Trash to Treasure: Waste Eggshells Used as Reactor and Template for Synthesis of Co$_9$S$_8$ Nanorod Arrays on Carbon Fibers for Energy Storage

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Supporting Information

ABSTRACT: The disposal of eggshell waste is an environmentally and economically challenging problem. We demonstrate here a novel application of waste eggshell as a multifunctional reaction system to regulate the reactants and pH inside the reactor and using eggshell membrane as protein-based and active substrates to collect the nanostructures formed in a controlled environment. We outline an idea of transferring waste eggshell (or “trash”) into a unique reaction system (or “treasure”) for the synthesis of 1-D nanorod arrays on eggshell membrane protein fibers. Subsequently, the intrinsic sulfur element contained in the eggshell membrane protein fibers is utilized to transform the Co(OH)$_2$ nanorod arrays into Co$_9$S$_8$ nanorod arrays. Meanwhile, the protein fibers are in situ carbonized into carbon fibers. The as-synthesized composite of crystalline Co$_9$S$_8$ nanorod arrays on carbon fibers is demonstrated to be a potential electrode for both lithium-ion and sodium-ion batteries. The idea of in situ carbonization and sulfurization based on proteins could be generalized for the synthesis of a composite of carbon and sulfides.

1. INTRODUCTION

The disposal of eggshell waste is an environmentally and economically challenging problem. A huge amount of eggshell waste is generated in food processing. For example, in the United States alone, nearly 76 billion eggs are consumed every year. Eggshell waste requires proper management. Local landfills are generally unwilling to accept eggshell waste because of the unpleasant odor (e.g., H$_2$S) and microbial growth that affect the working environment and neighboring community. Therefore, eggshell waste is required to be hauled to more-distant landfills, which is more costly. It is always interesting to transform eggshell waste into high-value products, or what we called a “trash to treasure” approach. The eggshell has two main parts: (1) calcified eggshell of calcium carbonate and (2) eggshell membrane of interwoven protein fibers. Eggshell can be used as a fertilizer by spreading it onto farmland, but field capacity may soon be saturated. Eggshell waste can be used as animal feed ingredients, calcium deficiency therapy, and catalyst for biodiesel, to immobilize heavy metals in contaminated soil. The eggshell membrane can be recycled as a dietary supplement for treating osteoarthritis. The existing approaches to recycle eggshell waste generally require the costly separation of the two parts. The eggshell waste with combined eggshell and eggshell membrane is considered useless. The integrated use of both eggshell and eggshell membrane utilizing their unique characteristics and compositions will be useful but not easy to accomplish.

The sophisticated eggshell formation mechanism can be a source of inspiration to develop alternative technologies for the integrated use of eggshell waste, and even to synthesize functional composites. In the formation of eggshell, the carbonate ions from the metabolism of an embryo could pass through the eggshell membrane and react with calcium ions from the uterus producing interstitial calcium carbonate structures on the external surface of the eggshell membrane, forming a robust and protective shell. The eggshell system provides an unique biological environmental for the embryo to avoid infection, control the gas exchange, prevent water loss, and provide a source of calcium for the embryonic skeleton. In other words, the eggshell system can be a robust container or reactor with semipermeability that can control the passage and concentration of reactants to create a unique reaction and/or nucleation environment for the formation of functional nanostructures. At the same time, the eggshell membrane is mainly consisted of protein fibers (e.g., collagen), which could be a rich biomass for making carbon fibers by carbonization. Additionally, the eggshell membrane also contains dermatan sulfate and chondroitin sulfated glycoproteins, which could be a
source of sulfur. In fact, one may already notice in daily life that a prolonged cooked whole egg has a greenish black coloration formed on the surface of the white yolk after peeling off the eggshell. The greenish black coloration is ferrous sulfide, where the sulfide is from the hydrogen sulfide released from decomposed sulfur containing compounds and the iron is from iron-containing compounds in the egg released by heating.6,7 Another notable characteristic one may notice in daily life is a rotten egg’s bad smell due to gas of \( \text{H}_2\text{S} \), also released by the decomposition of sulfide proteins in eggs. In other words, the eggshell membrane can be a source for sulfur. Therefore, the eggshell membrane can be used as a biotemplate for the formation of both carbon fibers and functional sulfides, based on in situ carbonization and sulfurization, achieving full utilization of its protein content. It is still intelligently interesting and technically challenging to develop a simple approach to achieve integrated use of eggshell waste, for example, making functional sulfides and carbon fibers for energy storage application.

Sulfides are attracting much attention for energy applications recently. For example, \( \text{FeS}_2, \text{NiS}_2, \text{and NiS}_2 \) have been demonstrated to be promising candidates for rechargeable batteries.8–10 Cobalt sulfides, including \( \text{CoS}_2, \text{CoS}_3, \text{Co}_2\text{S}_3, \text{CoS}_4, \text{CoS}_5, \text{CoS}_6 \), and \( \text{Co}_2\text{S}_6 \), have also been widely explored for various applications.11–16 In particular, nanostructured \( \text{CoS}_2 \) has demonstrated promising applications in catalysis,17–19 magnetic materials,20,21 supercapacitors,22,23 lithium-ion batteries,24,25 solar cells.26,27 Various nanoscale \( \text{Co}_2\text{S}_6 \) structures have been reported, including nanoscale spheres,28 tubes,29 rods,30 wires,31 and flowers.32 Nanostructured \( \text{CoS}_2 \) could be prepared by high-temperature solid-state synthesis,33 solvothermal methods,34,35 coprecipitation,36 thermal decomposition,37 and chemical vapor deposition.38 The synthesis of \( \text{CoS}_6 \) typically requires high pressure, complex procedure, toxic solvents, expensive precursors, and advanced instruments.28,39,33 Also, it is extremely dangerous to handle \( \text{H}_2\text{S} \) gas for synthesis of \( \text{CoS}_6 \). On the other hand, it is accepted that the composite of carbon with \( \text{CoS}_6 \) can enhance the electrochemical performance of the later in batteries.35–37 It is still technically challenging to develop a facile method to prepare \( \text{CoS}_6 \) nanoarrays using biological waste proteins as a source for sulfide. For example, eggshell membrane may supply a source of carbon and sulfur enabling the integrated use of the eggshell waste, based on in situ carbonization and sulfurization, achieving a composite of carbon and cobalt sulfide, which can find application in batteries.

Herein, we demonstrate a novel procedure to achieve integrated use of eggshell waste as a multifunctional bioreactor and eggshell membrane as multifunctional biotemplate. The overall idea is illustrated in Figure 1. The semipermeability nature of the eggshell system is used to separate the two reactants involved; or in other words, the eggshell is used as a unique reactor (Step 1). To illustrate the main idea outlined here, we selected a model couple of sodium hydroxide (\( \text{NaOH} \)) and cobalt sulfate (\( \text{CoSO}_4 \)) solutions to be put outside and inside of the eggshell, respectively, for the formation of \( \text{Co(OH)}_2 \) nanostructures. The exchange of reactants across the eggshell is used as a means to control the concentration of the reactants and \( \text{pH} \) inside the reactor. Eggshell membrane in the form of pieces of interwoven protein fibers can be inserted inside the reactor as the biotemplate to collect the product of \( \text{Co(OH)}_2 \) formed and coated on the protein fibers (Step 2). The eggshell membrane coated with the \( \text{Co(OH)}_2 \) will be heat-treated under argon. The eggshell membrane of protein fibers will be carbonized to carbon fibers. At the same time, hydrogen sulfide released from decomposed sulfur-containing proteins could react with \( \text{Co(OH)}_2 \) forming \( \text{CoS}_6 \) preserving the nanostructure of the precursor (Step 3). In such a way, we could obtain a piece of composite materials of interwoven carbon fibers coated with \( \text{CoS}_6 \) nanostructures, which can be used for many applications, including as electrodes for batteries. We believe that there are many other reaction couples that can work in our reaction system, including but not limited to metal oxides, sulfides, phosphates, chlorides, sulfates, carbonates, and so on. The idea outlined here provides numerous opportunities for the integrated use of eggshell waste and at the same time to synthesize functional nanostructures. Our method to use waste eggshell as a reactor system is different from those impregnation and infusion-based syntheses using the eggshell membrane.38–45 However, we also recognize that the direct use of nature waste eggshells as reactors for large-scale synthesis may require further optimization and engineering.

2. EXPERIMENTAL SECTION

Materials Synthesis. In a typical procedure, eggshell waste with both eggshell and eggshell membrane was obtained from fresh hen eggs purchased from a nearby grocery store by removing the liquid content of yolk and white via a hole cut in
the eggshell. The eggshell waste was washed by DI water. To the eggshell “container”, a 30 mL water solution of 1 M CoSO₄ with 10 mM CTAB was added. A separate piece of pre-prepared eggshell membrane (1.5 × 3 cm²) was inserted inside the eggshell container. The eggshell membrane was easily separated from the eggshell by exposing the intrinsic eggshell to a 2.5 M HCl solution for 15 min. The eggshell reactor was then partially immersed in a 1 M NaOH solution inside a beaker, and the two solutions were separated by an eggshell (Figure S1 in Supporting Information). The beaker was covered with Parafilm and maintained at 50 °C for 4 days. The as-coated eggshell membrane piece was taken out and washed with water thoroughly and dried in an oven. The color change as compared to bare eggshell membrane indicated that the eggshell membrane was coated with Co(OH)₂ (Figure S2 in SI).

The as-coated eggshell membrane was then heated at a ramp rate of 10 °C/min to 650 °C and kept at the set temperature for 2 h under argon protection to transform the eggshell membrane coated with Co(OH)₂ to carbon fibers coated with Co₉S₈. The chemical composition and morphology of the as-obtained products and intermediates were thoroughly characterized by XRD, SEM, TEM, and SAED according to standard procedure.⁴⁶

Electrochemical Test. The as-obtained composite of eggshell-membrane-derived interwoven carbon fibers coated with Co₉S₈ nanorods as active materials were ground and mixed with a binder (polyvinylidene fluoride), a conductivity enhancer (Super C65 carbon black) at a mass ratio of 8:1:1 in N-methylpyrrolidone, in a mortar to make the slurry. The slurry was casted on copper foil as current collector and dried in vacuum oven at 100 °C. Coin cells were assembled similarly but using lithium foil as the counter and reference electrode, 1 M solution of LiPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1. Lithium-ion testing cells filled with an electrolyte of 1 M NaClO₄ in a mixture of EC and DEC as the electrolyte. The coin cells were tested galvanostatically at room temperature on a MTI BST8-WA battery tester.

3. RESULTS AND DISCUSSION

The successful synthesis of Co₉S₈-coated carbon fibers by the procedure outlined in Figure 1 was confirmed by XRD characterization (Figure 2b). All the diffraction peaks would be assigned to crystalline Co₉S₈ (JCPDS no. 86-2273), indicating high phase purity. The absence of carbon peaks suggest that carbon fibers converted from eggshell membrane protein are mainly amorphous, which could be attributed to the relatively low carbonization temperature of 650 °C. Based on the Scherrer equation, the crystalline size of Co₉S₈ was estimated to be about 18 nm. The precursor of Co(OH)₂ nanorods-coated eggshell membrane fibers after reaction in an eggshell system shows no detectable peaks, indicating that amorphous Co(OH)₂ was formed (Figure 2a). In contrast, when the same two solutions of 1 M CoSO₄ solution with 10 mM CTAB and 1 M NaOH solution were mixed directly under the same experimental conditions, only flake-like Co(OH)₂ microparticles were formed (Figure S3 in SI). XRD analysis evidenced the formation of highly crystalline β-Co(OH)₂ with sharp diffraction peaks (Figure S3a in SI).

Figure 2. XRD analysis of (a) the as-formed composite of amorphous Co(OH)₂ nanorods-coated eggshell membrane protein fibers and (b) the derived composite of crystalline Co₉S₈ nanorods-coated carbon fibers.
The morphologies of the as-synthesized amorphous Co\((\text{OH})_2\) nanorods-coated eggshell membrane protein fibers and the derived composite of crystalline Co\(_9\text{S}_8\) nanorods-coated carbon fibers were thoroughly characterized (Figure 3 and 4).

![Figure 3](image1)

Figure 3. FESEM images of (a,b) original eggshell membrane, (c,d) amorphous Co\((\text{OH})_2\) nanorods-coated eggshell membrane protein fibers, (e,f) crystalline Co\(_9\text{S}_8\) nanorods-coated carbon fibers, at (a,c,e) low and (b,d,f) high magnifications.

The bare eggshell membrane is formed by protein fibers network (Figure 3a). The surface of the original protein fiber is smooth (Figure 3b). After reaction inside the eggshell system, the protein fibers were fully covered with nanorod arrays (Figure 3c). The observation suggests that the coating of the nanorod arrays on the eggshell membrane could occur on any surface exposed to the solution of reactants. The zoom-in view of a section of the coated protein fiber shows that covered protein fiber is highly rough (Figure 3d), in contrast to that of bare protein fiber (Figure 3b). The nanorods have one end free-standing, and the other end is attached on the protein fiber and both are cross-linked and connected. After transformation by heating treatment, the overall morphology was well-preserved (Figure 3e,f), although their chemical compositions have been changed. The low-magnification image clearly shows the overall fiber-like morphology preserving that of eggshell membrane protein fibers (Figure 3e). A section of a broken fiber also clearly reveals the carbon core of the fiber (Figure S14 in SI). The well-preserved morphology after heat treatment also suggests that the 3-D distribution of the derived crystalline Co\(_9\text{S}_8\) nanorods on the carbon fibers is both thermally and mechanically stable.

TEM was used to further characterize the 1-D nanostructures formed (Figure 4). TEM samples were prepared by ultrasonic treatment of the composites to peel off the Co\((\text{OH})_2\) nanorods attached on the eggshell membrane protein fibers. A few nanorods aggregated after they were peeled off from the surface of the protein fiber (Figure 4a). The lack of distinguishable diffraction spots or sharp diffraction rings in SAED pattern suggests that the Co\((\text{OH})_2\) nanorods are mainly amorphous (inset of Figure 4a), which agrees with the XRD result. It is always interesting to explore methods for the synthesis of amorphous Co\((\text{OH})_2\) under mild conditions, in contrast to that of Co\((\text{OH})_2\) nanorods synthesized under high temperature conditions.\(^52,53\) The nanorods are not cylindrical in shape, but they have needle-like structures (Figure 4b). Close examination of the tip and base of a typical nanorod suggests that the nanorod was formed by curled nanosheet with a tubular structure, as evidenced by the light contrast inside the tube and relatively dark contrast around the tube (Figure 4b). The overall structure of the nanorods was well-maintained upon heat treatment and conversion (Figure 4c,d). The as-derived Co\(_9\text{S}_8\) nanorods were highly crystalline as evidenced by clear diffraction spots in SAED pattern (inset of Figure 4c). The diffraction from (311) and (440) planes of Co\(_9\text{S}_8\) are easily assigned in the SAED pattern.\(^21\) The high-magnification view of a typical Co\(_9\text{S}_8\) nanorod shows that also has needle-like structure, similar to its precursor (Figure 4d). The tubular structure is also observed in the Co\(_9\text{S}_8\) nanorod, but the shell is formed by crystalline Co\(_9\text{S}_8\) with nonuniform contrast distribution along the shell and the tubular space is relatively narrow.

To investigate the possible mechanism of formation involved, time-course experiments were carried out (Figure S7 in Supporting Information) and the p\(\text{H}\) environment inside the eggshell reactor was monitored. The plausible formation
A mechanism is proposed as outlined in Figure 5. After the eggshell reactor was filled with the CoSO₄ aqueous solution and immersed into the solution of NaOH, the pH inside the eggshell reactor was immediately measured to be 4.6 maintaining its original acidic nature. This observation suggests that the eggshell could function as a diaphragm to avoid the direct and immediate mixing of the two solutions. The mixing of the two solutions directly will lead to the formation of crystalline β-Co(OH)₂ microparticles (Figure S3 in SI). On the other hand, the eggshell membrane is semipermeable, allowing...
ions to be transferred. One typical example would be salted eggs. The eggshell is dominantly made of porous calcium carbonate stabilized by ~5% protein matrix with air pores (Figure S8a in SI). Therefore, ions could slowly diffuse and cross the eggshell diaphragm. The diffusion of the OH⁻ ions into the eggshell reactor could increase the pH to about 6.2 after 1 day. The presence of additional OH⁻ ions inside the eggshell reactor could create a mild pH environment for the formation of amorphous Co(OH)₂ nanosheets on the eggshell membrane inserted inside the reactor. At the same time, the air pores on the eggshell could be filled by Co(OH)₂ microflake aggregates (Figure S8b in SI). The experimental observation suggests that Co²⁺ ions diffused outward could be immediately consumed by the high concentration of OH⁻ ions presented outside of the eggshell reactor and deposited in the form of crystalline β-Co(OH)₂ aggregates. The deposited crystalline β-Co(OH)₂ microflake aggregates could partially block the air pores or reduce the rates of ion diffusion. In other words, the amount of OH⁻ ions entered the inside of the eggshell reactors could be controlled. Experimentally, the pH increased to only about 7 even after 4 days, which clearly suggests that the pH inside the eggshell reactor was regulated. In other words, the eggshell system provided the right conditions with mild pH for the formation of amorphous Co(OH)₂ instead of β-Co(OH)₂ inside the eggshell reactor. The morphology evolution from Co(OH)₂ nanosheets into nanorods on the eggshell membrane fibers could follow the dissolution-recrystallization mechanism as evidenced by time-course experiments (Figure S7 in SI). Upon heat treatment, hydrogen sulfide released from decomposed sulfur-containing proteins could react with amorphous Co(OH)₂ forming Co₉S₈, preserving the nanostructure of the Co(OH)₂ precursor. At the same time, the eggshell membrane of protein fibers will be carbonized to carbon fibers. The idea of in situ carbonization and sulfurization based on proteins could be generalized for the preparation of various composites of carbon and sulfides for many applications, including batteries, which is our research focus in the near future. Our preliminary results also indicated that the type of Co salts (e.g., Co(NO₃)₂, CoCl₂) selected could dramatically change the morphology and composition of the products using the same egg-shell reactor system (Figure S13 in SI). Our ongoing efforts are to gain better understanding of the mechanism.

The potential application of the as-derived crystalline Co₉S₈ nanorods-coated carbon fibers for lithium-ion batteries was preliminarily evaluated (Figure 6). The cyclic voltammetry (CV) analysis shows broad peaks at around 0.8 and 0.5 V in the first cathodic scan (Figure 6a), which could be associated with the reduction of Co₉S₈ to Co and decomposition of electrolyte and the formation of electrolyte interphase. The cathodic peaks shifted positive potential to around 1.2 and 1.4 V for second and third cycle, indicating the reduced electrode polarization after first-cycle activation. The two reductions peaks in the second and third cycles suggest that two-step reduction of Co₉S₈ occurred. The highly reversible anodic peak at around 2 V could be attributed to the oxidation of Co to Co₉S₈. The first three cycle discharge–charge profiles were also analyzed (Figure 6b). The first cycle discharge profile shows a small plateau around 1.2 V, which could be attributed to the reduction of Co₉S₈ to metallic Co. This plateau shifted upward to around 1.4 V in the second and third cycles, indicating reduced polarization. The charge profiles show a distinct plateau around 2 V, which could be assigned to the oxidation of Co. Therefore, the charge–discharge profiles agree well with the CV results, as expected. The overlap between second and third cycles suggests that the reaction is highly reversible. As a control, bare carbonized eggshell membrane prepared under the same experimental conditions was electrochemically characterized similarly (Figure S10 in SI). The CV curves of carbonized eggshell membrane did not show any reduction peaks around 1.2–1.4 V nor any oxidation peaks around 2 V. Similarly, the charge–discharge profiles did not show plateaus around those voltage. Therefore, the electrochemical characterization provided additional evidence to show the formation of Co₉S₈.

The rate performance of crystalline Co₉S₈ nanorods-coated carbon fibers were evaluated by testing under various currents at 10-cycle intervals each (Figure 6c). A reasonably high capacity of ~530 mAh g⁻¹ was achieved after the 10th cycle of testing at 0.1 A g⁻¹. Subsequently, a capacity of ~465 mAh g⁻¹ was achieved at the 20th cycle of testing at 0.2 A g⁻¹, ~411 mAh g⁻¹ at the 30th cycle of testing at 0.4 A g⁻¹, ~365 mAh g⁻¹ at the 40th cycle of testing at 0.8 A g⁻¹, and 351 mAh g⁻¹ at the 50th cycle of testing at 1 A g⁻¹, indicating relatively good rate performance. Interestingly, when the testing current was set back to 0.1 A g⁻¹, a highly stable capacity of ~515 mAh g⁻¹ was resumed, indicating good electrode stability. Excellent cycling performance was achieved over 300 cycles, and a capacity of about 540 mAh g⁻¹ was maintained (Figure 6d). The dramatically improved rate and cycling performance as compared to Co₉S₈ could be attributed to unique rod-like structure firmly attached on the carbon fibers, which could enhance the electrode/electrolyte contact and facilitate the ion and electron transfer, as well as the mechanical stability.

We note that Co₉S₈ and carbon composites in the form of microspheres prepared by using H₂S gas and in the form of embedded in carbon nanowires using S power for sulfurization also demonstrated comparable performance to our composite. Given that we recycled the S from the waste eggshell membrane proteins, no external S source is required and, therefore, simplified the synthesis. In another preliminary investigation, the application of the as-synthesized crystalline Co₉S₈ nanorods coated on carbon fibers in sodium storage was also demonstrated (Figure S11 in SI). Our ongoing efforts are to optimize their electrochemical performances and also explore other applications, including catalytic applications. The results will be reported once available.

4. CONCLUSION

In summary, we demonstrated a novel application of waste eggshell as a multifunctional reaction system to regulate the reactants and pH inside the reactor and using eggshell membrane as active substrates. We outlined an idea of transferring waste eggshell or “trash” into a unique reaction system or “treasure” for the synthesis of 1-D Co(OH)₂ nanorod arrays on protein fibers. Subsequently, the sulfur element contained inside the protein was utilized to transform the Co(OH)₂ nanorod arrays into Co₉S₈ nanorod arrays, and the protein fibers were in situ converted into carbon fibers. The synthesized composite was demonstrated to be a good electrode for battery applications. We believe the idea of using an eggshell as a multifunctional reactor will enable the synthesis of many different kinds of materials on various substrates. The idea of using both sulfur and carbon contained in proteins at the same time will offer new opportunities in the preparation of composites of sulfides and carbon for many
applications. Our ongoing efforts are aligned in those directions.

ASSOCIATED CONTENT

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Additional results, including optical image, FESEM images, EDS, XRD, control, and sodium storage (PDF)

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Author Contributions
Da Deng conceived the idea and wrote the paper; Xinghua Meng carried out all the experiments and collected the results.

Notes
The authors declare no competing financial interest.

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