Electronic supplementary information (ESI)

Excellent anti-corrosive pretreatment layer on iron substrate based on three-dimensional porous phytic acid/silane hybrid

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S1. Effect of MTES / PA molar ratios

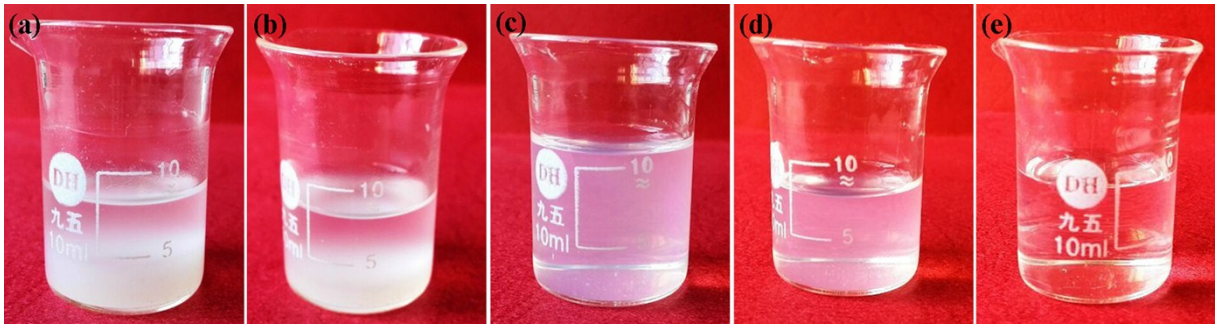

Fig. S1 A set of digital photos of various PAS hybrid materials synthesized at different molar ratios of MTES to PA: (a) 0.32, (b) 0.16, (c) 0.08, (d) 0.04, and (e) 0.02.

S2. Dependence of microstructure and morphology of the pretreatment layers on film-forming time

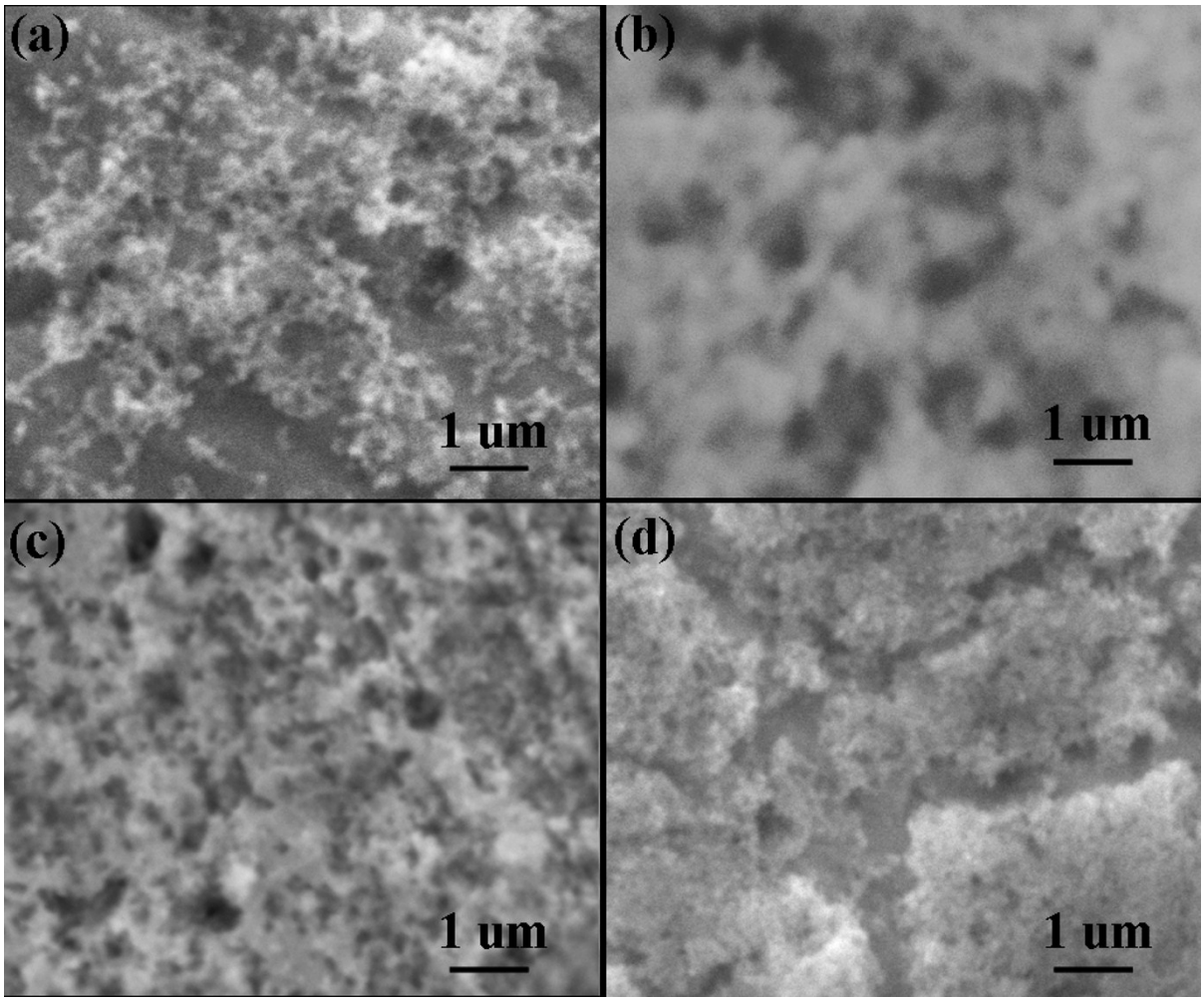

Fig. S2 SEM images for the iron plate samples covered with conversion coatings by immersing the iron samples in the PAS hybrid hydrosol for 20 (a), 40 (b), 60 (c) and 80 (d) minutes.

The influences of film-forming time on structural and morphological features of PAS pretreatment layers were investigated by SEM observations. It is clearly seen from Fig. S2, in the case of shorter film-forming time (*e.g.* 20 minutes), the iron surface was partially covered by the PAS coatings and some areas remained uncovered. If the film-forming time increased to 40 minutes, the uncovered areas were reduced significantly. In particular, when the film-

forming time increased to 60 minutes, the whole iron surface was completely covered with the PAS coatings, leaving only a small amount of holes with the diameter of ~220 nm. However, in the case of the longer film-forming time (*e.g.* 80 minutes), some microcracks would appear in the pretreatment layer. The SEM observations reveal that the optimal formation time for obtaining the high-quality undoped PAS layers is around 60 minutes.

S3. Effect of film-forming time on the corrosion resistance performance of the PAS pretreatment layers

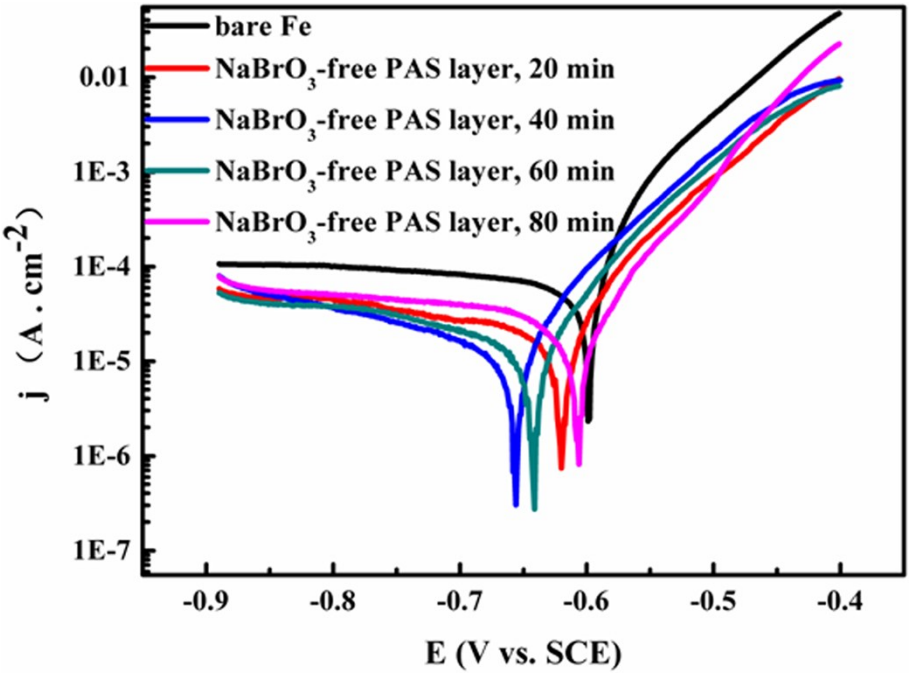

Fig. S3 Polarization curves of the iron electrodes untreated and treated with undoped PAS coatings.

The PAS layer modified electrodes showed the lower anodic and cathodic current densities than the bare electrode, and the degree of decrease was dependent on the film-forming time. When the film-forming time was between 40 to 60 minutes, the pretreatment layers exhibited the excellent anti-corrosion performance. Some important electrochemical parameters, including corrosion potentials (E_{corr}), corrosion current densities (i_{corr}), and anodic Tafel

slopes (b_a), were calculated out and collected in Table S1. Based on the variation trend of PE with the film-forming time, one would found that, PE values first increased and then decreased as the film-forming time changed from 20 to 80 minutes. The highest PE value was 85.9% in the case of 60 minutes.

Table S1

Electrochemical parameters obtained from the polarization curves of different iron electrodes shown in Fig. S3

	b_a (mV decade^{-1})	i_{corr} (A cm^{-2})	E_{corr} (mV)	PE%
Bare iron	83.8	1.48×10^{-4}	- 599	-
$NaBrO_3$-free PAS layer, 20 min	80.5	3.04×10^{-5}	- 620	79.4
$NaBrO_3$-free PAS layer, 40 min	80.0	2.12×10^{-5}	- 656	85.7
$NaBrO_3$-free PAS layer, 60 min	74.2	2.08×10^{-5}	- 641	85.9
$NaBrO_3$-free PAS layer, 80 min	69.4	3.33×10^{-5}	- 606	77.5

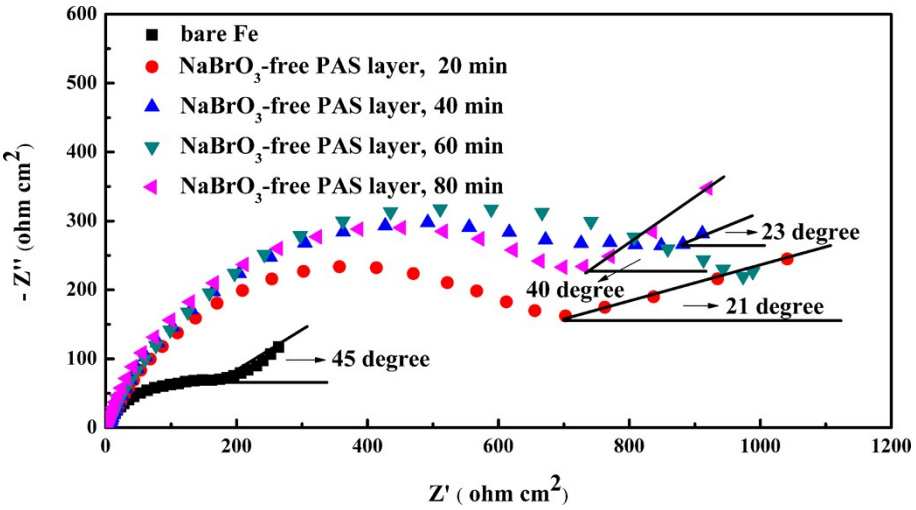

Fig. S4 Nyquist spectra for the iron electrodes untreated and treated with undoped PAS coatings.

For the iron electrodes modified with the undoped PAS layers, in the case of shorter film-forming time (*e.g.* 20 minutes), the capacitive loop was much larger in size than that of the bare iron, meanwhile the angle of the straight line reduced to around 22.5º. When the film-forming time was controlled in the range of 40 to 60 minutes, the diameters of capacitive loop further became larger and the straight lines in low frequency were not obvious or almost disappeared, which indicates that the pretreatment layers became compact. However, if the film-forming time increased to 80 minutes, the diameter of the capacitive loop decreased to a certain extent and the straight line appeared again. This is because the escape of hydrogen across the dense precursor film did some damage to the compactness of the film.