Anticorrosion coating for magnesium alloys: electrospun superhydrophobic polystyrene/SiO$_2$ composite fibers

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Abstract: Superhydrophobic nanocomposite coatings for magnesium surfaces with remarkable corrosion resistance were fabricated by electrospinning in the presence of fluorosilane-functionalized silica (SiO$_2$) nanoparticles. The effects of surface-modified silica (mod-SiO$_2$) nanoparticles on the superhydrophobicity and corrosion resistance of polystyrene (PS)/mod-SiO$_2$ fiber coatings were evaluated. The incorporation of the SiO$_2$ nanoparticles endows PS fibers with rough surfaces exhibiting a water contact angle (WCA) of 165°. The surface wettability, corrosion resistance, and their relation to the inorganic content in the PS fibers and the contact angle of the composite coatings were explored. Analysis of the corrosion results confirmed that the PS/mod-SiO$_2$ coating protected the Mg surface from corrosion. In addition, PS fibers containing mod-SiO$_2$ nanoparticles showed improved hydrophobicity, and excellent corrosion resistance was achieved with PS fibers containing 4 wt% SiO$_2$ nanoparticles.

Key words: AZ31 magnesium alloy, electrospinning, nanocomposite, polystyrene/SiO$_2$, superhydrophobicity

1. Introduction

Magnesium is the lightest structural engineering metal because of its high strength-to-weight ratio.$^1$ Hence, it is an alternative to steels, cast irons, copper-based alloys, and aluminum alloys, and it contributes to fuel economy and emission reduction.$^2$ However, the disadvantages of magnesium including poor corrosion resistance, high reactivity, and high-temperature strength have become major issues in the automotive and aerospace industries.$^{3,4}$ The main reasons for these are internal galvanic corrosion (caused by second phases), and the fact that the oxide/hydroxide film on magnesium is less protective than the surface film on other metals.$^{5,6}$

Alloying is an important method that can improve the corrosion resistance of magnesium. However, different types of coating methods, including chemical-conversion coatings, anodic-conversion coatings, painting, electroless nickel plating, micro-arc oxidation, electroplating, and electrospinning, have been developed for protecting magnesium because alloying is insufficient when magnesium is in contact with electrodes.$^{2,4}$ Among these methods, most coatings and paintings are based on organic polymers, which are used in decorative and protective applications.$^{7,8}$ Typically, organic coatings comprise a binder or vehicle, pigments, and additives.

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such as dryers, hardening agents, stabilizing agents, surface-activating compounds, and dispersing agents. These types of coatings act as barrier layers that separate the metal substrate from its surroundings. A general coating process of a specimen with a polymer involves preparing a solution or an emulsion, applying it to the substrate, and drying or curing for a certain time (as in the case of thermosetting resins). In general, industrial coating methods with polymers are cheaper and easier than other types of coating methods such as conversion and plasma electrolytic oxidation coatings. Therefore, for the corrosion protection of magnesium, one potential approach is to employ polymer coatings.

During the last decade, coatings to obtain superhydrophobic surfaces (typically defined as having water contact angle (WCA) greater than 150°) have been studied to impart water repellency to materials that could also provide excellent inhibition of the corrosion of magnesium alloys. High surface roughness, low hysteresis, and low surface free energy are the main properties of superhydrophobic surfaces, which make them nonstick and self-cleaning. It is well known that corrosion resistance can be improved by increasing the hydrophobicity and chemical stability of a surface. Therefore, the formation of a suitable layer on a sensitive surface is one of the main techniques to protect the surface of substrates from corrosive environments. To fabricate a superhydrophobic surface, two approaches are generally used, namely, (a) trapping air bubbles in the surface hierarchies, and (b) coating the surface with intrinsically hydrophobic materials such as wax and organic layers; these standard approaches have both been used by a number of researchers.

In addition, electrospinning is another effective way to obtain superhydrophobic surfaces. One prominent example was introduced by Gringard et al. by using electrospun perfluorinated copolymer layers to protect alumina substrates from corrosive ions. Recent progress has indicated that surfaces with ideal roughness and microtextured structures have low interfacial free energies and remarkably high contact angles, as in the case of lotus leaves, the contact angle (CA) of which is about 161.0 ± 2.7°. Organic/inorganic electrospun composites have been used to fabricate superhydrophobic, highly porous, and breathable surfaces. By mixing epoxy-siloxane-modified SiO$_2$ nanoparticles with a poly(vinylidene fluoride) (PVDF) solution, superhydrophobic PVDF membranes have been obtained using electrospinning by Wang et al. In their experiment, the CA and water-sliding angle were controlled by the mass ratio of epoxy-siloxane-modified SiO$_2$ nanoparticles/PVDF, and the contact angle increased with increasing amounts of modified SiO$_2$ nanoparticles. Radwan et al. used one-step electrospinning to obtain a superhydrophobic PVDF-ZnO nanocomposite coating for aluminum. They stated that the nanocomposite electrospun coating had 35 times higher corrosion resistance than pure PVDF, and that the superhydrophobic coating formed a barrier that increased the charge-transfer resistance occurring at the coating–substrate interface. Kim et al. recently applied polycaprolactone (PCL) and ZnO nanoparticle composite coatings onto AZ31 Mg via electrospinning. The corrosion test results of the coating indicated that increase in the content of ZnO NPs improved both the coating adhesion on Mg substrate and the corrosion resistance.

Electrospinning is used to efficiently prepare superhydrophobic, protective surfaces with ultrafine fibers. This approach has attracted much attention due to its wide applicability and low cost, which make the preparation of large-scale superhydrophobic surfaces with proper roughness possible. Herein, we focus on the fabrication of corrosion resistant and durable superhydrophobic coatings for AZ31 Mg alloys by electrospinning. To the best of our knowledge, the corrosion behavior of fluorosilane-functionalized SiO$_2$ nanoparticle-loaded polystyrene nanofiber coatings is addressed here for the first time. The effect of electrospun composite nanofiber coatings on the Mg alloy using a low-cost polymer, PS, and mod-SiO$_2$ nanoparticles has been explored. Mg-based alloys were selected as coating substrate due to growing demand for lightweight engineering applications.
such as fuel cells, hydrogen storage, and high energy batteries, and in the air and automotive industry.\textsuperscript{28} The versatility of electrospinning makes our coating method extendable to a large variety of easily corroded materials, such as iron and copper. Furthermore, various composite protective coating layers can be fabricated via electrospinning with the combination of biodegradable polymer (such as chitosan, polycaprolactone, etc.) and biologically active nanoparticles.

2. Results and discussion

The use of inorganic nanoparticles to obtain functional and porous surfaces has attracted considerable attention. Silica (SiO\textsubscript{2}) nanoparticles in particular have been used to endow surfaces with superhydrophobicity or superhydrophilicity due to ease of synthesis and surface modification. Herein, we synthesized monodispersed SiO\textsubscript{2} nanoparticles by a sol–gel method, and the particles were subsequently hydrophobilized by fluorosilane. The modified SiO\textsubscript{2} (mod-SiO\textsubscript{2}) nanoparticles were dispersed in a polystyrene/\textit{N}, \textit{N}-dimethylformamide (PS/DMF) solution for electrospinning. A superhydrophobic PS/mod-SiO\textsubscript{2} nanofibrous coating to protect magnesium against corrosion was prepared (see the photographic image of a water droplet on the fiber coated magnesium substrate in Figure S1). A schematic diagram of the synthesis of mod-SiO\textsubscript{2} and the superhydrophobic coating via electrospinning is depicted in Figure 1. A silica precursor sol–gel was prepared in the presence of a silicon alkoxide (TEOS), oligomeric media (PEG), and mineral acid (HCl) as a catalyst. The process involves transetherification of TEOS and subsequent polycondensation of the reaction adducts. Upon heat treatment, the oligomeric part associated with silica clusters was removed.

![Synthesis of superhydrophobic SiO\textsubscript{2} NPs](image)

\textbf{Figure 1.} Schematic of the preparation of fluorinated silica nanoparticles and corrosion resistant fiber coatings.
Figure 2 shows a scanning electron microscopy (SEM) micrograph and the size distribution of the synthesized SiO$_2$ nanoparticles. It is possible to observe the formation of SiO$_2$ nanoclusters through extremely small individual nanoparticles (Figure 2a). Estimation of the silica nanoparticle size was performed using dynamic light scattering (DLS). The particle size analysis indicates that more than 95% of the particles are less than 80 nm in diameter (Figure 2b). This result suggests that the nanoparticles form clusters or aggregates of smaller particles.

Figure 2. (a) A SEM micrograph and (b) particle size distribution of the synthesized SiO$_2$ nanoparticles.

Hydrophobilization of SiO$_2$ nanoparticles was carried out using fluoroalkyl silane. The surface compositions of bare and fluorosilane-functionalized SiO$_2$ nanoparticles were analyzed using X-ray photoelectron spectroscopy (XPS). Figure 3 shows the wide-scan XPS spectra obtained for the samples and the high-resolution spectrum of C1s. In Figure 3a, the Si2p signals centered at 104.4 eV arise from the silica particles. The intense feature at 532.8 eV may correspond to the oxygen in the Si–O–Si bonds, and O1s binding energy at 533.4 eV can be attributed to the oxygen in the Si–O–H bonds of SiO$_2$ nanoparticles. These values are reasonably close to the binding energy values reported earlier for O1s in Si–O–Si and Si–O–H.$^{29}$ The O KLL signal centered at 979.4 eV for both spectra represents the Auger emission associated with the de-excitation of the O1s core level.$^{30}$ In addition, a weak C1s signal appears at 285.5 eV, which might be due to the incomplete hydrolysis of the alkoxide precursor during the synthesis of silica nanoparticles.$^{31}$

In the case of modified SiO$_2$ nanoparticles, the Si2p signal centered at 104.2 eV is attributable to the silica particles. The O1s profiles are similar to those of bare SiO$_2$, indicating that it belongs to structural O in the material. The intensities of the O1s features at 533.0 eV (Si–O–Si) and 533.7 eV (Si–O–H) are lower for modified SiO$_2$ nanoparticles. The less intense O1s signal may be attributed to the replacement of surface hydroxyl groups with fluoroalkyl silanes. Moreover, the fluorosilane functionalization of SiO$_2$ nanoparticles leads to the development of an F1s feature centered at 689.4 eV and confirmatory F KLL signal at 835.7 eV (Figure 3b). Similar binding energies to those assigned have been reported previously for tridecafluorooctyl triethoxysilane-modified SiO$_2$ nanoparticles.$^{32}$ The photoelectron profile of C1s shows two distinct signals at 284.9 and 292.1 eV. These features can be attributed to three different C environments in the fluorinated SiO$_2$ nanoparticle structure, namely, C–C, C–H, and C–F environments (Figure 3c). On the basis of the binding energies, it is possible to say that the silica nanoparticle surfaces were successfully covered by fluorosilanes.
Figure 3. XPS wide-scan spectra of (a) SiO$_2$ and (b) mod-SiO$_2$ nanoparticles, and (c) the C1s photoelectron profile for mod-SiO$_2$ nanoparticles.

By simultaneous electrospinning of fluorosilane-functionalized SiO$_2$ nanoparticles and polystyrene solution, superhydrophobic PS fibers were successfully fabricated with the aim of developing corrosion resistant fibrous coating. To provide evidence of the presence of hydrophobic silica nanoparticles within the PS fibers, attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FTIR) was used. Figure 4 shows the FTIR spectra of the electrospun PS and PS/mod-SiO$_2$ composite fibers. All the characteristic bands of polystyrene are present on the surface of both fibers. The band at 696 cm$^{-1}$ is attributed to the out-of-plane ring deformation of the monosubstituted benzene ring, and the bands at 1450 and 1493 cm$^{-1}$ correspond to C–H bending vibrations.$^{33,34}$ The aromatic C=C stretching vibration in the benzene ring of PS appears at 1601 cm$^{-1}$. The bands at 2851 and 2923 cm$^{-1}$ are attributed to the symmetric and asymmetric stretching vibrations of CH$_2$, respectively. The wavenumbers of 3024, 3059, and 3083 cm$^{-1}$ are assigned to the aromatic C–H stretching vibration.$^{35}$ For the PS/mod-SiO$_2$ composite fibers, there are additional bands at 804 and 1087 cm$^{-1}$ arising from Si–O–Si asymmetric and symmetric vibrations, respectively.$^{36}$ Furthermore, the Si–O–Si band has a shoulder at around 1203 cm$^{-1}$ due to the presence of C–F stretching vibrations,$^{32,37}$ which supports the successful surface modification of SiO$_2$ nanoparticles as well as their incorporation into the PS fibers.
The morphology of the electrospun PS and PS/mod-SiO₂ composite fibers was examined by SEM. Figure 5 shows the SEM micrographs of fibers electrospun from 10 wt% PS solutions in DMF. The average fiber diameter of the electrospun composite fibers increased from 600 ± 250 nm to 750 ± 100 nm as the amount of the mod-SiO₂ nanoparticles increased in the solution (Figures 5a–5d). PS solution containing 8 wt% mod-SiO₂ nanoparticles yielded beaded fibers (Figure 5d). In the case of high particle concentrations, the bead formation may induce aggregation of the nanoparticles in the bead structures. This phenomenon can be explained by considering a critical nanoparticle concentration in parallel with the viscosity of the solution. Increasing the concentration above a critical value (8 wt% SiO₂ in this case) hinders the flow of the solution from the needle to the collector, which brings about beaded fibers. It should also be noted that the instability of the electrospinning jet is another factor for the fiber morphology obtained on the collector. As the charge density carried by the jet decreases, the capillary instability leads the jet to collapse into separated droplets, solidifying to form bead structures. Furthermore, the size of the silica particles also affects their aggregation state within the electrospun fibers. Jin et al. reported that SiO₂ nanoparticles having a diameter of 140 nm aggregated; on the other hand, nanoparticles larger than 260 nm formed necklace-like structures aligning along the fiber. As seen in Figure 6, the WCA of the coating was improved from 135° to 163° by increasing the mod-SiO₂ nanoparticles up to 4 wt% (see also the Table). Increased hydrophobic properties of fluorosilane-functionalized SiO₂ have been obtained with increasing amount of mod-SiO₂ nanoparticles because of the small dipole and low polarizability properties of the C–F bond, which enables reduction of surface energy. A slightly lower CA with a higher standard deviation was observed for PS/mod-SiO₂ (8 wt%) fiber coating. In general, a high CA would be expected for beaded fibers with a rough surface. This can be explained by considering that during electrospinning with high amounts of inorganic particles the solution eventually blocks the needle, which then affects the coating thickness even though the time was fixed to be the same (3 min) to ensure equal thickness.

Table. Corrosion resistance and water contact angle (CA) data of prepared samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>CA(°)</th>
<th>E_corr (V)</th>
<th>I_corr (µA/cm²)</th>
<th>η (%)</th>
<th>δ_α (mV/dec)</th>
<th>δ_α (mV/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ31 Mg</td>
<td>21 ± 2.0</td>
<td>-1.54</td>
<td>89</td>
<td>0.00</td>
<td>116</td>
<td>120</td>
</tr>
<tr>
<td>PS fiber</td>
<td>135 ± 2.0</td>
<td>-1.44</td>
<td>5.30</td>
<td>94.04</td>
<td>151</td>
<td>250</td>
</tr>
<tr>
<td>PS/mod-SiO₂ (2 wt%)</td>
<td>155 ± 3.0</td>
<td>-1.43</td>
<td>0.85</td>
<td>99.04</td>
<td>75</td>
<td>205</td>
</tr>
<tr>
<td>PS/mod-SiO₂ (4 wt%)</td>
<td>163 ± 2.0</td>
<td>-1.42</td>
<td>0.38</td>
<td>99.57</td>
<td>54</td>
<td>185</td>
</tr>
<tr>
<td>PS/mod-SiO₂ (8 wt%)</td>
<td>152 ± 4.0</td>
<td>-1.47</td>
<td>6.30</td>
<td>92.93</td>
<td>62</td>
<td>215</td>
</tr>
</tbody>
</table>
Figure 5. SEM micrographs of electrospun PS/mod-SiO$_2$ fibers containing different amounts of SiO$_2$ nanoparticles: (a) 0 wt\%, (b) 2 wt\%, (c) 4 wt\%, and (d) 8 wt\%.

Figure 6. Contact angles of PS/mod-SiO$_2$ fibers coated AZ31 Mg alloy.
The corrosion resistances of the PS and PS/mod-SiO$_2$ fiber coatings on Mg alloys were determined by measuring Tafel polarization curves. Figure 7 shows the polarization curves of bare Mg, PS, and PS/mod-SiO$_2$ fiber coatings with different amounts of SiO$_2$ nanoparticles in simulated sea media. The corrosion test results are summarized in the Table. The corrosion potential for bare Mg is $-1.54$ V and that for the PS fiber coating is $-1.44$ V. The corrosion potential for the PS/mod-SiO$_2$ (4 wt%) fiber coating is more positive than those for the other samples, which suggests that the composite coatings are more passive than PS fiber coatings. Not surprisingly, the corrosion current density ($I_{corr}$) for the bare Mg alloy is much higher than those for the coated samples. The corrosion current densities for PS/mod-SiO$_2$ fibers with 2 wt% and 4 wt% SiO$_2$ nanoparticles are almost 10 times lower than that for the PS fiber coating, and therefore they exhibit higher corrosion resistance compared with the other coatings.

These results may suggest a synergistic effect between SiO$_2$ nanoparticles and polystyrene on the corrosion protection as well as a uniform distribution of SiO$_2$ nanoparticles along the fibers at low concentration. In other words, the presence of SiO$_2$ nanoparticles entrapped in the polystyrene chain provides nanoparticle reinforcement to the polystyrene, which reduces the degradation of polymer chains in saline conditions. Radwan et al. also found that ZnO nanoparticles in PVDF fiber coatings increased the corrosion resistance of bare Al substrates owing to the superhydrophobic nature. The relation between superhydrophobicity and corrosion resistance can be explained as follows. According to the mechanism of superhydrophobicity, by increasing the WCA the trapped air on the surface is increased. The trapped air molecules act as a barrier to the diffusion of corrosive ions, resulting in a reduced corrosion current density. Moreover, the size and chemical stability of the nanoparticles are important for the fabrication of uniform coatings. At high nanoparticle concentrations (PS/mod-SiO$_2$ fibers with 8 wt%), the number of large agglomerated particles on the surface
increases, leading to a high concentration of surface impurities and a low coating performance. It can be concluded that the significant reduction in the corrosion current density in PS/mod-SiO$_2$ fiber-coated Mg alloy proves the existence of a suitable superhydrophobic layer and its effective corrosion protection performance.

Similarly, Zomorodian et al.$^{47}$ have also reported that higher amounts of hydroxyapatite nanoparticles (5\%) incorporated into polyether imide (PEI) and cross-linking agent blend cause particle agglomeration, which decreases the corrosion protection performance of the coating due to the formation of hillocks on the surface.

In summary, SiO$_2$ nanoparticles have been synthesized via a sol–gel method and hydrophobilized by fluoroilane, and the modified SiO$_2$ nanoparticles have been used as an additive in polystyrene fibers by electrospinning. AZ31 magnesium alloy was selected as a model substrate, and it showed a lower corrosion and dissolution rate than bare Mg$^{48}$ when coated with the electrospun composite fibers. The superhydrophobicity of the coating was increased by increasing the SiO$_2$ nanoparticle content. The maximum WCA obtained was around 165° for PS/mod-SiO$_2$ (4 wt\%) fibers. PS/mod-SiO$_2$ (4 wt\%) fiber coatings showed more than 13 times lower corrosion current density than PS fiber coatings, and therefore exhibited a relatively high corrosion resistance. The corrosion protection efficiency of the fibrous coating was found to be greater than 99\%, indicating the highly protective nature of the composite fibers.

### 3. Experimental

Polystyrene (PS; $M_w = 350$ kg/mol), poly(ethylene glycol) (PEG; $M_w = 400$ g/mol), $N,N$-dimethylformamide (DMF; 99\%), chloroform, hexane, dichloromethane, hydrochloric acid, and acetone were obtained from Aldrich. (Heptadecafluoro-1,1,2,2-Tetrahydrodecyl) dimethyl chlorosilane (HDFTHD) was obtained from Gelest Inc. All reagents were used as received without further purification. Silica (SiO$_2$) nanoparticles were synthesized by a sol–gel method according to the procedure reported by Gorji et al.$^{49}$ Briefly, 5.0 g of TEOS was introduced into a solution of 80 g of PEG (5 wt\%). After mechanical stirring (250 rpm) for 30 min, this solution was added dropwise (~1 mL/10 min) into a 30-mL HCl (0.001 N) solution at room temperature under continuous stirring. Homogenization of the solution was then carried out in a homogenizer (19000 rpm) for 30 min, followed by stirring (250 rpm) to avoid particle aggregation. The resulting pH of the solution was adjusted to around 2.0 by adding 10 mL of 0.1 N HCl. The solution was then heated to 80 °C, followed by heat treatment from 200 to 1000 °C at a heating rate of 4 °C/min. SiO$_2$ nanoparticles with a surface area of 152 m$^2$/g were obtained.

### 3.1. Synthesis of superhydrophobic SiO$_2$

Hydrophobilization of SiO$_2$ nanoparticles was carried out by treating them with fluoroilane. In a typical experiment, SiO$_2$ nanoparticles (2.0 g) were suspended in 60 mL of chloroform in a 250-mL round-bottom flask. Next 0.430 mL of fluoroilane was dispersed in 20 mL of chloroform, assuming a grafting density of 5 $\mu$mol/m$^2$, and then added dropwise into the round-bottom flask while the solution was stirred and refluxed for 3 h. After modified SiO$_2$ nanoparticles were recovered by filtering at room temperature under vacuum, they were purified by extracting three times each in equal volumes of hexane and dichloromethane to ensure the elimination of any noncovalently bound fluoro-functional silane derivatives and other surface impurities. After the extraction, the modified SiO$_2$ nanoparticles were collected and dried at room temperature for 1 day.
3.2. Fabrication of electrospun PS/mod-SiO$_2$ fiber coatings

A sample of PS or PS/mod-SiO$_2$ was dissolved in DMF by stirring. The polymer content of the solution was 10 wt%. The concentration of mod-SiO$_2$ in the polymer solution was varied from 2 to 8 wt%. The resulting viscous dispersion was loaded in a plastic syringe connected with polyethylene tubing. The electrospinning experiments were carried out using a commercial platform (Inovenso Basic Setup). The positive electrode was applied to the spinneret, and AZ31 Mg alloy was used as a grounded counter electrode. The round AZ31 Mg alloy with dimensions of 150 mm $\times$ 150 mm $\times$ 3 mm was prepared with 600, 1500, and 2000 grade SiC emery paper, followed by 5 min ultrasonic degreasing in acetone at room temperature, and then washed with distilled water. Then the sample was treated with 1 M HNO$_3$ for 2 min, subsequently cleaned in ethanol, and dried. The rate of the polymer solution was maintained at 2.0 mL h$^{-1}$ and a potential of 15 kV was applied. The tip-to-collector distance was 15 cm and the electrospinning time was fixed to 3 min to ensure equal thickness. Electrospun fiber-coated AZ31 Mg alloy samples were dried using nitrogen gas for 1 min to remove any residual solvent.

3.3. Characterization methods

Surface morphologies of SiO$_2$ nanoparticles and PS/SiO$_2$ electrospun fibers were obtained using scanning electron microscopy (SEM; Philips XL 30SFEG). The diameter of the fibers was calculated from SEM micrographs using the Fiji/ImageJ software. Particle sizes and their distribution were analyzed using a DLS instrument (Malvern Nano Zetasizer ZS 90, UK) with a scattering angle of 176.1°. Surface compositions were determined by X-ray photoelectron spectroscopy (XPS; K-Alpha Surface Analysis, Thermo Scientific). The spectra were recorded in the constant analyzer energy (CAE) mode with analyzer path energies of 150 eV for the survey spectra and 1000 eV for the high-resolution spectra. ATR-FTIR measurements of PS and PS/SiO$_2$ fibers were performed using a Thermo Scientific Nicolet iS5 FTIR spectrometer. The CA measurements were carried out on fiber-modified Mg AZ31 alloys using a KSV Attension Theta Lite Optical Tensiometer with a sessile drop method. Water droplets of 4.5 $\mu$L were deposited on the sample surfaces with manually controlled Hamilton syringe. All the measurements were performed in triplicate at room temperature.

Electrochemical studies were carried out using a Metrohm Autolab electrochemical workstation (PGSTAT204). The polarization curves were obtained using the NOVA 1.10 software. A standard three-electrode cell in an aqueous solution of 3.5 wt% NaCl was used. A platinum wire and a saturated calomel electrode were used as counter and reference electrodes, respectively. The electrode was immersed for 30 min to moderate the electrochemical system into a stationary state. The polarization curves obtained in a potentiodynamic mode with a potential scanning speed of 1 mV/s were initiated from the corrosion potential, $E_{corr}$. Then the higher negative potentials were followed by a sweep from $E_{corr}$ to the higher positive potentials. The efficiency of protection value was determined by Eq. (1).

$$
\eta = (1 - \frac{i_{corr}^{\text{protected}}}{i_{corr}^{\text{base}}}) \times 100
$$

$i_{corr}^{0}$ and $i_{corr}$ are the current densities for the corrosion of the Mg AZ31 alloy before and after fibrous coating, respectively, which are achieved by the extrapolation of cathodic and anodic Tafel right to the corrosion potential (Figure S2). Electrochemical parameters ($E_{corr}$, $i_{corr}$, $b_a$, and $b_c$) were determined by using the software OriginPro 8 from the polarization curves according to the Stern–Geary equation.$^{50}$ The anodic, $b_a$, and the cathodic constant, $b_c$, are described according to the slope of ($\beta$) on the logarithmic scale.
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References

Supporting Data

Figure S1. Photograph of a water droplet on the electrospun PS/mod-SiO$_2$ fiber-coated AZ31 Mg alloy.

The $I_{\text{corr}}$ based on its theory can be measured by electrochemical instrument software and controlled manually. $E_{\text{corr}}$ and $I_{\text{corr}}$ values can be directly determined from the cross-over point as shown in the figure below. At the corrosion potential, $E_{\text{corr}}$, the rate of cathodic reduction is equal to the rate of anodic reaction (metal corrosion).

![Tafel plot](image)

Figure S2. Tafel plot to estimate the $E_{\text{corr}}$ and $I_{\text{corr}}$ values.

$E_{\text{corr}}$ and $I_{\text{corr}}$ values can be directly calculated from the cross-over point, obtained from the extrapolating linear lines on the anodic and cathodic curves. We calculated these values for the uncoated and coated samples by using this method. Figure S2 shows the determination of the $E_{\text{corr}}$ and $I_{\text{corr}}$ values for the polystyrene/SiO$_2$ fiber-coated Mg substrate.