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Synergistic effect of low and high intensity ultrasonic irradiation on the direct growth of ZnO nanostructures on the galvanized steel surface: investigation of the corrosion behavior



Zahra Sharifalhoseini^{a,*}, Mohammad H. Entezari^{a,b,*}, Mohsen Shahidi^c

^a Sonochemical Research Center, Department of Chemistry, Ferdowsi University of Mashhad, 91779 Mashhad, Iran

^b Environmental Chemistry Research Center, Department of Chemistry, Ferdowsi University of Mashhad, 91779 Mashhad, Iran

^c Samed Chemical Inds. Co., Mashhad, Iran

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ABSTRACT

Considering the current interest in the preparation of modified surfaces with fixed nanostructures, in this research, the hot water treatment was chosen as a simple and efficient procedure for the direct growth of ZnO nanostructures (ZnO NSs) on the metallic surface. To improve the method and reduce the cost of experiments, the commercial galvanized steel (steel containing a thin layer of zinc) was used as the base substrate. The use of the galvanized steel as an inexpensive and available metal surface has advantages compared to the pure Zn foil (used in other researches). In addition, in the present work, the effective pretreatment of the base substrate surface by applying the chemical etching under the low intensity ultrasonic irradiation facilitated the reaction progress (Zn \rightarrow ZnO) in a shorter time and relatively low temperature in comparison to many reports. To find the effect of acoustic energy on the final ZnO morphology, the hot water treatment was carried out under conventional and sonochemical conditions. Finally, as a practical application, resulting surfaces were coated with electroless Ni-P deposits and the effect of as-grown ZnO NSs (as the sublayer) on improvement in the corrosion protection of binary Ni-P deposits was evaluated by the electrochemical method.

1. Introduction

Engineering materials in nano-scale and improving desired properties of nanomaterials by the implantation of nanotechnology have attracted intensive research efforts in various fields of science. Practical applications of this advanced technology in sustainable energy systems [1], electronics and computer science [2], environmental remediation [3] and construction of biosystems [4] make a long list of nanotechnology benefits. Despite these positive aspects, risks of nanomaterials to health and environmental safety should be carefully considered. The increased mobility and reactivity of nanomaterials raise the possibility of harmful effects on the human life. Between two main categories of nanomaterials, including fixed and free nanoparticles, the second one is an immediate concern [5].

Over the past few decades, several groups have devoted their attention to the preparation of modified surfaces with fixed nanostructures (mainly through the immobilization of nanoparticles on solid substrates). Among a wide range of organic and inorganic materials developed for the modification of various matrixes, zinc oxide (ZnO) as an important multifunctional material has been the focus of considerable research. This metal oxide is found as a safe and nontoxic compound that possess high thermal and chemical durability. Furthermore, this metal oxide as an antibacterial and antifungal agent is widely used to fabricate the ZnO coated textile [6], paper [7], glass [8], polyethylene films [9], and metal surfaces [10]. These productions reduce the spreading of secondary pollutions and provide a more sterile environment. Additionally, types of ZnO NSs and nanoclusters are used as building blocks for electronic, photoelectronic and sensor devices [11-14]. This bio safe material also shows high catalytic and photochemical activities in the removal of the dye and other organic pollutants [15,16]. The formation of various nanoconfigurations of ZnO including nanobelts, nanocages, nanocombs, nanosprings, nanohelixes, nanotubes, nanowires, nanoneedles, and nanorings is another major priority of this ceramic oxide [17-19]. Along with a large variety of methods developed to produce fixed and free ZnO nanoparticles (e.g. solvothermal, microwave-assisted method, sol-gel, electrochemical deposition, ultrasound-assisted procedure), some modern techniques, including pulsed-laser deposition, magnetron co-sputtering, molecularbeam epitaxy, chemical-vapor deposition, ion beam sputtering have been widely used to grow or deposit fixed ZnO NSs on various matrixes

* Corresponding authors. E-mail addresses: z.sharif@um.ac.ir (Z. Sharifalhoseini), entezari@um.ac.ir (M.H. Entezari).

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[20–28]. For instance, the direct growth of vertically aligned ZnO nanorods (ZnO NRs) on the window by sputtering method, the growth of the 3D ZnO nanowall network on the ITO/glass by pulsed laser deposition, and the fabrication of the well aligned and separated ZnO NRs using reactive magnetron sputtering on the Si substrate could be referred [29–31]. The use of resulting surfaces in the construction of antireflective, self-cleanable and electrically conductive windows, as photoanodes in dye sensitized solar cells, and as excellent matrixes for biosensor applications has been investigated in mentioned literatures.

The research on preparation of surfaces modified with nanostructures is also attended by scientists with the aim of improving the corrosion protection under different corrosive environments. Nanostructure designing as an efficient procedure has offered a promising method to fabricate superhydrophobic surface with the enhanced corrosion resistance for applications in metallic and nonmetallic surfaces [32,33].

The need of sophisticated instruments and the complexity of some procedures used to grow or deposit nanomaterials (here with the main emphasis on zinc oxide) on solid surfaces have resulted in developing more feasible and efficient methods. Herein, scientists have conducted some experiments on the production of fixed ZnO NSs through the direct growth of ZnO on the pure Zn foil by the hot water treatment [34–36]. Despite the simplicity of this method, the high crystallization temperature ($\approx 300^{\circ}$ C), long reaction time, and expensive pure Zn foil (as the substrate and the Zn source) can be mentioned as important limitations of this technique.

In this regard, in the present research, the new strategy has been aimed to produce the metal surface containing the ZnO NSs. For this purpose, the commercial galvanized steel (CGS) has been chosen as the solid support and Zn source too. As it is known, the mass production of CGS plates is performed through the galvanization that is the process of applying a protective zinc coating to steel or iron, to prevent rusting [37]. Therefore, the CGS is found as a cheap and abundantly available metal surface compared to the pure Zn foil (used in other researches). In addition, an appropriate pretreatment process involving the chemical etching under the low intensity ultrasonic irradiation has been applied to CGS plates. This step through the effective surface activation eliminated the need of harsh conditions for the Zn oxidation. Consequently, the conversion of the Zn into ZnO phases (using the hot water treatment) occurs in a shorter time and at relatively low temperature compared to other scientific reports. Furthermore, to find the effect of the acoustic energy transfer on the final ZnO morphology, the hot water treatment has been performed in the presence and absence of high intensity ultrasonic irradiation. Resulting surfaces are useful for a wide range of applications (e.g. in the field of medical research or investigate its wettability property), but here the performance of as-grown ZnO NSs on the improvement in the corrosion protection of the binary electroless Ni-P coating has been targeted. Attractive features of the electroless Ni-P layer, including, excellent corrosion, wear and abrasion resistance, high uniformity of the coating and good adherence to the substrate make the electroless technique as a powerful tool for the surface modification in engineering applications. Due to the importance of this technique, successful efforts have been made to manipulate final characteristics of the Ni-P layer through changing reaction conditions (e.g. bath composition and plating parameters) [38,39]. Over the past few decades, many researchers have reported the improvement in the structure and corrosion resistance of Ni-P by incorporation of inert particles or whiskers ceramic reinforcements (e. g. nitrides, carbides, silicon, titanium and diamond) in the Ni-P matrix [40,41]. Regarding this aspect, ZnO is used as an anticorrosive pigment in organic coatings [42], whereas this feature of zinc oxide in metal (or alloy) coatings has been less attended. Thereby, in this research, substrates containing asgrown ZnO NSs have been coated with the electroless Ni-P plating (EN plating) and the corrosion resistance of EN plated surfaces with and without the sublayer of ZnO NSs have been evaluated by the electrochemical method. Moreover, chemical and physical effects that may be responsible for the enhanced corrosion resistance of samples containing of zinc oxide have been discussed in detail.

2. Experimental

2.1. Materials

The chemicals, including hydrochloric acid (HCl, 12 M) (used for the surface pretreatment), ammonia solution (for the pH adjustment), nickel sulfate, NiSO₄ (H₂O)₆, sodium hypophosphite, NaPO₂H₂, trisodium citrate, Na₃C₆H₅O₇, lead acetate, Pb(CH₃COO)₂, (used for the nickel plating) and sodium chloride, NaCl (used for the corrosion test) were purchased from Merck and used without additional purification. In this series of experiments, the sheet of commercial galvanized steel was chosen as the metal substrate and as the precursor of Zn²⁺ too.

2.2. Pretreatment and activation of the substrate surface

Before each test, plates with the desired dimensions (40 mm \times 20 mm \times 1 mm) cut from sheet of the commercial galvanized steel were degreased with an aqueous detergent solution. The use of a mild detergent solution does not attack the galvanized coating and results in an effective removal of the grease and any contaminants from the surface. The results of our primary experiments confirmed that the effective surface activation is a necessary step to oxidize the Zn. After the examination of different conditions, the immersion of cleaned plates in a diluted hydrochloric acid solution (0.01 M) under the sonication for 5 min at room temperature was found as suitable conditions. Next, plates were drawn from the acid solution, rinsed with distilled water, and then transferred to the glass cell for following steps. A bath sonicator (Branson 8510E-DTE, internal dimensions: 49 cm \times 29 cm \times 16 cm) was used for the ultrasonic irradiation. Ultrasonic parameters, including frequency and intensity (determined by the calorimetric method [43]) were 40 kHz and 0.3 Wcm⁻², respectively. The creation of active sites on the surface under applied conditions facilitated the conversion of the zinc into zinc oxide. It should be noted that the instability of zinc in the acid medium, leads to the rapid corrosion of zinc and zinc-coated products. Hence, the immersion time of target plates in the acid medium as well as the acid concentration and the temperature should be regarded as crucial factors in the maintenance of the Zn coating.

2.3. Oxidation of Zn layer

For this step, a water-jacketed cell containing 100 mL of distilled water was chosen as the reaction container. The temperature of water in the cell was adjusted at 80°C and for a reliable control, the temperature was checked by an external thermometer during the reaction. The cell containing active plates was taken under two different conventional and sonochemical conditions. Details of each procedure are described in following sections.

2.3.1. The conventional method

For this route, the experiment was carried out under the constant stirring (300 rpm) for 60 min at temperature 80 °C. To fix the plate position, a Teflon holder was used, which was designed for tightening two plates in the reaction vessel. Therefore, after each experiment, two similar samples were obtained that has the desired effect on the reduction of experimental errors. To prevent the heat from exiting, a piece of aluminum foil was wrapped around the cell. Fig. 1(A) shows schematically details of test setup used in this part. After 60 min, plates were removed, rinsed with distilled water, and dried at room temperature. The sample prepared through this method was named as the sample IA (or the conventional sample).



Fig. 1. The schematic view of the experimental setup used in; (A) conventional, and (B) sonochemical conditions. In both cases, temperature was measured by an external thermometer.

2.3.2. The sonochemical route

Here, instead of stirring, an ultrasonic apparatus equipped with a horn (model XL 2020) was used to irradiate the reaction medium. The diameter of the extender probe attached to the horn was 13 mm (12.7 cm length). The frequency and intensity of the sonicator were 20 kHz and 35 W cm⁻², respectively. To have a meaningful comparison between conventional and sonochemical samples, other conditions, including the time, temperature and the reaction vessel were the same applied in the previous section. The sample prepared by this method was named as the sample IB (or the sonochemical sample). The schematic view of the experimental design is shown in the Fig. 1(B). Samples IA and IB were used for the characterization and EN plating.

2.4. Coating by the electroless plating method

For the electroless nickel plating, the basic bath was chosen. The acid baths are not suitable due to the low stability of the ZnO in the acid medium and its dissolution at pH < 6. The bath was composed of nickel sulfate (as a source of the Ni²⁺ ions), sodium citrate (as the complexing agent that controls the release of Ni²⁺ ions) and sodium hypophosphite (as the reducing agent). For the pH adjustment (at 8.0 - 8.3), ammonia solution was used. Moreover, to prevent the bath from the decomposition, a small amount of lead acetate was added to the bath as the stabilizer agent. Composition and operating conditions applied for the EN plating are summarized in Table 1.

 Table 1

 Composition and deposition parameters of the used bath.

Deposition parameters	Amount		
Nickel sulfate	2.50 (g/100 mL)		
Sodium citrate	0.75 (g/100 mL)		
Sodium hypophosphate	3.00 (g/100 mL)		
Lead acetate	≈ 1 ppm		
θ (temp.)	70 (°C)		
time	15 min		
рН	8.0-8.3		

For all experiments, the volume of the bath was 100 ml and EN plating was carried out in the same vessel described in the Section 2.3. During the EN plating, the medium was agitated continuously by a magnetic stirrer (300 rpm) and the coating lasted 15 min at temperature 70°C. After completion of the coating, samples were removed from the bath, rinsed with distilled water, and dried with a heater. Conventional and sonochemical products after EN plating were labeled as samples IIA and sample IIB, respectively. Sample names and reaction conditions of all samples are presented in Table 2.

2.5. Evaluation of the Zn and the Ni-P thickness

The strategy applied to evaluate the thickness of the Zn layer on the

Table 2

Synthesis conditions of different samples.

Conditions	Step	Sample IA	Sample IB	Sample IIA	Sample IIB
Surface modification	1	ZnO growth (A)*	ZnO growth (B)**	ZnO growth (A)	ZnO growth (B)
	2	-	-	Ni-P coating	Ni-P coating
Reaction time (min)	1	60	60	60	60
	2	-	-	15	15
Temperature (°C)	1 2	80 ± 2 -	80 ± 5 -	80 ± 2 70	80 ± 5 70

* & ** are attributed to conventional (A) and sonochemical (B) methods, respectively.

galvanized steel as follows: firstly, the galvanized plate with the dimensions 40 mm \times 20 mm \times 1 mm was weighed using an analytical balance (precision 0.0001 g), then the specimen was placed into the beaker containing HCl solution (1 M). The white layer of the Zn starts to dissolve due to the exposure to the acid solution. After complete dissolution (lasted about 2 min) and observation of the fresh surface of the bare steel, the sample was removed from the beaker and weighed again. By the assumption of the uniform Zn coating and the density of 7 g cm³, thickness of the Zn layer was evaluated. In the case of the Ni-P coating, the thickness was estimated by weighing the sample before and after 15 min electroless plating. In addition, it was assumed that the overall surface was deposited uniformly and the final Ni-P composite coating has the density of 8 g cm⁻³. All measurements were repeated in duplicate to get more accurate results.

2.6. Corrosion study

To evaluate the corrosion resistance of obtained samples, potentiodynamic polarization (PDP) measurements were carried out using a potentiostat/galvanostat (SAMA 500; Electro-analysis System). A three-electrode setup used for electrochemical measurements was composed of the corroding sample (or test sample) as the working electrode, the silver/silver chloride (Ag/AgCl) as the reference electrode and the platinum auxiliary electrode. In the electrochemical cell, electrodes were immersed in a NaCl solution (3.5 wt.%, pH \approx 6.9) as an electrically conductive solution (corrosive medium). Before any test, species were left for 30 min to stabilize. After determination of the open circuit potential (E_{OCP}), polarization curves were collected at the potential interval between 200 mV below E_{OCP} and 200 mV above E_{OCP} at a scan rate of 1 mV s⁻¹. The surface exposed to the electrolyte solution was 1 cm² of each plate and other parts of samples were isolated from the corrosive medium by the epoxy resin. All measurements were conducted at room temperature ($\approx 25^{\circ}$ C).

3. Results and discussion

3.1. Characterization of samples

3.1.1. SEM analysis

The surface morphology of target samples was viewed under a 3D microscope (LEO 1450 VP). Fig. 2(A-C) displays SEM images of the galvanized sample surface before any treatment.

As seen in the Fig. 2(A), the surface of the CGS is not smooth. Small depressions are observed on the surface, which are marked with green circles drawn on the Fig. 2(B) (this figure is a magnification of the yellow rectangle on the Fig. 2(A)). These depressions and cracks (indicated by green squares on the Fig 2(C)) are attributed to the alloy manufacturing process (Fig 2(C) is a higher magnification of the red area shown on the image (B)). The surface morphology of the conventionally hot-water treated sample (sample IA) is depicted in the



Fig. 2. Micrographs of the commercial galvanized surface; (B) is related to the yellow area marked on the image (A), and (C) is a magnified view of the red area marked on the image (B).

Fig. 3(A-C).

These micrographs reveal that this surface is not smooth and many pores are formed on the surface. Furthermore, in higher magnifications (Fig. 3(B) & (C), needle-shaped zinc oxide nanorods are observed inside and the around of these holes.

SEM micrographs of the sonochemically heat-treated sample (sample IB) are shown in the Fig. 4(A-C). The Fig. 4(A) & (B) demonstrates that hexagonal disks of ZnO nanostructures are grown on the overall surface of the activated galvanized steel (Fig. 4(B) is a magnified view of the yellow area marked on the image (A)). Besides, the detailed morphological study of the surface indicated that some of hexagonal disks are grown preferentially along the c-axis (Fig. 4(C).

Comparison between conventionally and sonchemically hot-water treated samples showed that ultrasonic irradiation had a significant influence on the final morphology of as-grown ZnO structures. Under conventional conditions, needle-shaped zinc oxide nanostructures are





Fig. 3. SEM images of the sample IA at different magnifications; (B) is higher magnification of image (A), and (C) presents some hexagonal disks are grown preferentially along the c-axis.

observed, whereas under the high intensity ultrasonic irradiation (35 W cm^{-2}), the crystallization progress occurs in another path. Under the sonication, the hexagonal wurtzite ZnO is formed that is more stable than the cubic zincblende ZnO phase.

To find the effect of ultrasonic intensity on the morphology, two other levels of intensity, including 17.5 and 8.5 Wcm⁻² were examined and the results are presented in the Fig. 5.

As depicted in this figure, in the low intensity ($\approx 8.5 \text{ Wcm}^{-2}$), the amount of ZnO structures grown on the CGS surface is low (Fig. 5(A) & (A')), while in the medium intensity ($\approx 17.5 \text{ Wcm}^{-2}$), more regions of the surface are covered with rod-like structures of ZnO (Fig. 5(B) & (B')).

In the case of the morphology, it seems that under high intensity irradiation, ZnO hexagonal shape is dominant, whereas under low and medium intensity levels, the rod-like ZnO crystals are synthesized.

For explanation of the growth mechanism of ZnO rod-like structures, hexagonal wurtzite ZnO crystals can be assumed as hexagonal

Fig. 4. SEM images of the sample IB; (A) shows hexagonal ZnO crystals in the flat form, (B) is a magnified view of the yellow area marked on the image, and (C) exhibits elon-gated ZnO nanorods.

prisms, including two hexagonal "basal" faces and six rectangular "prism" faces. The basal faces are found as polar planes, including the (001) face (or zinc-terminated plane) and the $(00\overline{1})$ face (or oxygenterminated plane). The (001) face, which belongs to the symmetry group (C6) has a higher symmetry compared to other perpendicular faces. According to scientific reports, the growth along the c-axis occurs in higher rate [44]. The formation of ZnO nanodisks in flat form on a large area of the sample IB and elongated ZnO hexagonal prisms in some regions of all sonochemical samples can be illustrated by harsh conditions of ultrasound, including the high temperature (5000 K) and high pressure (20 MPa) produced in the hot spots. The extension of hexagonal ZnO prisms along their c-axis in some areas may occur due to the uneven distribution of the ultrasound within the reaction container. Note transferring more acoustic energy to the medium (in high intensity irradiation) provides the proper conditions for the formation of more nucleation sites on the surface.

To study the effect of time on the morphology, two other samples



Fig. 5. SEM micrographs of samples prepared in; (A) & (A') low intensity, and (B) & (B') medium intensity. (A') and (B) are magnifications of (A) and (B), respectively,



Fig. 6. The surface morphology of the sonochemical sample treated in hot water for 90 min. (B) is the magnified view of the yellow part shown on image (A), and (B) is the magnification of red rectangle marked on image (A). Additionally, (D) is higher magnification of green part shown on image (B).

were treated by thermal oxidation for 5 min (as a short treatment time), and 90 min (as a long treatment time) under high intensity ultrasonic irradiation (other conditions were similar to those described in Section 2.3.2). At the low synthesis time (5 min), the most areas of the surface are free ZnO (Supplementary data. Fig. 1S). Moreover, at the long time (90 min), the surface is damaged (Fig. 6(A-D). It seems that the exposure of the CGS surface to energetic waves of ultrasound has the negative effect on the surface. Different ZnO morphologies with highly unequal distribution on the damaged base surface can be seen in high magnifications (Fig. 6(C) & (D)).

Fig. 7(A-C) and Fig. 8(A-D) display the morphology of samples IIA

and IIB, respectively.

The uniform and the compact layers of Ni-P are observed in both figures (for the chemical composition see the Section 3.2). An interesting point about the sample IIB is the formation of the nanoscale dimension of Ni-P structures (see Fig. 8(C), which is higher magnification of the red part shown on the Fig 8 (B)). To have a good picture of this morphology, in addition to the secondary electrons (that produce SEM images), the signals include the backscattered electrons were applied to the solid surface to produce the BSE image of the surface (Fig. 8 (D)). This technique is useful to guide the eye for the recognition of the boundaries between the Ni-P phases. Some of nano-sized Ni-P



Fig. 7. The surface morphology of the sample IIA.

structures are marked with the yellow circles on this figure. Since in our previous work, the nanostructures didn't observed on the nickel-phosphorous coating that directly deposited on the bare steel (see the Ref. [45]), the formation of the EN film with nanoscale dimensions could be assigned to the existence of as-grown ZnO nanoconfigurations as the sublayer in the present work. However in the case of the sample IIA, these nanoscale dimensions are not observed, which could be interpreted by the microscale roughness of this sample before EN plating, originating from many micro pores on the overall surface of the sample IA.

3.2. EDS analysis

Fig. 9 (A-D) shows the analytical spectra and corresponding EDS analysis. The EDS equipment used to determine the elemental analysis was attached to the SEM microscope already mentioned. The results confirmed the presence of Zn for CGS and the zinc and oxygen for samples IIA and IIB. The detection of the oxygen and the zinc on samples IA and IB was considered as an evidence for the formation of



Fig. 8. The morphology of sample IIB. The uniform and the compact layer of Ni-P is observed in the (A) & (B). (C) is the higher magnification of the red part marked on (B), and the (D) is the BSE image of the surface.



Fig. 9. the analytical spectra and corresponding EDS analysis of the samples. The EDS equipment. (A), (B), (C) and (D) are related to the galvanized surface, sample IA, sample IB and the sample IIB, respectively. Au peaks (marked with red diamonds on the EDS spectra) are due to the coating of samples with gold for the SEM analysis (in the reported values, the portion of Au is omitted).

the ZnO phases due to the hot-water treatment in conventional and sonochemical conditions. In the case of the sample IIB, the elemental analysis exhibited the presence of expected elements including nickel and phosphorous. As it is known, the EN plating is an auto-catalytic chemical technique resulting in the formation of the alloy deposition of nickel and phosphorus depending on the reducing agent (e.g. sodium hypophosphite). These alloys have the different percentage of phosphorus, ranging from 1-4 (low phosphorus), 4-9 (medium phosphorus), and > 9 (high phosphorus) [46]. Although the values of the chemical composition obtained by the EDS analysis is not the exact, the content of phosphorous in the sample IIB (\approx 8 weight percent) and the measurements on the other regions on the surface (showed the same trend) suggested the medium phosphorus EN deposit. This classification has a smaller crystalline size and tends to be semiamorphous compared to the low-phosphorous deposits [46].

Fig. 10 shows schematically the procedure applied for the surface activation, hot water treatment in classical and sonochemical routes and obtained ZnO morphologies to investigate the corrosion protection of EN coatings.

3.3. Zn and Ni-P thickness

According to the strategy described in the Section 2.5, the thickness of the Zn layer on the galvanized steel surface and the Ni-P layers was determined. Based on our measurements the thickness of the Zn and the Ni-P layers (in samples IIA and IIB) is about 20 and 3 µm. An average of two measurements is reported for each specimen.

3.4. Corrosion study

Electrochemical measurements were performed and Tafel curves obtained from these PDP measurements are shown in the Fig. 11.

Electrochemical data extracted from Tafel plots, including anodic and cathodic Tafel slopes (β_a , β_c), corrosion current (i_{corr}), and

corrosion potential (E_{corr}) are summarized in the Table 3. By using the Stern-Geary equation, the polarization resistance (Rp) of samples (considered as the corrosion resistance too) was evaluated and values are reported in this table.

According to the obtained data, the EN plated steel has lower corrosion current compared to the bare and galvanized steel. The value of Rp for the EN coated surface is about 10,000 Ω cm². Additionally, EN deposited plates with the sublayers of the ZnO NSs (samples IIA and IIB) show higher polarization resistance (or lower the current density) compared to other samples. The values of this parameter for samples IIA and IIB are about 27,000 and the 31,000 Ω cm², respectively. For the bare sample composed mainly of iron, the corrosion process is comprised of anodic oxidation that creates Fe²⁺ ions and cathodic reduction that consume the electrons released from the anodic reaction. Two reactions mainly occur during corrosion, as follows:

At anode:
$$\operatorname{Fe}^{0}(s) \rightarrow \operatorname{Fe}^{2+}(\operatorname{aq}) + 2e^{-}$$
 (1)

And, at cathode : $O_2(g) + 2H_2O(l) + 4e^- \rightarrow OH^-(aq)$ (2)

These two reactions complement each other so that impeding one of them slows the overall corrosion process [47]. In this study, the corrosion potential of the bare steel is about 0.776 V (vs. Ag/AgCl). When the surface of the bare steel covered with a layer, the corrosion potential shifts positively or negatively depending on the nature of the coating. In the case of the CGS (steel coated with Zn layer), this shift is negative (corrosion potential of used CGS is about -1 V (vs. Ag/AgCl)). The Ni-P layer, which is known as a protective coating with good corrosion resistance efficiency, shifts the potential positively (Ecorr \approx -0.4 V (vs. Ag/AgCl)). The more positive shift in the value of the E_{OCP} (or E_{Corr}) and low current density observed in the sample IIB could be assigned to uniform and compact ZnO NSs formed on surfaces. The improvement in the corrosion resistance of samples IIA and IIB could be illustrated by physical and chemical effects of ZnO. The formation of nanosized ZnO structures results in higher surface contact to adhere the



Fig. 10. The schematic representation of the procedure applied in this research including the surface activation, the classical and the sonochemical hot water treatment of the activated galvanized steel, the direct growth of the ZnO NSs to investigate the corrosion protection of the EN coatings.



 Table 3

 Electrochemical data for all samples

Sample	E _{Corr} (V vs. Ag/ AgCl)	β_a (V/dec)	β _c (V/dec)	B [*]	i _{Corr} (μA/cm ²)	R_p^{**} (k Ω cm ²)
Bare steel Ni-P coated steel	-0.776 -0.404	0.16 0.27	-0.06 -0.18	0.0189 0.0469	22.105 4.727	0.855 9.920
Galvanized steel	-1.043	0.06	-0.13	0.0178	8.768	2.030
Sample IIA	-0.390	0.27	-0.18	0.0469	1.717	27.320
Sample IIB	-0.378	0.28	-0.20	0.0506	1.621	31.253

* B= $\frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)}$

up-layer of Ni-P to the base substrates. In addition, based on scientific reports, structures with nanometric dimensions exhibit higher electrical resistivity. This phenomenon is due to additional scattering centers, mainly from surface and grain boundaries [48]. Furthermore, trapping electrons by zinc oxide (chemical effect) was proposed as a probable mechanism of this semiconductor in the organic coatings modified with ZnO NPs [42]. In the similar way, in our case study, the ZnO NSs lead to a reduction in electron transferring, which is accompanied by a decrease in the metal dissolution and consequently a decrease in the corrosion current.

4. Conclusions

To produce the fixed ZnO NSs on the metallic surface, the hot water treatment was applied. Firstly, the plate of the commercial galvanized steel was chosen as the solid support and the Zn source. The use of the commercial galvanized steel as an inexpensive and available metallic surface eliminates the need of the pure Zn foil. The well-treated surfaces through the chemical etching and the low intensity irradiation facilitated the Zn oxidation in a shorter time and at relatively low temperature compared to many scientific reports. The hot water treatment under in the presence and absence of high ultrasonic irradiation disclosed the role of the acoustic energy on the morphology of ZnO NSs. The resulting surfaces were deposited by the EN plating in order to study the effect of as-grown ZnO structures as sublayers on the corrosion resistance of the binary Ni-P coatings. The results of electrochemical measurements confirmed the positive influence of the ZnO on the improvement in the corrosion protection of electroless nickel deposits. Finally, doing more research on the access to various shapes and sizes of fixed ZnO NSs on the metal support by changing in conditions of the feasible, efficient, cost effective, and the free catalysis procedure applied in this research is suggested because resulting surfaces have the considerable potential for many industrial applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ultsonch.2018.02.046.

References

- [1] Y. Li, J. Yang, J. Song, Structural model, size effect and nano-energy system design for more sustainable energy of solid state automotive battery, Renew. Sustainable Energy Rev. 65 (2016) 685–699.
- [2] Z. Wang, W. Wang, Z. Jiang, D. Yu, Low temperature sintering nano-silver conductive ink printed on cotton fabric as printed electronics, Prog. Org. Coat. 101 (2016) 604–611.
- [3] Q. Gao, H.T. Li, Y. Ling, B. Han, K.S. Xia, C.G. Zhou, Synthesis of MnSiO₃ decorated hollow mesoporous silica spheres and its promising application in environmental remediation, Microporous Mesoporous Mater. 241 (2017) 409–417.
- [4] J. Qiao, X. Mu, L. Qi, Construction of fluorescent polymericnano-thermometers for intracellular temperature imaging: A review, Biosens. Bioelectron. 85 (2016) 403–413.
- [5] C. Buzea, I. I. P. Blandino, K. Robbie, Nanomaterials and nanoparticles: Sources and toxicity, Biointerphases 2 (2007) MR17-MR172.
- [6] I. Perelshtein, G. Applerot, N. Perkas, E. Wehrschetz-Sigl, A. Hasmann, G.M. Guebitz, A. Gedanken, Antibacterial properties of an in situ generated and simultaneously deposited nanocrystalline ZnO on fabrics, Appl. Mater. Interfaces. 1 (2009) 361–366.
- [7] N.C.T. Martins, C.S.R. Freire, C.P. Neto, A.J.D. Silvestre, J. Causio, G. Baldi, P. Sadocco, T. Trindade, Antibacterial paper based on composite coatings of nanofibrillated cellulose and ZnO, Colloids Surf. A. 417 (2013) 111–119.
- [8] G. Applerot, N. Perkas, G. Amirian, O. Girshevitz, A. Gedanken, Coating of glass with ZnO via ultrasonic irradiation and a study of its antibacterial properties, Appl. Surf. Sci. 256S (2009) S3–S8.
- [9] R. Tankhiwale, S.K. Bajpai, Preparation, characterization and antibacterial applications of ZnO-nanoparticles coated polyethylene films for food packaging, Colloids Surf. B. 90 (2012) 16–20.
- [10] J. Karbowniczek, L. Cordero-Arias, S. Virtanen, S.K. Misra, E. Valsami-Jones, B. Rutkowski, K. Górecki, P. Bała, A. Czyrska-Filemonowicz, A.R. Boccaccini, Electrophoretic deposition of organic/inorganic composite coatings containing ZnO nanoparticles exhibiting antibacterial properties, Mater. Sci. Eng., C 77 (2017) 780–789.
- [11] X. Deng, L. Zhang, J. Guo, Q. Chen, J. Ma, ZnO enhanced NiO-based gas sensors towards ethanol, Mater. Res. Bull. 90 (2017) 170–174.
- [12] X. Wu, S. Xiong, Z. Mao, Y. Gong, W. Li, B. Liu, S. Hu, X. Long, In-situ deposited ZnO film-based sensor with controlled microstructure and exposed facet for high H₂ sensitivity, J. Alloy. Compd. 704 (2017) 117–123.
- [13] R. Yoo, S. Yoo, D. Lee, J. Kim, S. Cho, W. Lee, Highly selective detection of dimethyl methylphosphonate (DMMP) using CuO nanoparticles /ZnO flowers heterojunction, Sens. Actuators, B 240 (2017) 1099–1105.
- [14] J. Shim, J.K. Kim, K.S. Lee, C.L. Lee, M. Ma, W.K. Choi, J.Y. Hwang, H.Y. Yang, B. Angadi, J.H. Park, K. Yu, D.I. Son, A facile chemical synthesis of ZnO@multilayer graphene nanoparticles with fast charge separation and enhanced performance for application in solar energy conversion, Nano Energy 25 (2016) 9–17.
- [15] H. Derikvandi, A. Nezamzadeh-Ejhieh, Increased photocatalytic activity of NiO and ZnO in photodegradation of a model drug aqueous solution: Effect of coupling, supporting, particles size and calcination temperature, J. Hazard. Mater. 321 (2017) 629–638.
- [16] A. Shirzadi, A. Nezamzadeh-Ejhieh, Enhanced photocatalytic activity of supported CuO–ZnO semiconductors towards the photodegradation of mefenamic acid aqueous solution as a semi real sample, J. Mol. Catal. A: Chem. 411 (2016) 222–229.
- [17] T. Sun, J. Qiu, C. Liang, Controllable Fabrication and Photocatalytic Activity of ZnO Nanobelt Arrays, J. Phys. Chem. C 112 (2008) 715–721.
- [18] Y.B. Li, Y. Bando, D. Golberg, ZnO nanoneedles with tip surface perturbations: excellent field emitters, Appl. Phys. Lett. 84 (2004) 3603–3605.
- [19] J. Wang, J. Cao, B. Fang, P. Lu, S. Deng, H. Wang, Synthesis and characterization of multipod, flower-like, and shuttle-like ZnO frameworks in ionic liquids, Mater. Lett. 59 (2005) 1405–1408.
- [20] G. Xu, X.L. Wang, G.Z. Liu, Facile solvothermal synthesis of abnormal growth of one-dimensional ZnO nanostructures by ring-opening reaction of polyvinylpyrrolidone, Appl. Surf. Sci. 329 (2015) 137–142.
- [21] M. Fang, Z.W. Liu, Controllable size and photoluminescence of ZnO nanorod arrays

on Si substrate prepared by microwave-assisted hydrothermal method, Ceram. Int. 43 (2017) 6955–6962.

- [22] Y. Natsume, H. Sakata, Zinc oxide films prepared by sol-gel spin-coating, Thin Solid Films 372 (2000) 30–36.
- [23] D. Gal, G. Hodes, D. Lincot, H.W. Schock, Electrochemical deposition of zinc oxide films from non-aqueous solution: a new buffer/window process for thin film solar cells, Thin Solid Films 361–362 (2000) 79–83.
- [24] Y. Peng, J. Ji, D. Che, Ultrasound assisted synthesis of ZnO/reduced graphene oxide composites with enhanced photocatalytic activity and anti-photocorrosion, Appl. Surf. Sci. 356 (2015) 762–768.
- [25] J.L. Zhao, X.M. Li, J.M. Bian, W.D. Yu, X.D. Gao, Structural, optical and electrical properties of ZnO films grown by pulsed laser deposition (PLD), J. Cryst. Growth 276 (2005) 507–512.
- [26] H.J. Ko, Y. Chen, S.K. Hong, T. Yao, MBE growth of high-quality ZnO films on epi-GaN, J. Cryst. Growth 209 (2000) 816–821.
- [27] Y. Zhao, C. Li, M. Chen, X. Yu, Y. Chang, A. Chen, H. Zhu, Z. Tang, Growth of aligned ZnO nanowires via modified atmospheric pressure chemical vapor deposition, Phys. Lett. A 380 (2016) 3993–3997.
- [28] S.W. Fu, H.J. Chen, H.T. Wu, K.T. Hung, C.F. Shih, Electrical and optical properties of Al:ZnO films prepared by ion-beam assisted sputtering, Ceram. Int. 42 (2016) 2626–2633.
- [29] D.H. Kim, J.H. Park, T.I. Lee, J.M. Myoun, Superhydrophobic Al-doped ZnO nanorods-based electrically conductive and self-cleanable antireflecting window layer for thin film solar cell, Sol. Energ. Mat. Sol. 150 (2016) 65–70.
- [30] N. Islavath, D. Das, S.V. Joshi, E. Ramasamy, Seed layer-assisted low temperature solution growth of 3D ZnO nanowall architecture for hybrid solar cells, Mater. Des. 116 (2017) 219–226.
- [31] R. Nandi, S.S. Major, The mechanism of growth of ZnO nanorods by reactive sputtering, Appl. Surf. Sci. 399 (2017) 305–312.
- [32] X.F. Zhang, R.J. Chen, J.M. Hu, Superhydrophobic surface constructed on electrodeposited silica films by two-step method for corrosion protection of mild steel, Corros. Sci. 104 (2016) 336–343.
- [33] D. Zhang, H. Qian, L. Wang, X. Li, Comparison of barrier properties for a superhydrophobic epoxy coating under different simulated corrosion environments, Corros. Sci. 103 (2016) 230–241.
- [34] W.K. Tan, K. Abdul Razak, K. Ibrahim, Z. Lockman, Oxidation of etched Zn foil for the formation of ZnO nanostructure, J. Alloy. Compd. 509 (2011) 6806–6811.
- [35] W. Tan, K.A. Razak, Z. Lockman, G. Kawamura, H. Muto, A. Matsuda, Formation of highly crystallized ZnO nanostructures by hot-water treatment of etched Zn foils, Mater. Lett. 91 (2013) 111–114.
- [36] W. Tan, K. Abdul Razak, Z. Lockman, G. Kawamura, A. Matsuda, Optical properties of two-dimensional ZnO nanosheets formed by hot-water treatment of Zn foils, Solid State Commun. 162 (2013) 43–47.
- [37] P. Pokorny, P. Tej, M. Kour`il, Evaluation of the impact of corrosion of hot-dip galvanized reinforcement on bond strength with concrete – A review, Constr. Build. Mater. 132 (2017) 271–289.
- [38] Y.S. Huang, F.Z. Cui, Effect of complexing agent on the morphology and microstructure of electroless deposited Ni-P alloy, Surf. Coat. Technol. 201 (2007) 5416–5418.
- [39] R. Elansezhian, B. Ramamoorthy, P. Kesavan, Nair, Effect of surfactants on the mechanical properties of electroless (Ni–P) coating, Surf. Coat. Technol. 203 (2008) 709–712.
- [40] H.L. Wang, L.Y. Liu, Y. Dou, W.Z. Zhang, W.F. Jiang, Preparation and corrosion resistance of electroless Ni-P/SiC functionally gradient coatings on AZ91D magnesium alloy, Appl. Surf. Sci. 286 (2013) 319–327.
- [41] H. Ashassi-Sorkhabi, M. Eshaghi, Corrosion resistance enhancement of electroless Ni-P coating by incorporation of ultrasonically dispersed diamond nanoparticles, Corros. Sci. 77 (2013) 185–193.
- [42] S. Dhoke, A. Khanna, T. Jai, Mangal Sinha, Effect of nano-ZnO particles on the corrosion behavior of alkyd-based waterborne coatings, Prog. Org. Coat. 64 (2009) 371–382.
- $[43]\,$ T.R. Bastami, M.H. Entezari, A novel approach for the synthesis of super-paramagnetic $\rm Mn_3O_4$ nanocrystals by ultrasonic bath, Ultrason. Sonochem. 19 (2012) 560–569.
- [44] A. Mclaren, T.V. Solis, G. Li, S.C. Tsang, Shape and size effects of ZnO nanocrystals on photocatalytic activity, J. Am. Chem. Soc. 131 (2009) 12540–12541.
- [45] Z. Sharifalhoseini, M.H. Entezari, Enhancement of the corrosion protection of electroless Ni-P coating by deposition of sonosynthesized ZnO nanoparticles, Appl. Surf. Sci. 351 (2015) 1060–1068.
- [46] A. Małecki, A. Micek-Ilnicka, Electroless nickel plating from acid bath, Surf. Coat. Technol. 123 (2000) 72–77.
- [47] D. Prasai, J.C. Tuberquia, R.R. Harl, G.K. Jennings, K.I. Bolotin, Graphene: Corrosion-inhibiting coating, ACS Nano 6 (2012) 1102–1108.
- [48] H. Marom, M. Eizenberg, The effect of surface roughness on the resistivity increase in nanometric dimensions, J Appl. Phys. 99 (2006), http://dx.doi.org/10.1063/1. 2204349.