

Covalent Grafting of Chitosan onto Stainless Steel through Aryldiazonium Self-Adhesive Layers

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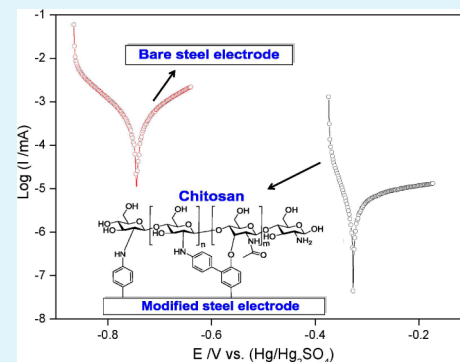
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S Supporting Information

ABSTRACT: Although the conventional methods for strong attachment of chitosan onto stainless steel require many steps in different solvents, it has been demonstrated in this work that covalent grafting of chitosan on a steel surface can be easily achieved through the formation of a self-adhesive surface based on aryldiazonium seed layers. Initially, a polyaminophenyl layer is grafted on a stainless steel surface by means of the one-step GraftFast™ process (diazonium induced anchoring process). The grafted aminophenyl groups are then converted to an aryldiazonium seed layer by simply dipping the substrate in a sodium nitrite acidic solution. That diazonium-rich grafted layer can be used as a self-adhesive surface for subsequent spontaneous coating of chitosan onto the steel surface. X-ray photoelectron and impedance electrochemical spectroscopies were used to characterize the pristine and modified steel samples. As evidenced from impedance and linear polarization results, the primary polyaminophenyl layer characterized by a high charge transfer resistance contributed to better protection against corrosion of the resulting chitosan-coated steel in sulfuric acid medium.

KEYWORDS: chitosan coating, stainless steel, diazonium chemistry, blocking effect, corrosion resistance



1. INTRODUCTION

Stainless steel is nowadays widely used in daily life, from the building industry to many other applications including the food industry, appliances, and implants in orthopedic surgery.^{1–3} To fulfill the requirements of real industrial utilizations, stainless steel has to be treated properly for better corrosion resistance without losing its physical and mechanical integrity.^{1–3} Organic coatings have already shown efficiency for protection against corrosion of stainless steel in different media,³ but novel strategies using green or low-cost polymeric films such as peptides, chitosan, poly(4-vinylaniline), polymethacrylate, and poly(acrylic acid) are urgently needed to fit the market requirements.^{1–13} Among these polymers, chitosan has appeared as a very attractive candidate because this bifunctional natural glucosamine is nontoxic, biodegradable, biocompatible, abundant in nature, and produced at low cost.^{5,6,13,14} It is, however, worth noting that chitosan and chitosan-based films are conventionally grafted onto stainless steel via catecholic anchors, which require multistep processes using different solvents.^{5–7,9–11} Furthermore, these processes require activating the steel surface in strongly acidic conditions to generate a hydroxyl-enriched surface. The treated surface then reacts with the initiator anchors bearing amine or hydroxyl moieties, e.g.,

dopamine, barnacle cement. The resulting modified surface will be further functionalized with a cross-linker containing selected groups such as aldehydes and carboxyls. The latter finally reacts with one of the hydroxyl or amine functionalities of chitosan. Indeed, as for many other processes used for organic coating, developing a simple and efficient strategy that allows a covalent attachment of chitosan onto stainless steel still remains a major challenge despite recent progress made in the field.^{2,3,15,16}

In comparison with these conventional catecholic chemistries for surface modification, electroreduction of aryldiazonium salts, first developed by Jean Pinson's group,¹⁵ has some advantages, as this simple one-step method can provide a conducting substrate with a polyphenylene layer bearing different desired functionalities (carboxylic, ester, alcohol, thiol, amine, and halogenated groups). Recently, this method has been applied to stainless steel.^{3,4} Here, another important point is that a grafted polyaminophenylene film (PAP) on stainless steel can be easily converted to an aryldiazonium salt.¹⁷ The obtained layer takes the versatility of the

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2.5. Electrochemical Impedance Spectroscopy. Impedance spectroscopy measurements were realized in a range of frequencies extending from 0.01 Hz to 100 kHz by a Solartron 1255 frequency analyzer and an electrochemical interface (SI1286) controlled by a computer with the Zplot software. To study the blocking behavior of the pristine and modified electrodes, all impedance measurements were evaluated in 0.01 M H₂SO₄ or 0.01 M Na₂SO₄ in the presence of redox probe species (5 mM Fe(CN)₆^{3−}/5 mM Fe(CN)₆^{4−}).

2.6. Corrosion Characterization. The polarization curves were recorded by a potentiostat/galvanostat (Autolab PGSTAT302) controlled by a computer. The linear voltammetry was performed in a potential range extending from −200 to +200 mV versus open-circuit potential at scan rate of 10 mV/min. All measurements were realized at room temperature. N₂ gas was bubbled for 10 min in the sulfuric acid solutions used as corrosive media before the linear voltammetric measurement, and during experiments.

3. RESULTS AND DISCUSSION

3.1. Covalent Grafting of a Polyaminophenylene Layer on Stainless Steel. According to the one-step GraftFast™ process described in section 2.2., the mechanism to graft a PAP layer on the steel surface involved preparing a 0.01 M solution of 4-aminophenyldiazonium cations (H₂N–C₆H₄–N₂⁺) from *para*-phenylenediamine, sulfuric acid, and sodium nitrite (Scheme 1i). It is important to point out that the acidic medium protects the remaining amine group from reacting with newly formed diazonium salts, which is likely to improve both the overall yield of grafting and the covering ratio. Then iron powder was added to reduce the aminophenyl diazonium cations (H₂N–C₆H₄–N₂⁺) to aminophenyl radicals (H₂N–C₆H₄·). Under our working conditions, protons will also be reduced to hydrogen. The reduction of diazonium may equally result in the generation of azophenyl radicals (H₂N–C₆H₄–N₂·) as an alternate reduction product (Scheme 1i). The grafting and growth of mixed layers involving phenyl and azophenyl radicals take place according to reactions (Scheme 1ii).^{17,25,26}

Figure 1 shows the XPS survey spectra of the bare and modified steel samples. As expected, the XPS signal of the pristine sample (Figure 1A) is identical to those of stainless steel surface published in the literature.^{3,9,28} Indeed, the Fe 2p spectrum shows a typical behavior for stainless steel, with the presence of Fe⁰, Fe³⁺ in the spectrum. Part of the large Fe³⁺ 2p signal can also be interpreted as the presence of the iron satellite (see Figure S1a, Supporting Information). In addition to iron, the steel surface XPS spectrum is also dominated by Cr 2p (575 eV), O 1s (531 eV), and C 1s (285 eV) signals. Full XPS characterization of the stainless steel surface was the subject of several published works in the field.^{3,9,28} Thus, it is out of the scope of the present paper. We will insist next on the presence of grafted aminophenylene groups that are critical for the subsequent grafting of chitosan. Introducing an aryl layer containing C and N elements onto the steel surface, as shown in Scheme 1ii, evidently leads to an increase in the intensity of the C 1s and N 1s peaks (Figure 1B). In contrast, the O 1s peak is less pronounced in comparison with that of the pristine steel sample.

The high resolution C 1s and N 1s spectra of bare steel and the PAP-grafted samples are shown in Figure 2. The C 1s spectrum of the pristine surface (Figure 2A) can be decomposed into three features: one located at 284.9 eV assigned to C–C bonds (this feature also includes surface contamination), one at 286.4 eV assigned to C–O bonds and the latter at 288.5 eV assigned to C=O bonds.^{3,28} With respect

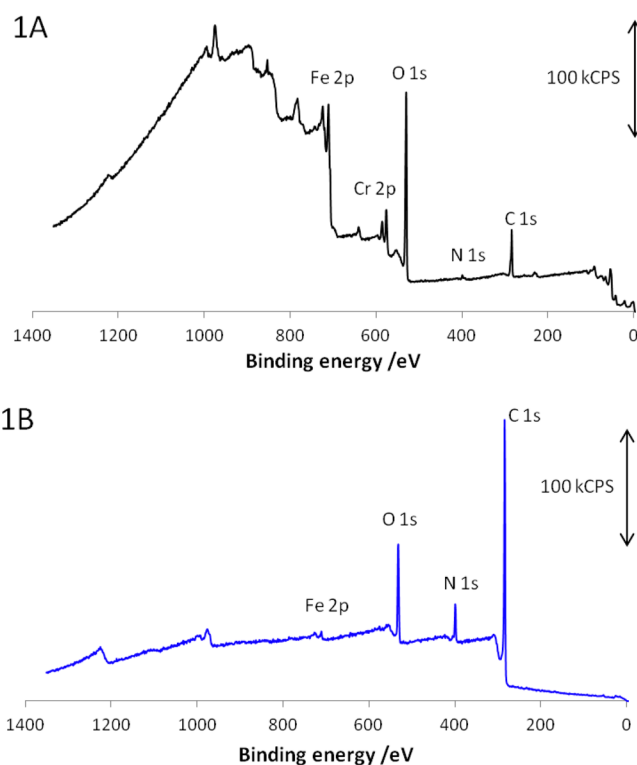


Figure 1. XPS survey spectra of the bare stainless steel (A) and the PAP-grafted sample (B).

to the functionalized surface, the C peak at 284.9 characterized by C–C bonds increases significantly as a phenyl layer is grafted on the surface (Figure 2B). The peak at 286.4 eV is more intense because this peak contains a certain amount of the C–N bonds²⁹ in parallel to the C–O bonds previously observed before modification. A minor C=O peak is observed at the same position compared to that of the pristine sample (288.5 eV).

Although the nitrogen content on the stainless steel surface, which is normally attributed to a fortuitous contamination, is rather negligible (Figure 2C), the N 1s core-level spectrum of the PAP-grafted surface (Figure 2D) can be decomposed very well by two components, one at 399.3 eV for aminophenyl functionalities and another at 400.1 eV for the –N=N–aryl linkages.^{15,29–33} As expected, there is no adsorption of diazonium salt on the obtained polymer film as shown by the absence of the characteristic peaks for the diazonium function at 403.8 and 405.1 eV.

Impedance electrochemical spectra was then used in this work because it was shown particularly efficient in the characterization of all phenylene layers grafted via the diazonium chemistry.^{3,34} Impedance electrochemical spectroscopy also provides a good understanding of the blocking effect, thus the resistance against corrosion, which is the main target of the last section.

Figure 3 shows the impedance spectra of the PAP-coated steel electrode in contact with 0.01 M H₂SO₄ and 0.01 M Na₂SO₄ solutions containing Fe(CN)₆^{3−/4−} as the redox probe (0.5 mM). It is important to point out that no straight line with a slope near unity is observed in the low frequency domain characteristic of semi-infinite diffusion phenomenon. Therefore, the PAP layer almost covers the entire surface of the electrodes and creates a physical barrier that impedes the diffusion of the

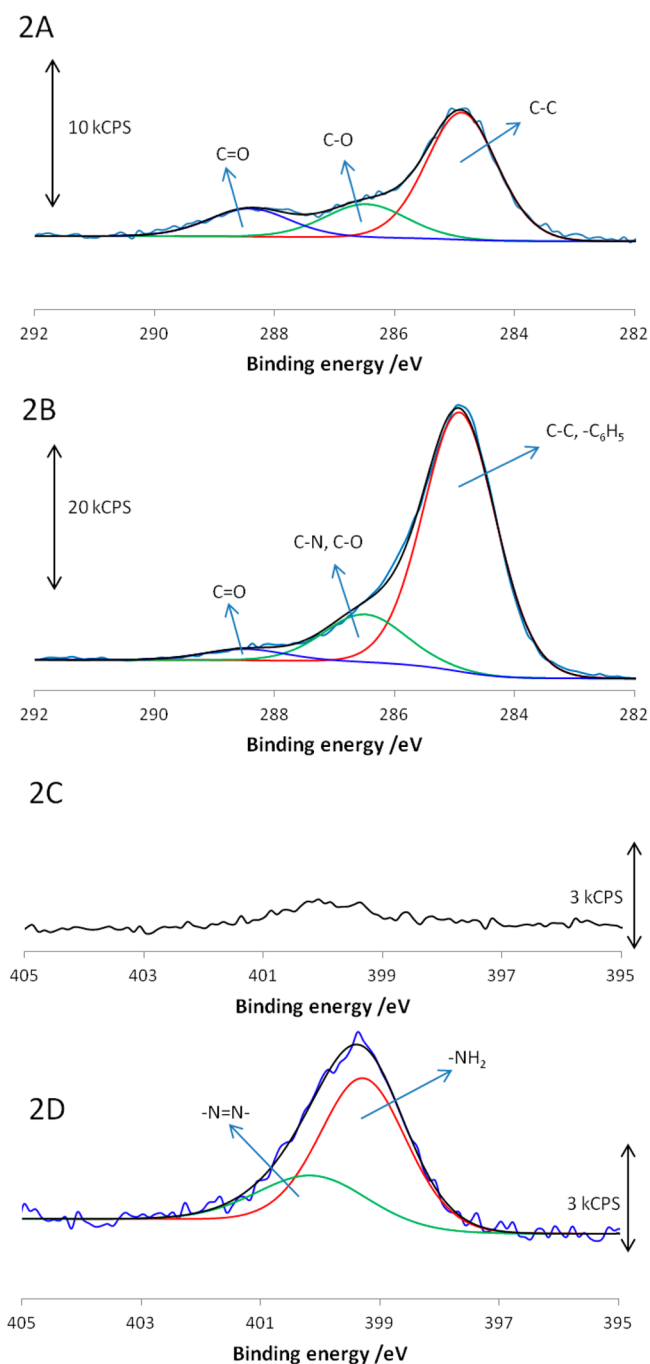


Figure 2. Core level C 1s (A,B) and N 1s (C,D) spectra of the bare stainless steel and the PAP-grafted sample.

$\text{Fe}(\text{CN})_6^{3-/4-}$ redox probe.³ The blocking effect of the PAP-grafted layer can have several origins and depends on (i) the nature of the electroactive species, (ii) the swelling properties of the polymer film, and (iii) the pH of the electrolyte.³ In our particular case, the pH of the electrolyte solution is crucial because the PAP-grafted film is supposed to bear amino groups. Actually, at low pH, amines are protonated and become positively charged while $\text{Fe}(\text{CN})_6^{3-/4-}$ redox probes are negatively charged. In contrast, at higher pH (in Na_2SO_4 at pH = 7), these amines are neutral and therefore create a more effective Coulomb barrier for $\text{Fe}(\text{CN})_6^{3-/4-}$. In acidic medium, the charge transfer resistance calculated from the semicircle diameter gives a relatively high value of 27 k Ω . In Na_2SO_4

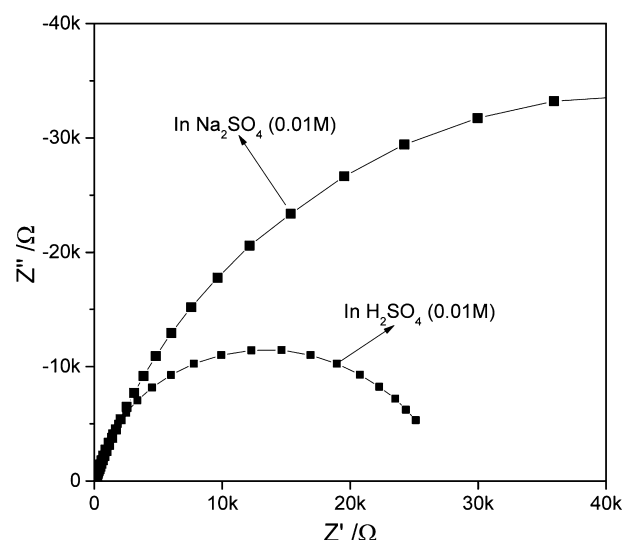


Figure 3. Impedance spectra of the PAP-grafted steel in contact with 0.01 M H_2SO_4 and 0.01 M Na_2SO_4 solutions containing $\text{Fe}(\text{CN})_6^{3-/4-}$ as redox probe (0.5 mM).

solution, the barrier effect is as expected more significant. The charge transfer resistance in this case is found to be 2.5 times higher than that obtained in the sulfuric acid medium (Figure 3). Those results are thus consistent with the presence of amino groups within the grafted layer, in accordance to the N 1s core-level XPS spectrum.

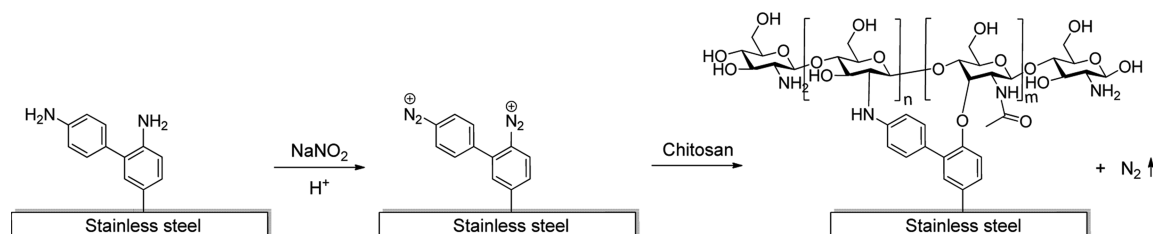
Impedance electrochemical spectroscopy clearly indicates that our primer PAP layer plays an important role for the blocking efficiency of the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox probe. This fact can be explained by taking into consideration the thickness of the PAP layer. The thickness of the PAP-grafted layers can be estimated from the attenuation of the Fe 2p peak intensities before and after modification:³⁰

$$\frac{I}{I_0} = \exp(-d/\lambda \sin \theta) \quad (1)$$

where d is the thickness layer, λ the photoelectron escape depth, θ the takeoff angle, and I/I_0 the ratio of the Fe 2p peak intensities of the bare and grafted surfaces (Figure S1, Supporting Information). In our experiment, the takeoff angle was 90° and λ was 10.9 nm.³⁵ The thickness of the PAP film is, at first approximation, found to be 9.8 ± 1.5 nm. Such a thick PAP film is likely responsible for the efficient blocking effect evidenced by impedance spectroscopy. More discussion in this regards will be given in section 3.3 in connection with the anticorrosive ability of the chitosan-coated steel samples.

3.2. Functionalization of Steel Surface with Chitosan via the Diazotization of the Primary Aminophenylene Layer. The immobilization of chitosan on the steel surface was obtained after the conversion of the aminophenylene groups into diazonium salts by simply dipping the substrate into a sodium nitrite acidic solution (Scheme 2). The chitosan hydrogel in slightly acidic medium was then dropped on that activated surface. Note that aryldiazonium salts are generally unstable compounds and storage in a cold and dark place is required. In previous work,¹⁷ we evaluated the lifetime of grafted aryldiazonium salts. After 2 h at 50°C , we observed complete disappearance of the IR signals from the aryldiazonium salts previously formed on the surface. A few minutes under UV light (200W) gave a similar result. The decomposition process

Scheme 2. Spontaneous Grafting of Chitosan with Aryldiazonium Self-Adhesive Surface



probably occurs via interaction with ambient water in air, which converts aryl diazonium salts to phenols. At room temperature, a diazonium-rich sample left for 24 h at 22 °C and 45% relative humidity exhibited no aryldiazonium signal. Consequently, it should be better to functionalize steel with chitosan by using only freshly prepared aryldiazonium-rich surfaces. In contact with chitosan, diazonium cations can react spontaneously with either the $-\text{OH}$ or $-\text{NH}_2$ groups of chitosan (Scheme 2).

Figure 4A presents the XPS survey spectrum of the chitosan grafted onto stainless steel. The observed behavior is similar to that published in the literature.^{5,6,11} The atomic percentages of C, O, and N elements are, respectively 61%, 32%, and 7% while they were 62%, 31%, and 7% in the work of Armalar and colleagues.³⁶ These experimental results are indeed comparable with the theoretical values calculated for chitosan with a 30% acetylation degree (56%, 36%, and 8%). Besides the quantification of the wide-scan spectra, the analysis of the high-resolution C 1s spectra bears evidence of the chitosan attachment. The shape of the C 1s spectrum recorded on our chitosan-grafted sample (Figure 4B) is, as predicted, typical of that for untreated chitosan particles as well as chitosan coated on steel surfaces by other modification methods.^{5,11,36–38} The carbon C 1s peak was best fitted with three components, a dominant one at 286.4 eV and two smaller ones at 284.9 and 288.0 eV. The dominant 286.4 eV peak is attributed to the carbon bound to nitrogen or oxygen ($\text{C}-\text{O}$, $\text{C}-\text{OH}$, or $-\text{C}-\text{NH}-\text{C}=\text{O}$). The others are ascribed to carbon in the $\text{O}-\text{C}-\text{O}$ bond of the saccharide ring or $-\text{HN}-\text{C}=\text{O}$ bond of the acetyl groups. The 284.9 eV peak is responsible for $\text{C}-\text{NH}_2$ group or $-\text{CH}_2$ saturated carbon group. Our C 1s high resolution results are in a good agreement with the carbon atoms present in the chitosan molecule. In combination with the C 1s spectrum, the N 1s spectrum matches with literature results.^{5,11} The N 1s core-level spectrum (Figure 4C) consists of a predominant amine group ($-\text{NH}_2$ at 399.4 eV) and a minor positively charged amino group (NH_3^+ at 401.6 eV) that is associated with the partial protonation of amine groups because chitosan is a weak polybase.^{5,11} Besides chitosan, the same strategy may extend to other polymers. In our previous work,¹⁷ aryldiazonium-rich surfaces were used to spontaneously graft pyridine-based compounds and polyamidoamine (PAMAM) dendrimers. The well-known spontaneous reactivity of aryldiazonium salts toward pyridine allowed us to successfully graft 4-vinylpyridine, acetylpyridine, ethyl-4-pyridylacetate, and poly-4-vinylpyridine (P_4VP) onto self-adhesive gold substrates. In the present work, we used the aryldiazonium seed layer to graft poly(acrylic acid), following the same droplet deposition method. The primary XPS results strongly support the presence of poly(acrylic acid) on a stainless steel surface (see Figure S2, Supporting Information). Hence, our self-adhesive surface strategy seems to be very suitable for grafting green polymers onto stainless steel.

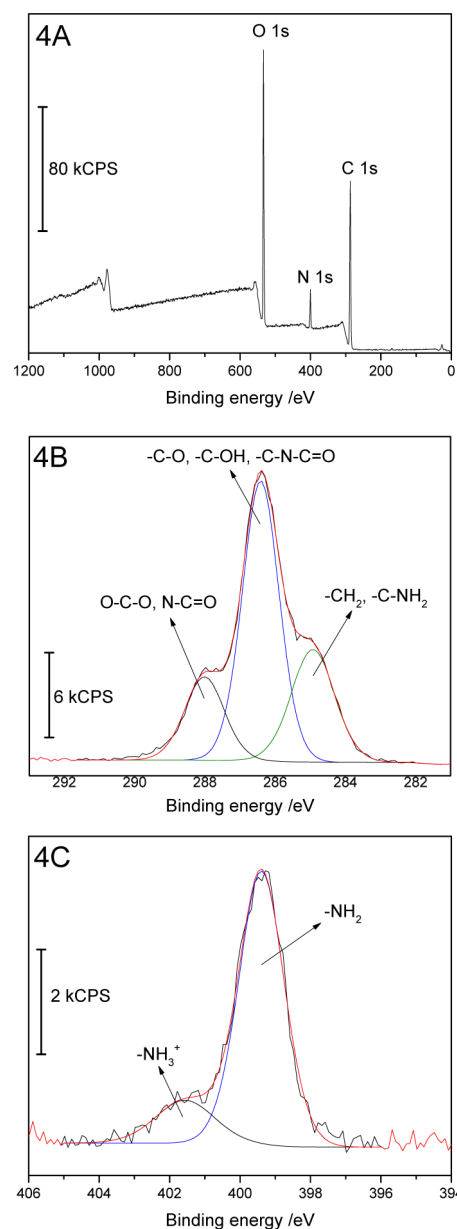


Figure 4. XPS survey spectrum (A) decomposed C 1s (B) and N 1s (C) core level spectra of the polyphenylene–chitosan-grafted stainless steel.

3.3. Protection against Corrosion of the Chitosan-Coated Steel Surface. As clearly indicated in section 1, in order for coated stainless steel to be used in real applications, resistance against corrosion in different media should be significantly improved with respect to bare stainless steel. A promising inhibition efficiency (up to 95%) has already been

achieved^{1,7,9,12,13} The purpose of this section is to evaluate the anticorrosive ability of our coated samples exposed to sulfuric acid medium in which it is normally subject to a high corrosion rate.

Figure 5 presents the potentiodynamic polarization curves of bare steel and polyphenylene–chitosan-grafted steel in contact

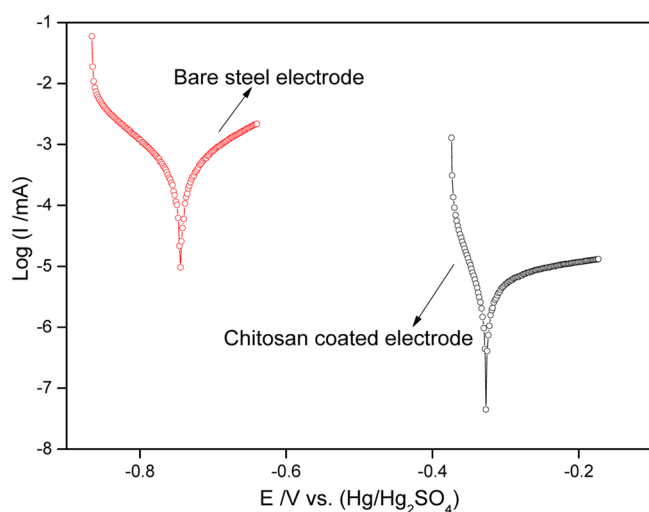


Figure 5. Logarithmic polarization curves of bare stainless steel and polyphenylene–chitosan-grafted stainless steel in 0.01 M H₂SO₄.

with 0.01 M H₂SO₄ solution. It is observed that, as for other polymeric films, the grafted chitosan film obtained via the self-adhesive strategy is characterized by a shift of the current–voltage curve toward less negative potential, i.e. the grafted polyphenylene–chitosan (PP–chitosan) plays the role of an anodic inhibitor for stainless steel. The inhibition efficiency of the modified samples, IE, was estimated as follows:

$$IE = 100 \left(1 - \frac{I_{\text{corr}}^{\text{film}}}{I_{\text{corr}}^0} \right) \quad (2)$$

Where, $I_{\text{corr}}^{\text{film}}$ and I_{corr}^0 stand for the current densities of the coated and bare steel electrodes, respectively. From the Tafel polarization curves presented in Figure 5, the corrosion current densities for bare steel and PP–chitosan-grafted steel were estimated to 0.45 and 0.001 $\mu\text{A cm}^{-2}$, respectively. An excellent inhibition efficiency was observed for the PP–chitosan-grafted steel surface (100%). The observed behavior is confirmed by measuring the charge transfer resistance of the PP–chitosan-coated steel electrode in sulfuric acid containing $\text{Fe}(\text{CN})_6^{3-/4-}$ as the redox probe (Figure 6): the charge transfer resistance is found close to 240 k Ω , which is much higher than that of the bare steel electrode (about 1 k Ω , as shown in the inset of Figure 6). In fact, the stainless steel surface is completely blocked by our grafted film, which consists of a polyphenylene layer topped by chitosan. In line with impedance spectroscopy results, iron and chromium peaks from the bare steel surface are no longer seen in the survey XPS spectrum of PP–chitosan-coated steel (Figure 4A).

The main difference between our grafted chitosan film and previously published ones lies in the presence of the primer PAP-grafted layer at the surface of stainless steel. Indeed, the covalently grafted polyphenylene layer is characterized by a high charge transfer resistance. We have recently found in previous work,³ that a thick-enough polyphenylene film able to

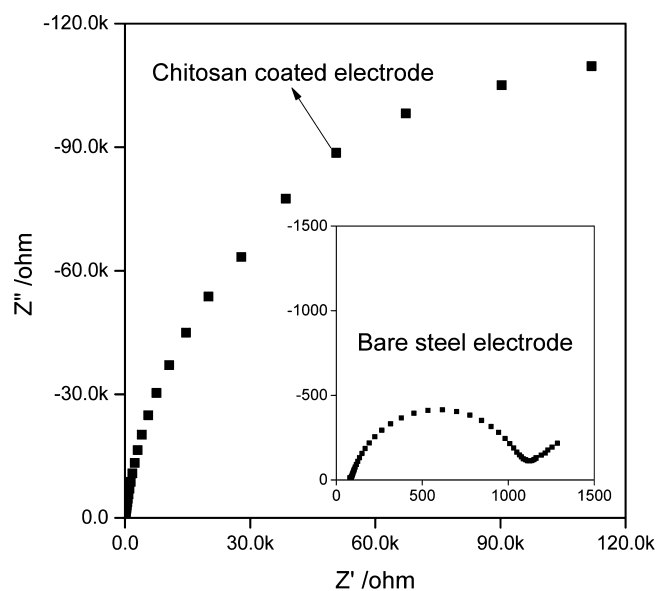


Figure 6. Impedance spectra of bare stainless steel and PP–chitosan-grafted stainless steel in contact with 0.01 M H₂SO₄ containing $\text{Fe}(\text{CN})_6^{3-/4-}$ redox probe (0.5 mM).

cover the entire steel surface creates itself an efficient physical barrier, thus leading to a high inhibition efficiency in sulfuric acid ($\geq 96\%$) without any further surface modification. The polyphenylene layer obtained in the present study has exactly the same effect. Our polyphenylene layer is quite thick and characterized by a high charge transfer resistance, as clearly pointed-out in section 3.1. Adding chitosan onto the top of the polyphenylene layer obviously introduces a more efficiently blocking effect which, in turn, causes an increase in the charge transfer resistance (from 27 to 240 k Ω).

With respect to the field of polymer grafting by way of diazonium chemistry, a similar strategy for grafting polystyrene on an iron surface with the aim of improving the protection against electrochemical corrosion in sulfuric acid was reported by Adenier et al.³⁹ It was clearly indicated that a benzoylphenyl layer grafted through the reduction of the diazonium salt can serve for a subsequent photochemical covalent attachment of polystyrene. As expected, the primary layer of benzoylphenyl groups, the thickness of which was estimated to be 6.8 nm, led to a blocking effect compared to the pristine iron surface. However, the secondary polystyrene film was not compact enough to bring additional protection of the iron surface. The observed behavior can be explained by noting that, after grafting, polystyrene appears as a dispersion of small particles. It is likely that the polymer chains do not attach to the benzoylphenyl groups either because of steric reasons or because the photochemical reaction, which must take place through the layer of polystyrene, is not efficient enough. Only 16% of the carbonyl groups on the top of the layer reacted with polystyrene under photochemical irradiation. Therefore, we believe that to obtain more protective layers, in place of polystyrene, a polymer that could undergo further polymerization and cross-linking is required. In the present case, the GraFFast process allows the grafting of a 9.8 nm thick primer layer onto stainless steel, which was eventually topped by chitosan through a spontaneous reaction between diazonium cations and either hydroxyl or amine functionalities of chitosan. These are probably the main reasons why PP–chitosan-coated steel behaves as a fully blocked surface in sulfuric acid and

hence leads to an excellent protection against corrosion, as discussed above.

4. CONCLUSION

We have reported here a simple two-step process for the covalent grafting of chitosan onto stainless steel in aqueous solutions. To the best of our knowledge, this is the first time that diazonium chemistry is used for functionalizing stainless steel with chitosan. The diazonium chemistry-based process proposed in this work takes advantage of both our patented GraftFast™ process and the self-adhesive surface strategy to provide strongly attached chitosan on a steel surface that exhibits an excellent anticorrosive ability in sulfuric acid. The polyaminophenyl layer primarily grafted via GraftFast™ on the steel surface is the key factor in this work, because it allows the easy formation of a self-adhesive layer for further coating chitosan and improves the overall resistance against corrosion of the resulting chitosan-coated steel samples. We believe that this success in grafting chitosan onto stainless steel via diazonium chemistry will be useful for advanced functionalization of diverse materials with carbohydrate polymers.

■ ASSOCIATED CONTENT

Supporting Information

Figure S1, XPS Fe 2p spectra of bare stainless steel and PAP-grafted steel samples; Figure S2, XPS survey and C 1s core-level spectra recorded on the surface of polyphenyl–poly(acrylic acid)-grafted steel sample. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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