Formation of Yolk–Shell MoS$_2$@void@Aluminosilica Microspheres with Enhanced Electrocatalytic Activity for Hydrogen Evolution Reaction

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Abstract: The development of low-cost electrode materials with enhanced activity and favorable durability for hydrogen evolution reactions (HERs) is a great challenge. MoS$_2$ is an effective electrocatalyst with a unique layered structure. In addition, aluminosilica shells can not only provide more hydroxyl groups but also improve the durability of the catalyst as a protective shell. Herein, we have designed a hard-template route to synthesize porous yolk–shell MoS$_2$@void@Aluminosilica microspheres in a NaAlO$_2$ solution. The alkaline solution can directly etch silica (SiO$_2$) hard templates on the surface of MoS$_2$ microspheres and form a porous aluminosilica outer shell. The electrocatalytic results confirm that the MoS$_2$@void@Aluminosilica microspheres exhibit higher electrocatalytic activity for HERs with lower overpotential ($104$ mV at the current density of $−10$ mA cm$^{-2}$) and greater stability than MoS$_2$ microspheres. The superior electrocatalytic activity of MoS$_2$@void@Aluminosilica microspheres is attributed to the unique structure of the yolk@void@shell geometric construction, the protection of the aluminosilica shell, and the greater number of active sites offered by their nanosheet subunits. The design of a unique structure and new protection strategy may set up a new method for preparing other excellent HER electrocatalytic materials.

Keywords: yolk–shell; MoS$_2$@void@Aluminosilica microspheres; hydrogen evolution reaction; hydrothermal and hard template method

1. Introduction

Over the past few decades, hydrogen, in particular, sustainable hydrogen production from water splitting, as a clean and renewable energy has received great attention regarding its potential to solve many environmental problems caused by fossil energy [1–5]. For an electrochemical hydrogen evolution reaction (HER), an excellent catalyst should possess lower overpotential and good stability in this important electrochemical process [6,7]. However, highly efficient HER electrocatalysts are Pt-based metals with higher cost and scarcity on the earth, which limits their widespread application [8–11]. Therefore, it is urgent to design an inexpensive and earth-abundant electrocatalyst to replace Pt-based metals and achieve lower overpotential and remarkable reaction kinetics.

In recent years, as an important family of functional materials, nanostructured transition metal sulfides have received intensive research interest due to their electrical conductivity and rich redox electrochemistry [12,13]. Among them, MoS$_2$, which is one of the layered transition metals dichalcogenides, has received more and more attention in diverse applications, such as solar cells [14], homogeneous biomolecules detection [15],...
photodetectors [16], sodium-ion batteries [17], and hydrogen storage [18]. In addition, the structure of the material is also an important factor affecting its performance. Taking these two factors (the material of MoS$_2$ and the structure) into account, preparing MoS$_2$ micro- and nanostructures with controllable morphologies and sizes has attracted lots of attention. For example, three-dimensional (3D) MoS$_2$ nanoflowers with large stretched “thin folding leaves” and considerable nanopores were synthesized by a polypyrrole-assisted one-pot hydrothermal routine [19]; nanostructured MoS$_2$ particles on a 3D carbon fiber paper substrate with preferentially exposed edge sites were successfully synthesized by the facile pyrolysis and sulfurization methods [20]; 2D MoS$_2$ monolayers with defect structures were prepared by direct sulfurization and chemical vapor deposition (CVD) [21]; a type of prickly-pear-like 3D porous MoS$_2$ was hydrothermally synthesized (ZT-MoS$_2$) with a zinc oxide (ZnO) rod template which deposited on quartz glass substrates [22]; zinc-doped MoS$_2$ material was prepared by a facile solvothermal method and using (NH$_4$)$_2$MoS$_4$ as precursors in DMF solution [23]; and an edge-rich MoS$_2$ nanoarray grown on an edge-oriented 3D graphene was prepared via CVD [24]. Although various reasonable progressions have been carried out in designs of the structure, there are still some inadequacies, such as complicated operation with inefficient catalytic activity and instability. In addition to the structures above, as a special extension of core–shell systems, the yolk–shell structure exhibits a distinctive yolk@void@shell configuration with an interspace between the core and porous shell (in most cases) which can provide a protective route for buffering the volume change and thus enhance the stability of the material [25]. For example, Wang et al. reported that yolk–shell ZnS@NC@MoS$_2$ nanoboxes can provide increased active sites and ion channels among the interfacial boundaries, high conductivity, and a stable structure for the sodium ion batteries (SIBs) anode [26]. However, MoS$_2$ electrocatalysts with aluminosilica protective shells have not been reported. Therefore, it is highly desirable to develop a facile and cost-efficient method to fabricate MoS$_2$-based catalysts with efficient catalytic performance and great stability.

In this work, we report that MoS$_2$@void@Aluminosilica microspheres with porous shells are prepared by a facile and robust method. In this experiment, SiO$_2$, which is first modified the surface of MoS$_2$ microspheres assembled by nanosheets, induced preferential generation and deposition of the porous aluminosilica shell. According to our research, this is the first report on the fabrication and electrocatalytic activity for HERs of monodispersed MoS$_2$@void@Aluminosilica microspheres. Most importantly, as an efficient electrocatalyst, MoS$_2$@void@Aluminosilica microspheres possess the following three features: (1) larger specific areas offered by their nanosheet subunits can provide more active sites for HER processes; (2) electrochemical kinetics are enhanced by the short diffusion lengths between the hierarchical MoS$_2$ microsphere core and the aluminosilica shell; (3) HER stability benefited from the porous aluminosilica shell.

2. Materials and Methods

2.1. Preparation of Hierarchical MoS$_2$ Microspheres Assembled by Nanosheets

In this experiment, 0.1 g of thioacetamide (TAA, 99%) and sodium molybdate (Na$_2$MoO$_4$ 2H$_2$O, 99%, 0.3 g) were dispersed in deionized (DI) water with continuous magnetic stirring. After 15 min, 0.2 g of polyethylene-polypropylene glycol, F68 (referred to as F68) was added to the mixed solution and stirred for 20 min. Then, the above solution was transferred to the 50 mL Teflon-lined, stainless-steel autoclave and kept at 180 °C for 12 h. When the autoclave was cooling down, the powder was washed with DI water and absolute ethanol three times and finally dried in a vacuum oven at 60 °C for 12 h.

2.2. Preparation of MoS$_2$@SiO$_2$ Microspheres

The SiO$_2$ was prepared on the basis of the Stöber method with some modification [27]. Briefly, 0.05 g of as-prepared MoS$_2$ microspheres was dispersed into a mixture solution including 20 mL ethanol and 4 mL deionized water under ultrasonication for 20 min. Then, 0.2 mL of tetraethyl orthosilicate (TEOS) and 0.25 mL of ammonia solution (25%) were
added to above solution and stirred for 3.5 h. The obtained products were washed with DI water and ethanol then dried under vacuum at 60 °C for 10 h.

2.3. Preparation of MoS$_2@$void@Aluminosilica Microspheres

The synthesis process of MoS$_2@$void@Aluminosilica microspheres was carried out according to our previous work [28], which is described briefly as follows: The MoS$_2@$SiO$_2$ microspheres (50 mg) were dispersed in 10 mL of DI water to form homogeneous solution A. A total of 0.05 g of sodium aluminate (NaAlO$_2$) was dissolved into 20 mL of DI water to form solution B. Then, solution A was poured into solution B to form a homogeneous suspension and then transferred to a Teflon autoclave (50 mL) and heated at 140 °C for 4 h. After cooling down to room temperature, the product was washed and dried in a vacuum oven at 60 °C overnight.

2.4. Electrochemical Measurements

The electrochemical property of the as-prepared samples was obtained by using a three-electrode system connected to a CHI 760E electrochemical workstation (Shanghai Chenhua Instrument Co., Shanghai, China). A total of 5 mg of as-prepared samples together with 10 µL of NaF solution was dispersed into 800 µL of ethanol and 200 µL of distilled water and sonicated for 30 min to form a homogeneous ink. Then, the ink was pipetted onto the FTO-coated glass and then used as the working electrodes. The Ag/AgCl electrode was employed as the reference electrode and a platinum plate as the counter electrode, and the 0.5 M H$_2$SO$_4$ solution was employed as electrolyte in all electrochemical tests. All of the electrochemical measurements were performed in a three-electrode system at room temperature. Linear sweep voltammetry (LSV) was conducted from 0 to −0.4 V versus (vs.) reversible hydrogen electrode (RHE) with a scan rate of 5 mV s$^{-1}$ at room temperature. Electrochemical impedance spectroscopy (EIS) measurement was conducted at the overpotential of 500 mV with a potential perturbation of 5 mV amplitude in the range from 10$^6$ Hz to 0.1 Hz. All potentials measured vs. Ag/AgCl were converted to RHE using the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + E^0_{\text{Ag/AgCl}}$$

where $E_{\text{RHE}}$ is the converted potential vs. RHE, $E_{\text{Ag/AgCl}}$ is the measured potential vs. the Ag/AgCl electrode, and $E^0_{\text{Ag/AgCl}} = 0.1976$ V at 25 °C.

2.5. Characterization

X-ray diffraction (XRD) patterns were measured on a Philips X’Pert Pro X-ray diffractometer (Holland Panalytical, Almelo, The Netherlands) with Cu Ka radiation (1.5418 Å). The main samples were characterized by taking TEM images using a JEOL JEM-2100 microscope (Hitachi Co., Tokyo, Japan). Scanning electron microscope (SEM) images were carried out at a SEM (Quanta 200 FEG, Tokyo, Japan) with an accelerating voltage of 10.0 kV. Specific surface areas of the samples were tested by Brunauer–Emmet–Teller (BET, Micromeritics ASAP 2020 M+C, Micromeritics Instrument Co., Atlanta, GA, USA) equipped with nitrogen adsorption and desorption. The static water contact angle (CA) measurement was tested on an optical CA meter system (Data Physics Instrument GmbH, Filderstadt, Germany).

3. Results and Discussion

The fabrication process for the MoS$_2@$void@Aluminosilica is shown in Figure 1. Firstly, the reactions of Na$_2$MoO$_4$ and S$^{2-}$ released from the TAA by hydrothermal method treatment at 180 °C formed the MoS$_2$ nanosheets. In addition, the MoS$_2$ nanosheets spontaneously assembled into MoS$_2$ microspheres with the addition of F68. In our experiments, it is supposed that the F68 intertwines to form a network structure in the solution and adsorbs on the surface of MoS$_2$ nanosheets due to the strong interaction between MoS$_2$ and
F68. Thus, the MoS$_2$ nanosheets encapsulated by F68 assembled to the MoS$_2$ microspheres in order to decrease the surface energy [29]. Secondly, SiO$_2$ was coated as the shell on the surface of the MoS$_2$ microspheres (MoS$_2$@SiO$_2$ microspheres) via the Stöber method at room temperature (TEOS as the SiO$_2$ source in alkaline solution was used in the reaction process). Finally, NaAlO$_2$ aqueous solution was employed as an alkaline solution to etch SiO$_2$ hard templates on the surface of the MoS$_2$ microspheres to form the monodispersed MoS$_2$@void@Aluminosilica microspheres with porous aluminosilica shell structures via the hydrothermal method at 140 °C.

Figure 1. Schematic illustration for the synthesis of the MoS$_2$@void@Aluminosilica microspheres.

The phase structures of the as-prepared products are tested with XRD (Figure 2). The XRD pattern of the MoS$_2$ sample shows that all the main diffraction peaks can be indexed to the (002), (100), (102), and (110) plane of the hexagonal MoS$_2$ phase (JCPDS No. 37–1492, P63/mmc). The (002) plane located at ~13.9° especially indicates that the MoS$_2$ is the graphene-like structure, and its corresponding d spacing is 0.62 nm, which was calculated based on Bragg’s equation. However, other peaks that slightly shift toward a lower angle of the diffraction peaks can be found. The reason for this phenomenon is caused by lattice strains derived from the folding and bending of the layers [30]. The typical XRD patterns of the MoS$_2$@SiO$_2$ microspheres and the MoS$_2$@void@Aluminosilica microspheres show almost the same features as those shown in MoS$_2$. There are no other diffraction peaks that can correspond to SiO$_2$ and aluminosilica because SiO$_2$ and aluminosilica are amorphous [28].

Figure 2. XRD pattern of the MoS$_2$ microspheres, the MoS$_2$@SiO$_2$ microspheres, and the MoS$_2$@void@Aluminosilica microspheres.
As shown in Figure 3a, as we can see, the MoS$_2$ was assembled by many monodispersed spherical particles with an average diameter of ~300 nm, which could work as seeds for further coating the SiO$_2$ shell on the surface of the MoS$_2$ microspheres to form core–shell composites [31]. The MoS$_2$ microspheres were further investigated by the TEM in Figure 3b,c, from which we found that the MoS$_2$ microspheres were assembled by nanosheets with a thickness of ~5.0 nm. As shown in Figure 3d, the MoS$_2$@SiO$_2$ microspheres possess a smooth SiO$_2$ shell, and the average particle diameter of the sample increased from 300 to 400 nm, which suggests that the thick shell of SiO$_2$ with ~100 nm was successfully coated onto the surface of the MoS$_2$ microspheres. TEM images in Figure 3e,f also suggest that the SiO$_2$ shell was successfully coated on the surface of the MoS$_2$ microspheres. In addition, the thickness of the shell was about 85 nm (Figure 3f). The aluminosilica shell and the MoS$_2$ core can be seen clearly in Figure 3g,h; the MoS$_2$@void@Aluminosilica microspheres possess yolk–void–shell structures. It is worth noticing that the SiO$_2$ shell is the key process for synthesizing MoS$_2$@void@Aluminosilica microspheres because the SiO$_2$ shell can induce the preferential generation and deposition of porous aluminosilica shells [28]. Compared to the MoS$_2$@SiO$_2$ microspheres with core–shell structure (Figure 3e,f), there is a clearer boundary between the outer aluminosilica shell, MoS$_2$ core, and the void space of MoS$_2$@void@Aluminosilica microspheres in the yolk–shell structures in Figure 3i. In addition, the SEM and TEM images of the SiO$_2$ microspheres are shown in Figure S1, and the SEM and TEM images of the hollow aluminosilica microspheres are shown in Figure S2. These aspects can be viewed in the Supplementary Materials.

The high-magnification TEM images of the MoS$_2$@void@Aluminosilica microspheres are shown in Figure 4a,b. In addition, Figure 4b shows that there are many mesopores (black circles) in the shell of the as-prepared sample. As shown in Figure 4i, the thickness of the shell of MoS$_2$@void@Aluminosilica microspheres is about 20 nm. Additionally, Figure 4i further reveals that the outer aluminosilica shell is amorphous, which is consistent with the SAED pattern (see inset of Figure 4i) and the XRD pattern (Figure 2). The HRTEM image (Figure 4k) shows that the MoS$_2$ core has a typical layered structure with interlayer
spacing at 0.62 nm, which corresponds to the (002) plane of hexagonal MoS$_2$ (JCPDS No. 37–1492). In addition, the electron mapping images in Figure 4c–h indicate Si-, O-, Al-, Na-, Mo-, and S-enriched areas of the MoS$_2$@void@Aluminosilica microspheres, respectively. The EDS analysis (Figure 4i) of the MoS$_2$@void@Aluminosilica microspheres further reveals the existence of Si, O, Al, Na, Mo, and S elements.

![Figure 4](image_url)

**Figure 4.** The images of the MoS$_2$@void@Aluminosilica microspheres: (a,b) low-magnification TEM images; electron energy loss: (c) “Si”, (d) “O”, (e) “Al”, (f) “Na”, (g) “Mo” and (h) “S”; (i) HRTEM image and the corresponding SAED pattern (inset in (i)); (j) EDS spectrum; (k) HRTEM image.

As shown in Figure 5, the MoS$_2$ microspheres and the MoS$_2$@void@Aluminosilica microspheres are of type IV isotherms, which indicates that both of them possess meso/microporous structures. The pore-size distribution curve of the MoS$_2$ microspheres shows a broad peak from 2–105 nm with a maximum of 90 nm. The MoS$_2$@void@Aluminosilica microspheres exhibit the same broad peak range but with a maximum of 85 nm. These results indicate that there are many mesopores/macropores in the above two mentioned samples. In addition, the mesopores may reflect the space between the nanosheets which assemble the MoS$_2$ microspheres or the MoS$_2$@void@Aluminosilica microspheres, while larger macropores can be concerned with the space between the MoS$_2$ microspheres or the MoS$_2$@void@Aluminosilica microspheres. For the MoS$_2$@void@Aluminosilica microspheres especially, larger mesopores may index to the void space between the yolk and shell of the sample, while the smaller mesopores can reflect the porosity of the aluminosilica shell. However, the porosity of the MoS$_2$@SiO$_2$ microspheres can be neglected.
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Figure 5. Nitrogen adsorption–desorption isotherms and the corresponding pore-size distribution curves (inset) of the MoS$_2$ microspheres, the MoS$_2$@SiO$_2$ microspheres, and the MoS$_2$@void@Aluminosilica microspheres.

The BET surface areas, average pore diameters, and pore volumes of the three main as-synthesized samples are summarized in Table 1. From the data, it can be clearly seen that the MoS$_2$ microspheres possess a larger specific surface area and bigger pore volume. After the SiO$_2$ was coated on the surface of the MoS$_2$ microspheres, the MoS$_2$@SiO$_2$ microspheres possessed the smallest specific surface area and pore volume, which indicates that solid SiO$_2$ reduced the amount of exposure active sites and blocked the ion channel. After being etched by an alkaline solution, the MoS$_2$@void@Aluminosilica microspheres possessed larger BET and higher pore volume, which indicates the porous aluminosilica shell can provide more exposure to active sites and more open ion channel.

Table 1. Some physical properties of the three main samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET (m$^2$/g)</th>
<th>Average Pore Diameter (Å)</th>
<th>Pore Volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$</td>
<td>27.35</td>
<td>140.5</td>
<td>0.096</td>
</tr>
<tr>
<td>MoS$_2$@SiO$_2$</td>
<td>24.96</td>
<td>40.8</td>
<td>0.025</td>
</tr>
<tr>
<td>MoS$_2$@void@Aluminosilica</td>
<td>36.49</td>
<td>110.0</td>
<td>0.100</td>
</tr>
</tbody>
</table>

As shown in Figure 6, a typical three-electrode system was employed to evaluate the HER performance of the as-prepared samples in the H$_2$SO$_4$ electrolyte. Figure 6a presents the LSV measurements performed at 5 mV s$^{-1}$. The MoS$_2$@void@Aluminosilica microspheres’ electrode showed a lower overpotential of 104 mV at a current density of $-$10 mA cm$^{-2}$ while the MoS$_2$ microspheres were 127 mV. In addition, the SiO$_2$ microspheres, the hollow aluminosilica microspheres, and the MoS$_2$@SiO$_2$ microspheres exhibited negligible electrocatalytic activities for HERs. The results show that the as-synthesized MoS$_2$@void@Aluminosilica microspheres hold great promise for electrocatalytic hydrogen evolution. The kinetics of the catalytic HER was commonly investigated and quantified by the Tafel slope, which can be readily determined from the LSV curves by recasting the data into the Tafel equation:

$$\eta = b \times \log |j| + a$$

with b being the Tafel slope and j being the current density (mA cm$^{-2}$). A smaller Tafel slope means a faster-increased rate of the HER with a rising potential [32]. As shown in Figure 6b, the Tafel slope of MoS$_2$@void@Aluminosilica microspheres was 123 mV dec$^{-1}$, which is lower than that of the MoS$_2$ microspheres (169 mV dec$^{-1}$), the MoS$_2$@SiO$_2$ microspheres (197 mV dec$^{-1}$), the SiO$_2$ microspheres (214 mV dec$^{-1}$), and the hollow aluminosilica microspheres (223 mV dec$^{-1}$), respectively, indicating the outstanding kinetic
performance of the MoS$_2$@void@Aluminosilica microspheres. The decrease of the Tafel slope for the MoS$_2$@void@Aluminosilica microspheres may be attributed to the formation of the aluminosilica shell on the surface of the MoS$_2$ microspheres as evidenced by their corresponding SEM and TEM morphologies because of the reduced corrosion of MoS$_2$ core. In addition, Table 2 presents a thorough overview of the reporting MoS$_2$-based materials toward the electrochemical property. Obviously, there are many methods to prepare MoS$_2$ electrocatalysts; however, the MoS$_2$@void@Aluminosilica microspheres in this work possess better performance than others. This much-enhanced electrocatalytic performance is also supported by the electrochemical impedance spectroscopy (EIS) in Figure 6c; the equivalent circuit diagram is shown in Figure S3. The impedance of the MoS$_2$@void@Aluminosilica microspheres was found to be much smaller than that of the MoS$_2$ microsphere and other samples (the SiO$_2$ microspheres, the hollow aluminosilica microspheres, and the MoS$_2$@SiO$_2$ microspheres, as shown in Figure S4), which is ascribed to the unique structure of the yolk@void@shell geometric construction, the presence of aluminosilica shell helps to adsorb the reactants in the solution, the greater number of active sites offered by their nanosheet subunits, and the enhancement of the hydrophilicity. It can be concluded that the MoS$_2$@void@Aluminosilica microsphere exhibits superior electrode kinetics and thus can enhance the electrochemical HER activity. As shown in Figure S5, the MoS$_2$@void@Aluminosilica microspheres show a capacitance value of up to 0.66 mF cm$^{-2}$, which is slightly lower than that of MoS$_2$ electrodes (0.67 mF cm$^{-2}$). The electrochemical active surface area (ECSA) of the MoS$_2$@void@Aluminosilica microspheres was 16.5 cm$^2$ while MoS$_2$ was 16.7 cm$^2$, indicating that the Aluminosilica shell cannot decrease the active surface area of MoS$_2$. To investigate the HER stability of the MoS$_2$@void@Aluminosilica microspheres, a long-term potential cycling test was performed at a scan rate of 10 mV s$^{-1}$. As shown in Figure 6d, only a slight activity loss of the MoS$_2$@void@Aluminosilica microspheres was observed, even after 500 continuous cycles, while there was a significant decline in potentials for the MoS$_2$ microspheres, which may be attributed to the MoS$_2$ core not corroded because it was protected by the aluminosilica shell. In addition, as shown in Figure 6e, after continuous testing at the static current density of $-10$ mA cm$^{-2}$, the potential of the MoS$_2$@void@Aluminosilica microspheres remained stable for a long period test and showed excellent stability under acidity conditions.

Table 2. The synthesis method and HER performance of the MoS$_2$-based electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Synthesis Method</th>
<th>$\eta$10 (mV) *</th>
<th>Tafel Slope (mV dec$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$ (activated)</td>
<td>Commercial activated method</td>
<td>—</td>
<td>180</td>
<td>[18]</td>
</tr>
<tr>
<td>3D MoS$_2$ nanoflowers</td>
<td>Hydrothermal method</td>
<td>350</td>
<td>95.5</td>
<td>[19]</td>
</tr>
<tr>
<td>se-MoS$_2$</td>
<td>Hydrothermal method</td>
<td>104</td>
<td>59</td>
<td>[33]</td>
</tr>
<tr>
<td>r-MoS$_2$</td>
<td>Microwave hydrothermal method</td>
<td>217</td>
<td>121</td>
<td></td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>Hydrothermal method</td>
<td>340</td>
<td>105</td>
<td>[34]</td>
</tr>
<tr>
<td>Zn-MoS$_2$</td>
<td>Hydrothermal method</td>
<td>290</td>
<td>110</td>
<td>[34]</td>
</tr>
<tr>
<td>MoS$_2$@3DC</td>
<td>Pyrolysis method</td>
<td>252</td>
<td>102.8</td>
<td>[35]</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>Hydrothermal method</td>
<td>400</td>
<td>157</td>
<td>[36]</td>
</tr>
<tr>
<td>3D MoS$_2$</td>
<td>Hard template method</td>
<td>270</td>
<td>112</td>
<td>[37]</td>
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<tr>
<td>MoS$_2$</td>
<td>Template sacrificial method</td>
<td>508</td>
<td>136</td>
<td>[38]</td>
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<tr>
<td>MoS$_2$ nanosheets</td>
<td>Hydrothermal method</td>
<td>308</td>
<td>201</td>
<td>[39]</td>
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<tr>
<td>MoS$_2$ microspheres</td>
<td>Hydrothermal method</td>
<td>127</td>
<td>169</td>
<td>[39]</td>
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<tr>
<td>MoS$_2$@void@Aluminosilica</td>
<td>Hydrothermal and hard template method</td>
<td>104</td>
<td>123</td>
<td>This work</td>
</tr>
</tbody>
</table>

* HER overpotential at $-10$ mA cm$^{-2}$ achieved at a given catalyst loading.

To probe the interface property of the electrocatalyst, the hydrophilicity of the MoS$_2$@void@Aluminosilica microspheres was investigated. As shown in Figure 6f, the contact angle of the MoS$_2$@void@Aluminosilica microspheres was $10^\circ$, which was smaller than that of the MoS$_2$ microspheres ($27^\circ$), suggesting the former has better hydrophilicity than the latter. More hydrophilic surface was conducive to contact between the reactants and active sites, enabling the facile release of evolved H$_2$ gas bubbles and facilitating electron...
transfer to improve water electrolysis [40]. Consequently, all the above results powerfully confirmed that MoS$_2$@void@Aluminosilica microspheres have greatly optimized the HER reaction kinetics and thus significantly enhanced the HER catalytic activity. The improved performance of MoS$_2$@void@Aluminosilica is attributed to the greater number of active sites offered by MoS$_2$ nanosheet subunits and hydrophilic hydroxyl groups on the surface of aluminosilica.

4. Conclusions

In conclusion, MoS$_2$@void@Aluminosilica microspheres have been successfully prepared by hydrothermal and hard template methods. The experimental results illustrate that MoS$_2$@void@Aluminosilica microspheres display great electrocatalytic activities and stability for HERs compared with MoS$_2$ microspheres. The excellent HER catalytic performance of MoS$_2$@void@Aluminosilica microspheres is ascribed to the unique structure of the yolk@void@shell geometric construction, the presence of aluminosilica shell, and the greater number of active sites offered by their nanosheet subunits. The products with the yolk@void@shell structures prepared by the simple protocol and unique protection strategy are prospectively applicable in the fields of electrocatalysis and batteries.
Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/en15239031/s1, Figure S1: SEM (a) and TEM (b) images of SiO$_2$ microspheres; Figure S2: SEM (a) and TEM (b) images of hollow aluminosilica microspheres; Figure S3: Equivalent circuit diagram ($R_s$ is the solution resistance; $C_{dl}$ is the double layer capacitance; $R_{ct}$ is the charge transfer resistance); Figure S4: Electrochemical impedance spectroscopy of the SiO$_2$ microspheres, the hollow aluminosilica microspheres, and the MoS$_2$@SiO$_2$ microspheres; Figure S5: Plots of the double-layer capacitances of MoS$_2$ and MoS$_2$@Void@Alumino silica.

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References
