Two Birds with One Stone: Concurrent Ligand Removal and Carbon Encapsulation Decipher Thickness-Dependent Catalytic Activity

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ABSTRACT: A carbon shell encapsulating a transition metal-based core has emerged as an intriguing type of catalyst structure, but the effect of the shell thickness on the catalytic properties of the buried components is not well known. Here, we present a proof-of-concept study to reveal the thickness effect by carbonizing the isotropic and homogeneous oleylamine (OAm) ligands that cover colloidal MoS$_2$. A thermal treatment turns OAm into a uniform carbon shell, while the size of MoS$_2$ monolayers remains identical. When evaluated toward an acidic hydrogen evolution reaction, the calcined MoS$_2$ catalysts deliver a volcano-type activity trend that depends on the calcination temperature. Rutherford backscattering spectrometry and depth-profiling X-ray photoelectron spectroscopy consistently provide an accurate quantification of the carbon shell thickness. The same variation pattern of catalytic activity and carbon shell thickness, aided by kinetic studies, is then persuasively justified by the respective limitations of electron and proton conductivities on the two branches of the volcano curve.

KEYWORDS: encapsulation, shell thicknesses, molybdenum disulfide, electrocatalysts, hydrogen evolution reaction

A pressing issue recognized by the catalysis community is that the applied solid catalysts often experience uncontrollable structural and compositional variations under harsh reaction conditions.$^{1-6}$ One solution that is being strongly pursued is to cover the catalysts with a carbon shell that protects the components beneath. These peculiar types of core–shell catalysts have demonstrated fascinating advantages, such as resistances to agglomeration, corrosion, and oxidation, reaction selectivity control, and an electron transfer effect.$^{7-9}$ However, the influence of the carbon shell structure on the buried core has been poorly elaborated due inevitably to the challenge of fine-tuning the shell structural factors while retaining identical inner cores.

One of the intriguing structural factors of a carbon shell is its thickness along the radial direction. A critical, yet often ignored, question is how the thickness of the carbon shell dictates the catalytic behavior, especially from the perspective of proton-coupled electron transfer that lays the foundation of many electrochemical reactions.$^{10,11}$ In the cases of single- and few-layer graphene, previous studies have verified that protons can penetrate through, allowing their accessibility to the core materials beneath.$^{12-16}$ However, a carbon shell that is too thick may block the reactants from accessing the active sites and detain the products from diffusing away. The shell thickness also affects the synergistic interactions between the metal core and the outer few carbon layers that are catalytically relevant. Theoretical calculations by Bao and co-workers revealed that the electron transfer between the carbon shell and metal core gradually intensifies and remains steady when the shell is thicker than three graphene layers.$^{17}$ Therefore, the effect of shell thickness deserves considerable attention to precisely evaluate the catalysts of interest, but relevant in-depth studies on this aspect are still lacking.

The key to deciphering the shell thickness effect is the controllable synthesis of carbon-encapsulated materials with well-defined structural parameters. Furnace pyrolysis is the prevailing route to yield metal-based cores embedded in carbon shells.$^{18-20}$ Nonetheless, it is extremely difficult to control the structures and compositions of both the core and shell because the process is largely empirical, making the precise discrimination of the catalytic contributions of core and shell difficult.$^{21-23}$ Colloidal synthesis in the presence of organic ligands has demonstrated its competence to tailor-make low-dimensional transition metal-based nanomaterials.$^{24-26}$ Calcination is often required to recover ligand-stripped catalysts, but what indeed occurs is that calcination does not remove all the ligands but turns part of them into carbon layers covering inner...
cores. In light of the colloidal nanomaterials with narrow size distributions and homogeneous ligand coverage, calcination of ligand-capped nanomaterials holds the potential to solve two problems at one time. On one hand, the detrimental ligands that sterically and chemically block the metal active sites can be efficiently eliminated. On the other hand, the isotropic and homogeneous surface ligands can be converted into uniform carbon shells with a well-defined and adjustable thickness. The resulting products thus serve as a desirable prototype to investigate the thickness effect of the carbon shell on the catalytic properties of encased cores.

Drawing on the preceding synthesis of ligated MoS$_2$ monolayers, we take one step further by calcining the monolayers at controlled temperatures in the range of 200–600 °C to carbonize the ligands without affecting the size of the MoS$_2$ core. The hydrogen evolution reaction (HER) activity in acids of the calcined products is found to be dependent on the calcination temperature, forming a volcano-type activity curve. Microscopic and spectroscopic characterizations unambiguously disclose the formation of a carbon shell around the MoS$_2$ monolayers. The relative thickness of the carbon shell is further quantified by Rutherford backscattering spectrometry and surface morphology of Super P and the calcined MoS$_2$-AP (Figure S5). This result is hence linked to the crystallinity of MoS$_2$. The absence of the (002) characteristic peak at 14.3° in Figure S4 further demonstrates the monolayer structure, in stark contrast to the highly crystalline commercial MoS$_2$ (c-MoS$_2$). The (004) peak originally located at 29.0° of standard 2H-MoS$_2$ is shifted to 18.5°, indicating an extended interplanar spacing along the c axis according to Bragg’s law.

To remove the ligands, we calcined the MoS$_2$-AP and MoS$_2$/C-AP at 200–600 °C. Analogous dark lines in MoS$_2$/C-400 (Figure 2b) are observed with an almost identical lateral size. Moreover, the monolayers are attached to an amorphous carbon substrate resulting from OAm carbonization (vide infra). In comparison, MoS$_2$/C is also annealed at 400 °C (Figure 2c). The spherical carbon particles of Super P with clear lattice fringes are discerned alongside the dark lines of MoS$_2$. Again, the average lateral size of MoS$_2$ monolayers barely vary from those of MoS$_2$-AP and MoS$_2$/C-400. XRD patterns in Figure 2d indeed show that the structure and size of MoS$_2$ are well retained at calcination temperatures of even up to 600 °C. Super P itself is very stable during sintering (Figure S5). This result is hence linked to the carbon shell that affords high sintering resistance and structural stability. Scanning electron microscopy unveils the consistent surface morphology of Super P and the calcined MoS$_2$/C (Figure S6), distinct from that of the calcined MoS$_2$ (Figure S7).
Figure 3a shows the ATR-FTIR spectra of calcined and as-prepared MoS$_2$/C. The prominent absorption peaks from the most representative aliphatic tail of OAm, enlarged in the right panel, hardly appear at 400 °C and above, manifesting the complete transformation of OAm. To preclude the effect of Super P carbon, we also compare the ATR-FTIR spectra of MoS$_2$-AP and calcined MoS$_2$ (Figure 3b). It is again found that a threshold of 400 °C is necessary for the total elimination of OAm ligands. The Raman spectra of supported MoS$_2$ in Figure 3c present two major peaks at 1350 and 1599 cm$^{-1}$, ascribed to the D and G bands of graphitic structures, respectively. The Raman spectra of the unsupported MoS$_2$ are displayed in Figure 3d. For both MoS$_2$-200 and MoS$_2$-AP, D and G bands are not observed. When the temperature is elevated to 300 °C, both D and G bands appear, directly evidencing the carbon formation.

A depth-profiling X-ray photoelectron spectroscopy (XPS) analysis coupled with 300 eV Ar$^+$ etching is further performed to probe the elemental composition and speciation at different depths. Commercial c-MoS$_2$ is included as a reference (Figure S9). All of the full survey XPS spectra of the calcined MoS$_2$ at three etching stages identify the elements C, N, O, S, and Mo (Figure S10). The inconspicuous C 1s peak changes of each sample before and after etching can be ascribed to the random orientation of MoS$_2$ monolayers throughout the carbon shell (Figure S11). In contrast, Figure S12 shows that the C 1s peak is the smallest for MoS$_2$-400 among the calcined MoS$_2$ etched for 90 s. The N 1s region is close to that of Mo 3p, and the XPS spectra are then deconvoluted into Mo$^{4+}$ 3p$_{3/2}$, Mo$^{6+}$ 3p$_{3/2}$, and N 1s (Figure S13). The N 1s peak shrinks with an increase in the calcination temperature and disappears at 400 °C, verifying the complete removal of OAm. The Mo 3d and S 2p XPS spectra after 90 s of etching are shown in Figure 3e,f, respectively. As the calcination temperature increases, all of the doublet peaks of Mo 3d move to lower binding energies, indicating that fewer 3d electrons are transferred from MoS$_2$ to OAm as OAm is being gradually removed. After OAm removal, the Mo$^{4+}$ 3d$_{5/2}$ and 3d$_{3/2}$ peaks are positioned at almost the same binding energy as that of c-MoS$_2$ (Figure S14). In Figure 3f, the S 2p$_{3/2}$ and 2p$_{1/2}$ doublets are shifted to higher binding energy, implying that fewer electrons are withdrawn from S atoms as OAm ligands are eliminated. This is in contradiction with the fact that more 3d electrons are available by Mo as fewer are transferred to N. It is inferred that N−H···S hydrogen bonds could be formed to allow electron withdrawal from adjacent H atoms to low-valent S atoms. Removal of OAm thus results in the upward shifting of the binding energy of S 2p electrons to the same positions as in c-MoS$_2$ (Figure S14).
The HER activity of the calcined MoS\(_2\)/C is assessed in Ar-saturated 0.5 M H\(_2\)SO\(_4\). Figure 4a shows the \(iR\)-compensated linear sweep voltammetry (LSV) polarization curves of the catalysts being studied. The overpotential at a current density of 10 mA cm\(^{-2}\) (\(\eta_{10}\)) is compared in the upward axis of the radar chart in Figure 4b. Despite the ultrafine lateral size of MoS\(_2\)/C-AP, its \(\eta_{10}\) value is found to be close to that of c-MoS\(_2\)/C, indicating the poor HER activity of MoS\(_2\)/C-AP. Calcination of MoS\(_2\)/C-AP at 200 and 300 °C leads to a gradually reduced \(\eta_{10}\) value and improved activity. When the calcination reaches 400 °C, \(\eta_{10}\) is reduced by 280 and 130 mV compared to the values for Super P and MoS\(_2\)/C-AP, respectively. However, at even higher temperatures, \(\eta_{10}\) starts to increase for MoS\(_2\)/C-500 and MoS\(_2\)/C-600, indicating their deteriorated HER activities. Figure 4c shows the Tafel plots, and the derived Tafel slopes are presented in the rightward axis of Figure 4b. MoS\(_2\)/C-400 delivers the smallest Tafel slope of 76 mV dec\(^{-1}\). The other catalysts annealed at lower or higher temperatures have values larger than 118 mV dec\(^{-1}\). As elaborated in Note S1, the rate-determining step (RDS) for c-MoS\(_2\)/C should be the Volmer step that involves electron transfer and proton adsorption at the active sites (H\(^*\)), in agreement with the facts that hydrogen adsorption

Figure 3. ATR-FTIR and Raman spectra of (a, c) the calcined, as-prepared MoS\(_2\)/C and Super P, and (b, d) the calcined, as-prepared MoS\(_2\) and c-MoS\(_2\). The right panel of (a) is an enlargement of the highlighted region that represents the C–H bond stretching vibration. The corresponding \(I_D/I_G\) ratios are indicated in (c, d). High-resolution XPS spectra of Mo 3d (e) and S 2p (f) regions of the calcined and the as-prepared MoS\(_2\).
to the 2H-MoS\(_2\) basal plane is thermodynamically unfavorable and electron transfer to semiconductive 2H-MoS\(_2\) is slow.\(^{43,44}\) For the catalysts calcined at temperatures either lower or higher than 400 °C, the Volmer step is also the RDS. In contrast, the Heyrovsky step is the RDS for MoS\(_2\)/C-400, manifesting the sluggish electrochemical desorption of H\(^*\) on the active sites.\(^{45-48}\) It is thus deduced that the electronic structure of MoS\(_2\) has been modulated by carbon encapsulation to favor the adsorption of H\(^*\).

Electrochemical impedance spectroscopy (EIS) measurements are carried out for all the catalysts, and the Nyquist plots are presented in Figure 4d. The solution resistance \(R_s\) is determined to be around 10 Ω, which is used for \(iR\) compensation. The charge transfer resistance \(R_{ct}\) represented by the semicircular diameter is compared in the leftward axis of Figure 4b. With an increase in calcination temperature, \(R_{ct}\) of the calcined MoS\(_2\)/C gradually decreases, indicating a reduced resistance in electron transfer at the electrode/electrolyte interfaces. This agrees with the higher graphitization degree or electrical conductivity of the carbon shell obtained at higher temperatures, as revealed by the Raman analysis in Figure 3d. The double-layer capacitance \((C_d)\) is calculated to assess the electrochemically active surface area. According to the non-Faradaic CV curves (Figure S15), the capacitive current density at 0.3 V\(_{RHE}\) is plotted against the scan rate (Figure 4e). After linear fitting, the obtained \(C_d\) is compared in the downward axis of Figure 4b. It is found that the \(C_d\) value of calcined MoS\(_2\)/C increases constantly with the calcination temperature. Given that carbon materials with a high specific surface area also exhibit capacitive behavior, the larger \(C_d\) value of MoS\(_2\)/C sintered at higher temperatures should be largely due to the carbon shell with a greater thickness. Nonetheless, according to the colored areas linking four key performance indicators in the radar chart of Figure 4b, a better catalyst should cover a larger area and MoS\(_2\)/C-400 thus has the best performance among all of the catalysts.

The preceding structural characterizations and catalytic performance hint that the shell thickness of MoS\(_2\)/C varies with the calcination temperature. The Rutherford backscattering spectrometry (RBS, Note S2) is then employed for quantification of the carbon shell thickness of calcined unsupported MoS\(_2\), in addition to the depth-profiling XPS. Graphite bulk and thin gold films are utilized to calibrate the energy offset and energy per channel (Figure S16). Figure 5a shows the experimental and simulated RBS spectra using the SIMNRA code.\(^{49}\) All of the materials present stair-shaped spectra featured by typical bulk samples, indicating their relatively high thicknesses deposited on silicon wafers. The simulated spectra of single-phase MoS\(_2\) and carbon films with different thicknesses and layer configurations are also given in Figure S17. The front edges at channels of 457, 657, 981, 1112, and 1564, representing the elements C, O, Si, S, and Mo, respectively, are indicated. The sharp peak at channel 451 is ascribed to non-Rutherford elastic backscattering. N is not detected due, probably to its low intensity and signal overlapping. Provided that the surface of calcined MoS\(_2\) should
be carbon layers, shifting of the front edges of buried Mo and S elements should be expected due to energy loss of incident ion particles traveling through the carbon layers. However, such shifting is not obvious in Figure 5a, indicating that the carbon layer has a thickness of several nanometers, as revealed by the simulations in Figure S17. The RBS spectra of blank silicon wafer show no major C peak, ruling out the potential origin of adventitious carbon from the solvent or other organic impurities (Figure S18).

Based on the fitted data, the average atomic percentage normalized to C, Mo, and S atoms together with the (Mo + S)/C atomic ratio (Table S1), which quantifies the relative thickness of the carbon shell, is plotted in Figure 5b. MoS$_2$-AP possesses a high C content that originates from the OAm ligands. Upon calcination, OAm ligands are vaporized, accounting for the ever-decreasing C contents of MoS$_2$-200, MoS$_2$-300, and MoS$_2$-400. At temperatures of 500 and 600 °C, carbonization of OAm ligands becomes the dominant process, leading to higher C contents in comparison to MoS$_2$-400. The smallest carbon shell thickness is then achieved at 400 °C. Furthermore, the relative thickness is also derived from the XPS data (Table S2). As presented in Figure 5c, the relative thickness derived from XPS follows the exact same variation as the RBS results. In addition to this observation, the Mo/S ratios are in good accord with the stoichiometric ratio of MoS$_2$.

Given the above, a rational explanation for the volcano-type HER activity trend can be made, which is briefly illustrated in Figure 5d. First, TEM and XRD results show that the lateral size and monolayer structure of calcined MoS$_2$ are well preserved, excluding the MoS$_2$ size effect on HER activity. As collectively revealed by multiple techniques, MoS$_2$/C-AP and MoS$_2$/C-200 are strongly capped by OAm, deactivate the surface-active sites for the HER. A Tafel analysis indicates that the Volmer step that involves proton-coupled electron transfer is rate-determining for these catalysts. Considering the large $R_{ct}$ from EIS measurements, we believe that the low electron conductivity should be held accountable for the poor activity of these OAm-ligated catalysts. Removal and translation of OAm by calcination gradually release the active sites and thus result in the enhanced HER activity of MoS$_2$/C-300 and MoS$_2$/C-400. In addition, the carbon shell tunes the electronic structure of the catalyst that eventually favors the adsorption of H*, changing the RDS to the Heyrovsky step. Further elevation of the calcination temperature leads to an intensified carbonization of OAm, and MoS$_2$ monolayers are thus coated by thicker shells. The RDS for both MoS$_2$/C-500 and MoS$_2$/C-600 is then shifted back to the Volmer step. By virtue of the improved graphitization degree and reduced $R_{ct}$ from EIS results, their degenerative kinetics should be attributed to the inadequate proton conductivity rather than the electron conductivity as above.

To summarize, we have investigated the effects of thermal calcination on the ligand carbonization and carbon shell thickness on the catalytic properties of MoS$_2$ by utilizing OAm-ligated MoS$_2$ monolayers. OAm is found to be gradually pyrolyzed into a carbon shell as the calcination temperature increases. When tested toward an acidic HER, the calcined catalysts deliver a volcano-type activity trend with MoS$_2$/C-400 presenting the highest activity. RBS and depth-profiling XPS results indicate that the best-performing MoS$_2$/C-400 is neither capped by excessive OAm ligands nor covered by thick carbon layers, in sharp contrast to other catalysts calcined at higher or lower temperatures. In this case, the proton and electron transfer are both improved to surmount the slow kinetics of the Volmer step. This study not only gives attention to the judicious
selection of calcination conditions for ligand removal but also unambiguously uncovers the shell thickness effect of core–shell structured catalysts on the catalytic activity.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.2c03181.

Experimental section, briefs of Tafel analysis and RBS, normalized elemental contents, and additional XRD, ATR-FTIR, SEM, XPS, CV, and RBS data (PDF)

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Notes
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