# Modification of a Cu Mesh with Nanowires and Magnesiophilic Ag Sites to Induce Uniform Magnesium Deposition

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Cite This: https://doi.org/10.1021/acsami.2c08470 **Read Online** ACCESS III Metrics & More Article Recommendations Supporting Information Ma<sup>24</sup> ABSTRACT: The nature of dendrite-free magnesium (Mg) metal Mg deposits Substrate Magnesiophilic laver anodes is an important advantage in rechargeable magnesium High batteries (RMBs). However, this traditional cognition needs to be reconsidered due to inhomogeneous Mg deposits under extreme current density Uneven Mg growth electrochemical conditions. Herein, we report a three-dimensional (3D) Cu-based host with magnesiophilic Ag sites (denoted as "Ag@ 3D Cu mesh") to regulate Mg deposition behaviors and achieve uniform Mg electrodeposition. Mg deposition/stripping behaviors Local are obviously improved under the cooperative effect of nanowire Uniform Mg growth structures and Ag sites. The test results indicate that nucleation overpotentials are reduced distinctly and cycling performances are prolonged, suggesting that the general rules of 3D structures and Low **Function of 3D structure** Function of coating layer

deposition/stripping. Besides, a unique concave surface structure can induce Mg to deposit into the interior of the interspace, which utilizes Mg more efficiently and leads to improved electrochemical performances with limited Mg content. Furthermore, in situ optical microscopic images show that the Ag@3D Cu mesh can attain a smooth surface, nearly without Mg protrusions, under  $8.0 \text{ mA cm}^{-2}$ , which prevents premature short circuits. This report is a pioneering work to demonstrate the feasibility of modification of Cu-based current collectors and the necessity of functional current collectors to improve the possibility of practical applications for RMBs.

KEYWORDS: rechargeable Mg batteries, Mg deposition, Cu-based current collectors, magnesiophilic Ag sites, limited Mg content

# 1. INTRODUCTION

Because of the increasing human demand for electrochemical energy-storage systems with lower cost and higher safety, nextgeneration "beyond Li-ion" batteries, have attracted extensive attention in recent years.<sup>1</sup> Among numerous candidates, rechargeable magnesium batteries (RMBs) are at the center of this research field due to their high theoretical volumetric capacity ( $3833 \text{ mAh cm}^{-2}$ ), high crustal abundance (the eighth most abundant element on earth), and relatively low standard reduction potential (-2.37 V vs standard hydrogen electrode (SHE)) of Mg metal.<sup>2–4</sup> More importantly, Mg metal tends to form a dendrite-free surface during the electrodeposition process and possesses a moderate chemical property of reacting with oxygen and water under air exposure, thereby earning the reputation of being safer than its counterpart Li metal.<sup>3–7</sup> Unfortunately, there is a lack of adequate in-depth and comprehensive studies on RMBs to achieve large-scale commercialization, and the development of RMBs is still in the primary laboratory evaluation stage.

affinity sites improve the durability and reversibility of Mg

After Aurbach et al. developed the first prototype of RMBs over two decades ago,<sup>8</sup> mainstream research has focused on the design of cathode materials for the rapid diffusion dynamics of Mg<sup>2+</sup> ions as well as electrolytes for compatibility

with electrodes and accomplished considerable advances.<sup>9–22</sup> Until recently, several original and unconventional studies were reported, which have intrigued researchers and inspired them to further scrutinize RMBs,<sup>23</sup> such as engineering an artificial solid–electrolyte interface (SEI) on Mg metal,<sup>24–28</sup> exploring the interface evolution process between Mg metal and noncorrosive electrolytes,<sup>29</sup> and regulating Mg electrodeposition behaviors.<sup>30–33</sup> The expected high safety, which is a significant incentive of Mg batteries, is also challenged by some novel studies.

Initial studies demonstrated that Mg forms homogeneous and smooth deposition layers during the electrodeposition process.<sup>34–37</sup> Nevertheless, there are now an increasing number of reports suggesting the growth of Mg dendrites under extreme conditions,<sup>38,39</sup> and caution needs to be exercised while ascertaining the absence of dendrite

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Figure 1. (a) Schematic illustration of the fabrication of the Ag@3D Cu mesh current collector. (b) Optical images of the four materials. (c, d) SEM of the Ag@3D Cu mesh at low and high magnifications. (e, f) XRD and XPS images of the Ag@3D Cu mesh. (g-i) EDS mapping images of the Ag@3D Cu mesh.

formation.<sup>40,41</sup> At least, it indicates that Mg metal can deposit nonuniformly at high current densities and high areal capacities, which is presumably harmful to the safety and cycling life of RMBs. Besides, potential nonuniform Mg deposition is likely to destroy the artificial SEI during the deposition/stripping process. To tackle a similar challenge of dendrites in Li-metal batteries, a three-dimensional (3D) host with lithiophilic sites was designed to delay the growth of Li dendrites.<sup>42,43</sup> This is attributed to the fact that the 3D substrate provides more free space, which can decrease the effective current density and has more active sites to induce homogeneous metal growth.<sup>44-47</sup> Therefore, according to this conception, designing an analogous 3D deposition substrate with abundant magnesiophilic sites can be of considerable use to regulate the uniform electrodeposition of Mg, and it is extremely critical for increasing the safety of RMBs, mitigating the challenge of modifying Mg metal anodes and promoting the possibility of practical applications. On the basis of this design principle, Lim et al. fabricated graphitic carbon nanosubstrates (GC-NSs) with a 3D microporous structure, realizing a more reversible and stable cycling performance over 1000 cycles compared with flat metal substrates.<sup>32</sup> Yang et al. reported 3D Mg<sub>3</sub>Bi<sub>2</sub> scaffolds via the electrochemical alloying reaction of reversible Mg plating/stripping.<sup>31</sup> Mg<sub>3</sub>Bi<sub>2</sub> alloy substrates avoided continuous electrochemical passivation and showed a lower nucleation overpotential compared with Mg foils. Cui et al. designed vertically aligned nitrogen- and oxygen-doped carbon nanofiber arrays on a carbon cloth (VNCA@C) as functional current collectors to guide uniform Mg electrodeposition.<sup>30</sup> The VNCA@C host delivered a lower overpotential and a longer cycling life at a high current density of 10.0 mA cm<sup>-2</sup>. Besides, they provided a structural design guideline based on theoretical calculations and experimental results for the first time in Mg batteries. Nevertheless, these magnesiophilic substrates were carbon-based or alloy-based

materials that are not commonly used in large-scale production currently. In contrast, Cu current collectors were widely applied in commercial Li-ion batteries to avoid anode alloy reactions.<sup>44,48</sup> However, some studies reported that the growth of Mg on Cu current collectors was extremely unfavorable, which indicated that normal Cu-based substrates were quite magnesiophobic and were incapable of being used as anode current collectors directly in RMBs.<sup>31,32,49</sup> Consequently, a 3D magnesiophilic Cu-based host is strongly desired for the practical application of Mg anodes. Besides, Yang and coworkers reported that better electrochemical performances can be obtained with a Ag substrate in RMBs, which is relevant to the formation of Mg-Ag alloys, suggesting the good magnesiophilicity of Ag metal.<sup>50</sup> The simulated Mg-Ag phase diagram illustrated a non-zero solubility value of Mg in Ag at room temperature, which further indicated the possibility of forming Mg-Ag alloys by the electrodeposition process.<sup>5</sup>

Herein, we elaborately fabricate a 3D Cu mesh with magnesiophilic Ag sites (denoted as "Ag@3D Cu mesh") as the high-performance and low-cost current collector for reversible Mg deposition/stripping. The magnesiophilicity of Ag is proved by systematic experiments. As expected, superior kinetics and more excellent electrochemical performances of the Ag@3D Cu mesh in RMBs are verified by various testing methods. The Ag@3D Cu mesh possesses a large 3D structure and affinity sites at the same time, which could be used as a study model, indicating the universality of modification rules for current collectors. Compared with the unmodified Cu mesh, the Ag@3D Cu mesh shows better adhesiveness of the grown Mg metal, which is attributed to the concave surface structure, and exhibits improved electrochemical performances with a limited Mg content. Moreover, in situ optical images reveal that the reason for the rapid short circuit that occurred in common current collectors under a high current density is



Figure 2. (a) CV curves of the Mg//Ag@3D Cu mesh, Mg//Ag@Cu mesh, and Mg//Cu mesh at 25 mV/s with a three-electrode system. (b) Nyquist plots of the Mg//Ag@3D Cu mesh, Mg//Ag@Cu mesh, and Mg//Cu mesh in the initial state. Voltage profiles of galvanostatic Mg metal deposition on the Ag@3D Cu mesh, Ag@Cu mesh, and Cu mesh at (c) 1.0 mA cm<sup>-2</sup> and (d) 8.0 mA cm<sup>-2</sup>.

the random growth of large Mg protrusions, and a smooth surface can only be obtained with a Ag@3D Cu mesh. In addition, the full cell with the Mg@Ag@3D Cu mesh could exhibit a higher discharge capacity and longer cycling reversibility.

#### 2. RESULTS AND DISCUSSION

Figure 1a schematically illustrates the fabrication of the Ag@ 3D Cu mesh from a pristine Cu mesh. First, a 3D Cu mesh was synthesized by a previously reported method.<sup>52</sup> A clean Cu mesh was immersed into an ammonia solution for 48 h to generate  $Cu(OH)_2$  nanowires. The growth of  $Cu(OH)_2$ nanowires could be optically observed through a gradual color change in both the solution and the Cu mesh during this reaction process. Subsequently, the as-prepared Cu(OH)<sub>2</sub>@Cu mesh was heated under a vacuum and a H<sub>2</sub>/Ar mixed atmosphere to obtain the 3D Cu mesh. The Ag@3D Cu mesh was synthesized by a simple replacement reaction between the 3D Cu mesh and AgNO<sub>3</sub> solution. It is worth emphasizing that this is the first and meaningful attempt to demonstrate the feasibility of modification of Cu-based current collectors for RMBs. This synthesis method with a simple procedure and mild reaction conditions is in accord with the idea of green chemistry and can also provide scientific guidance for future large-scale preparation of anode current collectors in RMBs. To verify the magnesiophilicity of Ag individually, we designed an intermediate sample by a replacement reaction similar to that mentioned above between pristine Cu mesh and AgNO<sub>3</sub> solution (denoted as "Ag@Cu mesh"). Figures 1b and S1a,b show the optical images of these samples. The clear colors of these products are consistent with previous reports, which indicate the successful synthesis of these materials.<sup>52,</sup> Scanning electron microscopy (SEM) images of the Ag@3D

Cu mesh reveal a 3D structure composed of nanowires (Figure 1c,d). These nanowires are evenly grown on the surface of the Cu mesh. The highly distributed Cu nanowires on the Cu mesh substrate surface possess large specific surface areas, which can decrease the local current density and provide more space for restoring Mg metal. SEM images of the Cu mesh and Ag@Cu mesh (Figure S2a-d) reveal that the surface texture before and after the replacement reaction between Cu and AgNO<sub>3</sub> is hardly changed. X-ray diffraction (XRD) patterns (Figures 1e and S3) show the characteristic peaks of Cu ( $\approx$ 43, 50, and  $74^{\circ}$ ), which match with the reference card of the Cu crystal phase (PDF#01-070-3038). The XRD patterns shown in Figure S4a,b also verify the crystal structure of intermediate products (Cu(OH)<sub>2</sub>@Cu mesh and 3D Cu mesh). However, there is no apparent characteristic peak of Ag in Figures 1e and \$3, which is due to the low content of Ag compared with the Cu host. To prove the existence of Ag, X-ray photoelectron spectroscopy (XPS) patterns were obtained, which are displayed in Figures 1f and S5. The four typical peaks can be attributed to Ag  $3d_{3/2}$  (368.6 eV), Ag  $3d_{5/2}$  (374.6 eV), Cu  $2p_{3/2}$  (932.9 eV), and Cu  $2p_{1/2}$  (952.6 eV).<sup>53</sup> These typical peaks clearly indicate the existence of metallic Ag and Cu. The corresponding energy-dispersive spectroscopy (EDS) mapping images of the Ag@3D Cu mesh (Figure 1g-i) and the Ag@Cu mesh (Figure S6) further demonstrate that the Ag metal is relatively uniformly distributed on the surface of the Cu-host structure. These Ag sites could serve as magnesiophilic sites to induce uniform Mg electrodeposition.

We chose the classic all-phenyl complex (APC) as the electrolyte in the whole electrochemical testing process. The APC electrolyte was prepared in our own laboratory (see Experimental Section for more details), and its performance was examined by Mg foil symmetric cells (Figure S7a,b). First,



**Figure 3.** Ex situ optical images of Mg//GF//Cu mesh cells after (a) 0.4 mAh cm<sup>-2</sup>, (b) 2.0 mA cm<sup>-2</sup>, and (c) 8.0 mA cm<sup>-2</sup> Mg deposition; Mg//GF//Ag@Cu mesh cells after (d) 0.4 mAh cm<sup>-2</sup>, (e) 2.0 mA cm<sup>-2</sup>, and (f) 8.0 mA cm<sup>-2</sup> Mg deposition; and Mg//GF//Ag@3D Cu mesh cells after (g) 0.4 mAh cm<sup>-2</sup>, (h) 2.0 mA cm<sup>-2</sup>, and (i) 8.0 mA cm<sup>-2</sup> Mg deposition at a current density of 1.0 mA cm<sup>-2</sup>. (j) Schematic illustration of the separating process on the common Cu-based substrate and Ag@3D Cu mesh substrate.

the kinetics of Mg deposition/stripping on the Ag@3D Cu mesh, Ag@Cu mesh, and Cu mesh were comparatively investigated by cyclic voltammetry (CV) with a three-electrode system. As shown in Figure 2a, the initial reduction potentials of these three current collectors are about -0.20, -0.35, and -0.45 V at a scan rate of 25 mV/s, respectively (shown in the inset in Figure 2a). Meanwhile, the response currents of the Ag@3D Cu mesh, Ag@Cu mesh, and Cu mesh decrease successively during the whole testing process. These results demonstrate that faster kinetics can be obtained by the Ag@ Cu mesh compared with the Cu mesh, which indicates the magnesiophilicity of Ag, and the Ag@3D Cu mesh is obviously superior to the others due to the cooperative effect of the large specific surface area and Ag sites. In addition, the Mg//Ag@ 3D Cu mesh cell shows a distinctive CV curve range of 0.55 to -0.45 V, which exhibits both the alloying reaction process of Mg-Ag and the Mg deposition process (Figure S8). The CV curves of the Mg//Ag@3D Cu mesh in the second and third cycles show no apparent further alloying reaction process and exhibit the normal deposition curve, which indicates that the alloying reaction process could occur only in the first cycle (Figure S9). Furthermore, the CV curves of the stripping processes of the Ag@3D Cu mesh, Ag@Cu mesh, and Cu mesh are almost the same, and so we speculate that the dealloying process could not happen during the CV scanning process. To acquire more kinetic information about these current collectors, we carried out electrochemical impedance spectroscopy (EIS) measurements. Figure 2b shows the Nyquist plots of the Mg//Ag@3D Cu mesh, Mg//Ag@Cu mesh, and Mg//Cu mesh in the initial state. As expected, the impedance data are in perfect agreement with the CV test results. The Ag@3D Cu mesh, Ag@Cu mesh, and Cu mesh all have semblable ohmic resistances ( $R_1 = 13.48 \ \Omega$  for the Ag@ 3D Cu mesh, 9.58  $\Omega$  for the Ag@Cu mesh, and 9.50  $\Omega$  for the

Cu mesh), confirming that the conductivities of the APC electrolyte in these three cell systems are almost the same.<sup>54</sup> A distinct difference could be observed in the interfacial resistances ( $R_2$ ). The  $R_2$  of Mg//Ag@Cu mesh cells (7918  $\Omega$ ) is smaller than that of the Mg//Cu mesh (18762  $\Omega$ ), indicating the magnesiophilic function of Ag sites. The Ag@3D Cu mesh current collector shows the lowest  $R_2$  (2407  $\Omega$ ) compared with both the Ag@Cu mesh and the Cu mesh, suggesting its excellent charge-transfer kinetics.

The electrochemical performances of galvanostatic Mg metal deposition on the Ag@3D Cu mesh, Ag@Cu mesh, and Cu mesh at current densities of 1.0 and 8.0 mA cm<sup>-2</sup> are shown in Figure 2c,d, respectively. The nucleation overpotential is usually defined by the difference in the value between the lowest point of the voltage dip and the subsequent flat electrodeposition plateau.55 The nucleation overpotential is used to overcome the heterogeneous nucleation energy barrier due to the unsatisfactory thermodynamic affinity between the substrate and the deposition metal. For the Cu mesh, the overpotential is obviously the highest among these three current collectors at both current densities of 1.0 mA cm<sup>-2</sup> (0.42 V) and 8.0 mA cm<sup>-2</sup> (0.58 V). In contrast, the overpotential of the Ag@Cu mesh decreases to a certain extent compared with that of the Cu mesh (0.34 V at 1.0 mA  $cm^{-2}$ and 0.48 V at 8.0 mA cm<sup>-2</sup>), and the Ag@3D Cu mesh shows the lowest overpotential (0.15 V at 1.0 mA  $cm^{-2}$  and 0.17 V at 8.0 mA cm<sup>-2</sup>), which correspond to the above consequences. The details of Mg deposition curves are shown in Table S1. These experimental results indicate that it is reasonable to believe that the better Mg deposition/stripping kinetics gained could be attributed to the excellent Mg affinity of Ag and the large 3D structure. It should be noticed that the voltage dip curve of only the Ag@3D Cu mesh at 1.0 mA cm<sup>-2</sup> is conspicuously pitched, whereas the others are nearly vertical,



**Figure 4.** SEM images of the Ag@3D Cu mesh electrode in different deposition/stripping states. Mg deposition of (a) 0.4 mAh cm<sup>-2</sup>, (b) 2.0 mAh cm<sup>-2</sup>, and (c) 8.0 mAh cm<sup>-2</sup> in the first cycle. Mg stripping of (d) 0.4 mAh cm<sup>-2</sup>, (e) 2.0 mAh cm<sup>-2</sup>, and (f) 8.0 mAh cm<sup>-2</sup> in the first cycle. Mg stripping of (g) 0.4 mAh cm<sup>-2</sup>, (h) 2.0 mAh cm<sup>-2</sup>, and (i) 8.0 mAh cm<sup>-2</sup> in the first cycle. Mg stripping of (g) 0.4 mAh cm<sup>-2</sup>, (h) 2.0 mAh cm<sup>-2</sup>, and (i) 8.0 mAh cm<sup>-2</sup> in the first cycle. Mg stripping of (g) 0.4 mAh cm<sup>-2</sup>, (h) 2.0 mAh cm<sup>-2</sup>, and (i) 8.0 mAh cm<sup>-2</sup> in the first cycle. Mg stripping of (g) 0.4 mAh cm<sup>-2</sup>, (h) 2.0 mAh cm<sup>-2</sup>, and (i) 8.0 mAh cm<sup>-2</sup> in the first cycle.

and that its galvanostatic deposition curves in the first cycle show a magnesiation plateau above 0 V (Figure S10), demonstrating that the formation of the Mg–Ag alloy could occur under very low local current density conditions during the Mg deposition process.

To examine the genuine electrodeposition situation of these three current collectors, they were first assembled into asymmetric coin cells with glass fibers (GF) as separators. After depositing different capacities (0.4 mAh cm<sup>-2</sup>, 2.0 mA cm<sup>-2</sup> and and 8.0 mA cm<sup>-2</sup>) of Mg metal at a current density of 1.0 mA cm<sup>-2</sup>, the coin cells were disassembled immediately in a glovebox filled with pure argon. The optical images are exhibited in Figure 3a-i. Interestingly, in both the Mg//GF// Cu mesh cells and the Mg//GF//Ag@Cu mesh cells, nearly all of the deposited Mg metal adheres to the GF separators rather than the current collectors (details are shown in Figure S11ah). In sharp contrast, only in the Mg//GF//Ag@3D Cu mesh coin cells, most of the deposited Mg metal is attached to the Ag@3D Cu mesh current collectors, revealing clean GF separators. These results indicate that the concave surface structure formed by the interspace among periodically arranged nanowires on the Ag@3D Cu mesh can induce Mg metal to deposit into the interior of the interspace construction without being stuck to the GF separators easily while separating (Figure 3j). However, for the normal mesh structure of the Cu mesh and Ag@Cu mesh, due to the lack of an analogous concave surface structure, the majority of the deposited Mg metal grows on the surface of the mesh and thus

it effortlessly adheres to GF separators. The Mg grown in GF separators produce dead Mg upon cycling, which results in an irreversible Mg loss and poor electrochemical performances ultimately.

The Mg electrodeposition morphology evolution process of the Ag@3D Cu mesh electrode is further investigated in detail. SEM images of the Ag@3D Cu mesh after Mg deposition show that a relatively uniform Mg deposition could be achieved at 0.4 mAh cm<sup>-2</sup> (Figures 4a and S12a), 2.0 mAh cm<sup>-2</sup> (Figures 4b and S12b), and 8.0 mAh cm<sup>-2</sup> (Figures 4c and S12c) capacities. It is clear that Mg deposits tend to fill up the inside channels and form a homogeneous surface eventually, proving the previous speculation that a concave surface structure could accommodate more Mg deposits without being stuck to the GF separators easily and that the Ag@3D Cu mesh current collector displays good reliability. Besides, even in the low-magnification SEM image (Figure S13a-c), no uneven accumulations of Mg deposits are observed. Subsequently, the corresponding structural stability of the Ag@3D Cu mesh current collector is further investigated by SEM after the first and tenth deposition/ stripping cycles at area capacities of 0.4, 2.0, and 8.0 mAh  $cm^{-2}$ . After all of the Mg metal is stripped off, the original nanowire structures of Ag@3D Cu are basically well-recovered without large Mg residues (Figure 4d–i), illustrating the good cycling reversibility and stability of the Ag@3D Cu mesh current collector during the Mg deposition/stripping process.



Figure 5. Voltage profiles of (a) Mg//Ag@3D Cu mesh cell, (b) Mg//Ag@Cu mesh cell, and (c) Mg//Cu mesh cell at 1.0 mA cm<sup>-2</sup> for 8.0 mAh cm<sup>-2</sup>. Voltage profiles of (d) Mg//Ag@3D Cu mesh cell, (e) Mg//Ag@Cu mesh cell, and (f) Mg//Cu mesh cell at 8.0 mA cm<sup>-2</sup> for 8.0 mAh cm<sup>-2</sup>. (g) Voltage profiles of Mg@Ag@3D Cu mesh//Ag@3D Cu mesh cell, Mg@Ag@Cu mesh//Ag@Cu mesh cell, and Mg@Cu mesh//Cu mesh cell at 1.0 mA cm<sup>-2</sup> for 1.0 mAh cm<sup>-2</sup>. (h) Rate performances of Mg//Ag@3D Cu mesh, Mg//Ag@Cu mesh, and Mg//Cu mesh at different current densities from 0.1 to 8.0 mA cm<sup>-2</sup>.

These results are also supported by XRD patterns (Figure S14a-c).

The electrochemical cycling stability of these three types of asymmetrical cells (Mg//Ag@3D Cu mesh, Mg//Ag@Cu mesh, and Mg//Cu mesh) are examined by comparing the galvanostatic deposition/stripping voltage profiles. At a current density of 1.0 mA cm<sup>-2</sup> with a deposition capacity of 8.0 mAh cm<sup>-2</sup>, these three types of asymmetrical cells show outstanding long-term cycling performances for over 200 h without exception (Figure 5a-c), indicating good reliability of each cell component and the excellent compatibility among Mg foils, APC electrolytes, and current collectors. When the current density increases to 8.0 mA cm<sup>-2</sup>, only the asym-

metrical cell of Mg//Ag@3D Cu mesh could still run well for at least 25 h (Figure 5d). In sharp contrast, the Mg//Ag@Cu mesh cell and Mg//Cu mesh cell become short-circuited rapidly in less than 12 and 6 h, respectively (Figure 5e,f). The Coulombic efficiencies (CEs) of the three types of current collectors are shown in Table S2. These experimental results clearly illustrate the remarkable cycling performance of the Ag@3D Cu mesh current collector even under an extreme electrochemical testing condition of 8.0 mA cm<sup>-2</sup> with 8.0 mAh cm<sup>-2</sup>. This might be attributed to the relatively uniform Mg deposition induced by the cooperative effects of the 3D nanowire structure and magnesiophilic Ag sites. The above experimental results indicate the essential roles of the 3D



Figure 6. In situ optical observation of the three types of asymmetric cells at 8.0 mA cm<sup>-2</sup> for 8.0 mAh cm<sup>-2</sup>. The time interval between two images is 30 min. (a-c) Mg//Cu mesh cell, (d-f) Mg//Ag@Cu mesh cell, and (g-i) Mg//Ag@3D Cu mesh cell. (j-l) Schematic illustrations of Mg deposition on the three types of current collectors.

structure and magnesiophilic sites for the durability and reversibility of the Mg deposition/stripping process under strict electrochemical testing conditions. Besides, we measured the Mg//Mg symmetric cell under 8.0 mA cm<sup>-2</sup> with 8.0 mAh cm<sup>-2</sup> and found that it also becomes quickly short-circuited after several cycles (Figure S15). This phenomenon indicates that the short circuit of the Mg//Ag@3D Cu mesh might be caused by the nonuniform Mg deposition at the Mg anode side. Compared with other current collectors, our work (Ag@ 3D Cu mesh) shows the lowest overpotentials at different current densities and the longest cycling time with a high capacity (Table S3). The electrochemical cycling stabilities with celgard2500 separators are also shown in Figure S16a–e.

The electrochemical performances of these three types of electrodes with a limited Mg content are also investigated. However, the electrochemical tests with a limited Mg content are crucial for the practical application of RMBs but do not get much attention. Besides, there were no reports on detailed methods for preparing the premagnesiated electrodes to our knowledge. Because of the low adhesiveness of the growth of Mg on the Ag@Cu mesh and Cu mesh, it is unrealistic to obtain premagnesiated electrodes from assembled coin cells directly. Hence, as an attempt, we used the premagnesiated current collectors without separating the GF separators (denoted as "Mg@Ag@3D Cu mesh", "Mg@Ag@Cu mesh," and "Mg@Cu mesh", respectively) to conduct the electrochemical test. At the outset, the limited Mg content was 2.0 mAh cm<sup>-2</sup> and the current density was 1.0 mA cm<sup>-2</sup>. In the first cycle, the nucleation overpotential of the Mg@Ag@3D Cu mesh//Ag@3D Cu mesh cell was approximately 0 V, which is the lowest compared with those of the other two cells (inset in Figure 5g). Furthermore, the Mg@Ag@3D Cu mesh//Ag@ 3D Cu mesh cell shows a steady galvanostatic voltage profile for about 50 h (whereas it is 35 h for the Mg@Ag@Cu mesh// Ag@Cu mesh cell and 15 h for the Mg@ Cu mesh//Cu mesh cell). The distortion of voltage curves during the charging/ discharging process is caused by the irreversible Mg capacity loss. When there is a limitation of Mg at the anode side, such as due to complete consumption by the Mg@Cu mesh or Mg@Ag@Cu mesh, the discharge curve would decline sharply (Figure S17). Thereafter, the current density is increased to 8.0 mA  $cm^{-2}$  with a limited Mg content of 8.0 mAh  $cm^{-2}$ .



Figure 7. (a) Schematic illustration of the key components and the working principle of RMBs. Full-cell performances using anodes of (b) Mg@ Ag@3D Cu mesh, (c) Mg@Ag@Cu mesh, and (d) Mg@Cu mesh. (e) Discharge capacity and Coulombic efficiency of the full cell with the three types anodes.

However, these three types of asymmetrical cells are all shortcircuited quickly after several cycles (Figure S18a-c), indicating that the performance of current collectors should be further improved or the method of preparing the premagnesiated electrodes should be optimized.

Rate performances of asymmetrical cells are also investigated (Figure 5h). The current densities were 0.1, 0.5, 1.0, 2.0, 4.0, and 8.0 mA cm<sup>-2</sup>. Neither the Mg//Ag@Cu mesh nor the Mg//Cu mesh cell was capable of running under a relatively high current density of 8.0 mA cm<sup>-2</sup> and became shortcircuited quickly, which might be caused by the random 3D growth of Mg deposits.<sup>56</sup> In contrast, the Mg//Ag@3D Cu mesh cell could operate stably even at a current density of 8.0 mA  $cm^{-2}$  for several hours, which is consistent with the above result. However, when the current density reverts to 0.1 mA  $cm^{-2}$ , the Mg//Ag@3D Cu mesh cannot run as well as expected. Subsequently, the highest current density decreases to 4.0 mA cm<sup>-2</sup>. The Mg//Ag@3D Cu mesh cell shows a stable and satisfactory voltage profile, consistent with the previous literature (Figure S19).<sup>30</sup> These results unequivocally demonstrate the superior rate performance of the Ag@3D Cu electrode during the Mg deposition/stripping process.

To further understand the reason for the premature short circuit under high current densities with high area capacities clearly, we used an in-situ optical microscope to observe the morphology of Mg deposits during the electrodeposition process at 8.0 mA cm<sup>-2</sup> for 8.0 mAh cm<sup>-2</sup> (Figure 6a–1). Gray

arrows represent the direction of Mg deposition. It must be mentioned that the structures of these three electrodes would be slightly but inevitably damaged during sample preparation. For the Cu mesh, large protrusions could be observed in the sectional views as the discharge time progresses, and its thickness is nearly the same as the initial size of the Cu mesh. These large Mg hemispherical deposits render a more nonuniform electric field distribution on the surface of current collectors, which could further accelerate the growth of inhomogeneous Mg deposits. The random growth of numerous large protrusions such as these might be the cause for the extremely poor electrochemical performance in a practical coin cell under a relatively high current density. When the large protrusions grow through the GF separator and contact the anode material of the Mg foil, the asymmetric cell would be short-circuited rapidly. As for the Ag@Cu mesh, this situation could be improved to a certain extent. Only some small protrusions are detected as the Ag metal induces a relatively uniform Mg deposition. In comparison, a smooth surface nearly without any protrusions could be obtained on the Ag@3D Cu mesh. Although some very small protrusions can still be found in the Ag@3D Cu mesh, this is because the deposition substrate in our work is a Cu-based mesh, which is not flat. Thus, as the growth of the Mg deposition is based on a curvilinear substrate, it is reasonable to find some very small protrusions on the Ag@3D Cu mesh. In addition, the interior space of arranged nanowires is occupied by Mg deposits

preferentially rather than the exposed Cu-host, the cross section of which confirms the mechanism of preferential growth on the microchannel. These visualization results further prove the magnesiophilicity of Ag sites and the superiority of the 3D nanowire structure. Moreover, it indicates that the morphology of Mg deposits in the APC electrolyte depends on both the substrate material and the local current density, and the transformation from kinetic control to diffusion control under a high current density leads to the growth of 3D Mgstacked spheres, which cause the premature short circuit eventually.

To simulate the practical operation situation, the performances of full cells are investigated with  $Mo_6S_8$  cathodes (Figure 7a-e). The XRD pattern of the  $Mo_6S_8$  material is shown in Figure S20. The full cell with the Mg@Ag@3D Cu mesh anode could deliver a specific capacity of about 64.73 mAh  $g^{-1}$ in the 200th cycle. In contrast, for the Mg@Ag@Cu mesh anode, the full cell displays a lower specific capacity of about 57.01 mAh  $g^{-1}$  in the 150th cycle. However, the full cell with the Mg@Cu mesh anode could exhibit a specific capacity of only about 8.87 mAh  $g^{-1}$  in the 120th cycle, which is the lowest. The low average discharge capacity of the Mg@Cu mesh and Mg@Ag@Cu mesh might be caused by the high overpotential at the anode side, which leads to a narrow practical cut-off charging/discharging voltage range during cycling. Moreover, the rapid decline of the discharge capacity of the Mg@Cu mesh//Mo<sub>6</sub>S<sub>8</sub> cell indicates the Mg anode capacity loss during the charging/discharging process and the poor Mg cycling reversibility of common Cu current collectors.

## 3. CONCLUSIONS

In conclusion, we prepared a modified Cu mesh with nanowires and magnesiophilic Ag sites, which could be used as a model to study the modification rules by a facile and lowcost method. The Cu nanowire structure formed in an ammonia solution was confirmed by SEM and XRD images, and the existence of an Ag metal introduced by the simple replacement reaction is proved by XPS and EDS mapping results. The systematic experimental results indicate the function of magnesiophilic Ag sites. Ex situ optical images illustrate a better adhesiveness of the synthesized Mg metal to the Ag@3D Cu substrate, which is attributed to the unique concave surface structure preventing the formation of dead Mg in GF separators, which in turn leads to improved electrochemical performances with a limited Mg content. The Ag@ 3D Cu mesh collector could achieve an obviously reduced nucleation overpotential under current densities of 1.0 and 8.0 mA cm<sup>-2</sup> and perform stably even at a high current density of 8.0 mA  $cm^{-2}$  with a high area capacity of 8.0 mAh  $cm^{-2}$  for over 25 h. In situ optical microscopy images show that the reason for the short circuit under a high current density is the random 3D growth of large protrusions, and only the Ag@3D Cu mesh could attain a smooth surface. This report is a pioneering work toward realizing uniform Mg deposition by the Cu mesh substrate, which indicates the potential of functional current collectors for large-scale application in Mg batteries.

#### 4. EXPERIMENTAL SECTION

**4.1. Fabrication of the Ag@3D Cu Mesh.** The pristine Cu mesh (50  $\mu$ m in thickness, canrd, >99.9%) was first immersed in diluted hydrochloric acid for about 10 min to remove surface oxidation layers, and then the Cu mesh was washed with deionized water and alcohol

in sequence. After that, the clean Cu mesh was soaked in an ammonia solution (15 wt %, Aladdin) for 48 h. During this process, a blue layer of  $Cu(OH)_2$  was generated on the Cu mesh surface. The as-prepared  $Cu(OH)_2@Cu$  mesh was heated at 200 °C for 5 h under a vacuum. Then, it was transferred into a tube furnace and reduced at 500 °C for 12 h in a H<sub>2</sub>/Ar mixed flow (10% H<sub>2</sub> in volume) to obtain the 3D Cu mesh. Finally, a Ag-modified 3D Cu mesh was fabricated by a simple replacement reaction. Typically, the 3D Cu mesh was immersed into a AgNO<sub>3</sub> (Aladdin, >99%) solution of 0.17 g/100 mL for 2 min. Afterward, the black Ag@3D Cu mesh was washed again with deionized water and alcohol in turn. The Ag@3D Cu mesh was dried and punched out into 16 mm circular disks for RMBs.

**4.2.** Preparation of the APC Electrolyte. The APC electrolyte consists of 0.4 M (PhMgCl)<sub>2</sub>–AlCl<sub>3</sub> with tetrahydrofuran (THF) solvent.<sup>57</sup> First, anhydrous AlCl<sub>3</sub> (Sigma-Aldrich, >99.9%) was slowly and carefully added to THF (Aladdin, >99.9%, anhydrous) under vigorous stirring to avoid a rapid temperature increase because the dissolution process was exothermic. After AlCl<sub>3</sub> was dissolved completely, commercial 2 M PhMgCl/THF (Aladdin, 2.0 M in THF) was added dropwise into the clear and transparent AlCl<sub>3</sub>/THF solution. Finally, the as-prepared APC electrolyte was magnetically stirred for 12 h at room temperature. Because of the high activity of the Grignard reagent, all synthesis processes were performed in a Braun glovebox filled with pure argon (water and oxygen contents were less than 1.0 ppm).

**4.3. Preparation of the Mg Foil Electrodes and GF Separators.** The pristine Mg foils (0.2 mm in thickness, >99.9%) were polished in an air environment and then washed with alcohol. After the alcohol was volatilized completely, the Mg foils were transferred to an argon-filled Braun glovebox immediately. The Mg foils were further thoroughly polished three times and then washed with pure THF solvent, and finally, they were punched out into 12 mm circular disks before use. GF separators (Whatman, GF/D) were punched out into 19 mm circular disks and transferred into the Braun glovebox mentioned above.

**4.4. Material Characterizations.** The crystal structure was characterized by XRD (Rigaku Corporation, Japan) with Cu K $\alpha$  radiation at room temperature, and the angle range was from 5 to 90° (2 $\theta$ ) with a scanning speed of 5° min<sup>-1</sup>. The surface morphology was measured by SEM (Hitachi S-4800). XPS spectral information was obtained with the PHI Quantum 2000.

4.5. Electrochemical Measurements. CR-2032-type coin cells were assembled for testing, in which Ag@3D Cu meshes served as cathodes, Mg foils served as anodes, and the GF served as separators. The amount of APC electrolyte used for coin cells was 200  $\mu$ L. All coin cells were aged for an additional 10 h before electrochemical measurements. The CV measurements were obtained on an electrochemical workstation (CHI 440B, Chenhua) with a voltage range of -1.0 to 2.0 V (initial electric potential is the open-circuit voltage; negative scanning): the counter electrode and reference electrode are Mg foils; the working electrode is a Cu mesh, Ag@Cu mesh, or Ag@3D Cu mesh. The EIS data were measured at a frequency range from  $10^5$  to  $10^{-2}$  Hz. The tests of asymmetrical cells were conducted with a discharge time of 1.0 h and a cut-off charge voltage of 1.0 V vs  $Mg^{2+}/Mg$ . The in situ optical images were obtained with an optical microscope (Olympus, Japan). The temperature for all electrochemical measurements was 25 °C.

#### ASSOCIATED CONTENT

# **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c08470.

Additional experiment details; characterization of materials (SEM, XRD, etc.); cycling performances and supporting tables (PDF)

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#### Notes

The authors declare no competing financial interest.

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