction between titanium species and PEI molecules, the presence of PEI molecules were incorporated into the structure of mesoporous TiO\textsubscript{2}, which contributed to maintaining the mesostructured stability, allowing formation of ultrahigh surface area mesoporous TiO\textsubscript{2}. When the amount of HOAc was more than 3 mL (MT3.0), the surface charges of titanium species have been transformed from negative to positive because the pH\textsubscript{i} (about 4.0) was lower than pH\textsubscript{e} of TiO\textsubscript{2}. Acetate groups could bind to titanium species through bridging modes and interact with PEI molecules by hydrogen-bonding interaction. Therefore, acetate groups served as a glue which bound PEI molecules around titanium species through organic–inorganic interaction mode (S\textsuperscript{+} X\textsuperscript{-} I\textsuperscript{+}). Compared to strong electrostatic interaction (S\textsuperscript{+} I\textsuperscript{-}), this interaction between titanium species and PEI was relatively weaker. After hydrothermal treatment, S\textsuperscript{+} X\textsuperscript{-} I\textsuperscript{+} was not strong enough to restrict the growth of TiO\textsubscript{2} nanocrystals under high temperature and high pressure environment, resulting in highly crystallized mesoporous TiO\textsubscript{2}.

Figure 2. a) XRD patterns and b) Raman spectra of mesoporous TiO\textsubscript{2}: MT1.0, MT2.0, and MT3.0. c) FT-IR spectra, d) solid state \textsuperscript{13}C NMR spectra, e) Ti 2p, and f) O 1s high-resolution XPS spectra of mesoporous TiO\textsubscript{2}: MT1.0 and MT3.0.
Under the guidance of mechanism studies, the polymer-oriented self-assembly strategy can be extended to synthesize other types of MMOs with ultrahigh surface areas, including 
ZrO2, NbO5, Al2O3, Ta2O5, HfO2, and SnO2. A large number of mesopores with uniform open pores of these MMOs can be clearly observed from TEM images (Figure 3a–f). XRD patterns indicated that most MMOs except for mesoporous Al2O3 were amorphous at atomic scale (Figure S11, Supporting Information). Crystalline Al2O3 consisting of agglomerated nanoflakes was obtained after calcining mesoporous AlOOH at 400 °C in air (Figure S12a–d, Supporting Information). Nitrogen sorption data (Figure 3g; Figure S13, Supporting Information) indicated that all these samples possessed ultrahigh surface areas, uniform pore size distributions, and large pore volumes. The S\textsubscript{BET} of these samples were as high as 422 m\textsuperscript{2} g\textsuperscript{-1} for ZrO2, 360 m\textsuperscript{2} g\textsuperscript{-1} for Nb2O5, 360 m\textsuperscript{2} g\textsuperscript{-1} for AlOOH, 393 m\textsuperscript{2} g\textsuperscript{-1} for Al2O3, 190 m\textsuperscript{2} g\textsuperscript{-1} for Ta2O5, 344 m\textsuperscript{2} g\textsuperscript{-1} for HfO2, and 174 m\textsuperscript{2} g\textsuperscript{-1} for SnO2 (Table 1).

MMOs can also be synthesized by using hydrochloric acid (HCl) as a pH regulator, and the corresponding results were shown in Figure S14a–g and Table S4 (Supporting Information). The resulting mesoporous TiO2 had a surface area of 550 m\textsuperscript{2} g\textsuperscript{-1}, which was lower than that of MT1.0 (733 m\textsuperscript{2} g\textsuperscript{-1}). This may be attributed to the complexation of HOAc that can modify the condensation kinetics of metal alkoxides. Moreover, under alkaline condition, our approach was still suitable for the synthesis of MMOs (Figure S15 and Table S5, Supporting Information). More importantly, that other nonsurfactant cationic polymers, such as PDADMAC, was also capable of directing the synthesis of MMOs (Figure S16 and Table S6, Supporting Information). These results confirmed that our synthesis system was very robust.

Photocatalytic water splitting for hydrogen production is one of the key technologies for addressing global energy problem.\textsuperscript{[54]} TiO2, one of the most important oxide semiconductors, has been proven to be a promising photocatalyst for photocatalytic hydrogen production, owing to its cheap price, abundance, low nontoxicity, and good stability.\textsuperscript{[55–57]} As part of this effort, we performed H\textsubscript{2} evolution experiment from water splitting to evaluate the photocatalytic activity of as-prepared mesoporous TiO2 (1 wt% Au loaded) with CH\textsubscript{3}OH as the sacrificial agent under a 300 W xenon lamp irradiation. With increasing the calcination temperature from 400 to 600 °C, the crystallinity of MT3.0 gradually improved while the corresponding S\textsubscript{BET} decreased from 152 to 40 m\textsuperscript{2} g\textsuperscript{-1} (Figure S17a–c and Table S7, Supporting Information). Figure 4a showed the temperature-dependent photocatalytic H\textsubscript{2} generation rates using obtained MT3.0 sample and commercial P25 TiO\textsubscript{2} as photocatalysts. The H\textsubscript{2} evolution rates increased with increasing the calcination temperature and reached a maximum at 500 °C, then decreased with further increasing the calcination temperature. The maximum H\textsubscript{2} evolution rate of 3.68 mmol h\textsuperscript{-1} g\textsuperscript{-1} for MT3.0-500 (MT3.0 calcined at 500 °C) was higher than that of commercial P25 TiO\textsubscript{2} (3.09 mmol h\textsuperscript{-1} g\textsuperscript{-1}), which was attributed to the large surface area and high crystallinity of MT3.0-500. The S\textsubscript{BET} of MT3.0-500 (101 m\textsuperscript{2} g\textsuperscript{-1}) was much larger than that of P25 TiO\textsubscript{2} (50 m\textsuperscript{2} g\textsuperscript{-1}). In general, the large surface area not only accommodated more catalysis active sites and accelerated the surface reaction kinetics, but also facilitated the transportation of reactant and product ions/molecules, which was responsible for photocatalytic activity.\textsuperscript{[58]} Furthermore, high crystallinity generally meant less defects and would be beneficial for the transfer and separation of photogenerated carriers.\textsuperscript{[59]} Thus, the photocatalytic activity of MT3.0-500 was higher than that of MT1.0-400. The photocatalytic activity of MT3.0-600 was lower than that of MT3.0-500, which was attributed to the occurrence of phase change and low surface area of MT3.0-600. Moreover, the temperature-dependent photocatalytic activities of MT1.0 were also investigated and the corresponding results were shown in Figure S18 and Table S8 of the Supporting Information. The MT1.0-400 exhibited a much higher photocatalytic H\textsubscript{2} generation rate of 4.49 mmol h\textsuperscript{-1} g\textsuperscript{-1} than those of other photocatalysts. Generally, stability was a crucial factor for photocatalysts in practical applications. To show its long-term durability and reusability, the photocatalyst was reused for photocatalytic H\textsubscript{2} production in 5 cycling tests within 20 h photocatalytic period. As shown

![Figure 3. a–f) TEM images and g) nitrogen sorption isotherms of MMOs.](image-url)
in Figure 4b, no noticeable decrease in H₂ production rate was observed, which indicated the photocatalyst possessed excellent stability.

To confirm the great influence of material structure on photocatalytic activity, photoluminescence (PL) spectra were performed, which is a very useful technique to disclose the photophysical processes of semiconductors, such as charge-transfer and separation. From PL spectra shown in Figure 4c, the lower emission intensity of MT3.0-500 than that of P25 TiO₂ was observed clearly, indicating a more efficient charge separation. The electrochemical impedance measurement was employed to further clarify the photogenerated charge transfer efficiency. As shown in Figure 4d, a smaller interfacial resistance for MT3.0-500 than that of P25 TiO₂ was observed, suggesting a higher separated efficiency of photogenerated electron–hole pairs. These results may contribute to the high photocatalytic activity of MT3.0-500.

3. Conclusion

In summary, a facile and general polymer-oriented self-assembly strategy, using water as a solvent and nonsurfactant cationic polymers as porogens, for the fast and scalable synthesis of a series of MMOs (e.g., TiO₂, ZrO₂, NbO₅, Al₂O₃, Ta₂O₅, HfO₂, and SnO₂) with ultrahigh specific surface areas and large pore volumes was developed. The presented strategy overcomes the defects associated with the traditional sol–gel-based self-assembly route in organic solvents synthesis system, which would strongly promote the industrial application of MMOs. These obtained MMOs possessing superior porous properties will be tailored for promising applications in energy conversion, catalyst, gas separation, and sensing. This approach may open up new opportunities for fabricating other high surface area mesoporous materials, such as mixed-metal oxides, metal phosphates, metal sulfides, and oxide nanostructures.

4. Experimental Section

Materials: TBOT, zirconiumn butoxide (Zr(OBu)₄), hafnium ethoxide, niobium ethoxide, tantalum ethoxide, aluminium ethoxide, tin(II) ethoxide, PEI (average Mw 600), and PDADMAc were purchased from Sigma-Aldrich Co. HOAc concentrated HCl and ammonium hydroxide (NH₃·H₂O) were of analytical grade and obtained from Shanghai Chemical Corp.

Synthesis of MMOs: All the MMOs were synthesized by the polymer-oriented self-assembly strategy using nonsurfactant cationic polymers as porogens and metal alkoxides as metal oxide precursors, certain quantity HOAc as the pH regulator and complexing agent, and distilled water as a solvent. A typical synthesis of mesoporous TiO₂: 3.4 mL TBOT, 1.6 g PEI, and a certain quantity HOAc were added into 30 mL distilled water. After stirring for 2 h, the obtained colloidal suspensions were transferred into an 80 mL autoclave and reacted at 100 °C for 24 h. The resulting powders were washed and then dried at 75 °C for 12 h. In order to investigate the effect of HOAc content on the pore structure and crystallinity of mesoporous TiO₂, the HOAc content verified from 0 to 8 mL in the reaction system.
The synthesis of other MMOs, except for mesoporous Al₂O₃, was completed identically to that outlined for mesoporous TiO₂. For the synthesis of mesoporous Al₂O₃, 10 mmol Al(C₂H₅O₂)₃·3H₂O, 1 mL HOAc, 1.6 g PEI were dissolved in 30 mL distilled water. After stirring for 2 h, the obtained colloidal suspensions were transferred into an 80 mL autoclave and reacted at 100 °C for 24 h. The resulting powders were washed and then dried at 75 °C for 12 h. The obtained mesoporous AlOOH was calcined at 400 °C in air for 5 h (ramp rate 2 °C min⁻¹) to obtain mesoporous Al₂O₃.

Photocatalytic Activity Measurements: The photocatalytic water splitting was carried out in an online photocatalytic hydrogen generation system (CEL-SPH2N-D9, Beijing Aulight Co., Ltd.) at ambient temperature. 50 mg of photocatalyst powder loaded with 1 wt% Au was dispersed in 50 mL of aqueous solution containing 10 mL of methanol and 40 mL of water. Prior to the 300 W xenon lamp irradiation, the mixture was evacuated for 30 min to remove oxygen and ensure that the reactor was in a vacuum condition. The resultant hydrogen was determined by an on-line gas chromatograph (GC7920-DTA) equipped with a TCD detector.

Photoelectrochemical Property: The electrochemical impedance measurements were performed using a three-electrode CHI 650D electrochemical workstation in a 0.5 M Na₂SO₄ electrolyte, with Pt foil as counter electrode, saturated calomel electrode as reference electrode, and photocatalysts used as working electrodes. A simulated AM 1.5 solar power system was used as light irradiation source. The working electrodes were prepared by dropping the suspension containing 20 mg of powder and 20 μL of absolute ethanol on F-doped tin oxide glass (0.5 cm x 0.5 cm).

Characterizations: XRD patterns were measured using a Bruker D8 Advance X-ray diffractometer with monochromatic Cu Kα irradiation. N₂ sorption isotherms were measured at 77 K with a Quantachrome Nova 4200e. Before measurements, all of the samples were degassed under vacuum at 100 °C for a minimum of 8 h. The specific surface area was calculated by BET equation. Pore size distributions were obtained using adsorption isotherms were measured at 77 K with a Quantachrome Nova 4200e. Before measurements, all of the samples were degassed under vacuum at 100 °C for 12 h. The obtained mesoporous AlOOH was calcined at 180 °C for 24 h. The resulting powders were washed and then dried at 75 °C and reacted at 100 °C for a minimum of 8 h. The specific surface area was calculated by BET equation. Pore size distributions were obtained using adsorption isotherms measured at 77 K with a Quantachrome Nova 4200e. Before measurements, all of the samples were degassed under vacuum at 100 °C for 5 h (ramp rate 2 °C min⁻¹) to obtain mesoporous Al₂O₃.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
high crystallinity, mesoporous metal oxides, photocatalytic hydrogen production, polymer-oriented self-assembly strategy, ultrahigh surface area

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