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# Sonication affects the quantity and the morphology of ZnO nanostructures synthesized on the mild steel and changes the corrosion protection of the surface



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# ABSTRACT

The several types of sonication methods were applied to access the different morphologies of ZnO nanostructures on the surface of mild steel. To achieve this goal, a sonictor equipped with the probe extender was used as a high intensity ultrasonic apparatus for direct sonication. Furthermore, an ultrasonic bath (low intensity) and a cuphorn system (high intensity) were applied for indirect sonication. To find the effect of the acoustic waves on the ZnO morphology, the micrographs of obtained surfaces were compared to the sample prepared by the conventional method using scanning electron microscopy (SEM). In this work, the beneficial effects of sonication were subjected on the breaking down the agglomerates to smaller size particles, metal surface activation, and on the facile approach to nanostructures synthesis. The influence of the resulting ZnO structures over the corrosion protection of the electroless Ni-P alloy coatings was evaluated by the potentiodynamic polarization technique (Tafel extrapolation).

# 1. Introduction

The phenomenon of acoustic cavitation in liquids causes the unique effects on the chemical reactions and processes. Increase in the reactivity of reagents, more efficient energy usage, more activation of the solid surface, and increase in the reaction output as the positive sonochemical effects have been led to the development of sonication as a powerful technique for many applications. The synthesis of a wide range of materials with the desirable properties (e.g. uniform size distribution and high surface area) under the normal conditions is one of the most important practical applications of ultrasound. In fact, sonochemistry by providing the proper conditions overcomes the most important limitations of the reaction, including the unfavorably high growth temperatures and long reaction time [1-3].

Based on the open literatures, the harsh conditions assigning to the cavitation process consist of transient temperatures of 5000 K, pressure of 1800 atm and cooling rates in excess of 1010 K/s facilities the achievement of the various compounds with at least one dimension in the nanorange. Herein, in the past decades, sonochemistry as an efficient and powerful technique has been attended in nanotechnology filed to the synthesis of large number of organic and inorganic compounds [4].

Among the inorganic materials, ZnO has been targeted. This metal oxide not only has nontoxicity effects, good biocompatibility effects, and chemical stability, but also shows high electron communication features [5-7]. Up to now, researchers have proposed several approaches to the synthesis of this ceramic oxide with various shapes [8-12]. Todays, several scientific reports have been published about the relation of ZnO morphology and its performance in optic, optoelectronic, and biomedical applications. For instance, the correlation between the morphology and the biological action of ZnO nanostructures has been studied by some researchers [13,14]. In addition, Li et al. reported the ZnO hierarchical nanostructures (as the three-dimensional ZnO morphology) with the high surface area show higher photocatalytic performance comparing to the other nanoparticle, nanosheet and nanorod structures [15]. The photodegradation of a wide range of pollutants in the presence of ZnO nanopowders could be referred as another practical application of this semiconductor [16–19].

Apart from a considerable amount of research has been devoted to the access of different ZnO morphologies in the powder form, the creation of various ZnO structures on the solid surface such as metal and glass substrates has received increasing attention. In this case, most of the successful attempts are focused on the synthesis of the one-dimensional (1D) zinc oxide nanostructures. More attention to these

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Fig. 1. Schematic view of the experimental setup applied in the direct sonication.

morphologies is due to superior electronic properties, giving them a great potential to manufacture the solar cells, sensors, short-wavelength light emitting and field effect devices. Currently, the well-aligned ZnO nanorods and nanowires due to desired properties have been extensively used in photodetectors, solar cells, piezoelectric generator, and supercapacitor [6,20–23].

In addition to the 1D ZnO nanostructures, producing the other ZnO shapes has been the subject of intense research in the past few years. In this field, the experiments have been conducted on the growth of the disks, rods, spindles, flowers, nanospike decorated sheets and nanowalls of ZnO on the solid substrates, and the morphology-dependent photoelectrochemical properties have been investigated [24–32].



Fig. 2. Schematic view of the cup horn and experimental setup used in the indirect method.

Among the wide variety of methods presented to ZnO synthesis, sonochemical assisted approaches towards the controllable synthesis of this valuable metal oxide could be referred [33–35].

Some synthesis processes that applied to grow the ZnO structures on the surface are complex and time-consuming. Hence, accessing to the pure phase of ZnO structures using the low-cost and available chemical materials through the simple and efficient procedures has been targeted. To our knowledge, approaching to the different ZnO morphologies through the similar procedure under the different types of ultrasonic irradiation has been rarely reported in the previous investigations. In this study, the effect of the different types of ultrasonic wave propagation through the reaction medium is shown on the content and the ZnO morphology coated on the metal substrate.

Another important feature of zinc oxide is the resistance of this ceramic oxide to high temperatures and high pressures. Regarding this aspect, zinc oxide as a protective ceramic oxide has been developed in the production of anticorrosive organic coatings [36], whereas the effect of this metal oxide on the corrosion resistance of the protective metal coatings has been less attended.

In this research, the efficiency of the synthesized ZnO structures (as the sub-layer) in the corrosion protection of the electroless nickelphosphorous (Ni-P) coatings has been evaluated. The electroless Ni-P layer is extensively used as a protective layer in engineering coating applications due to its real advantages, including excellent corrosion, wear and abrasion resistance, hardness, uniformity and adherence [37,38]. Despite these positive features, a wide range of researches has focused on the improvement in the performance of the binary electroless Ni-P film.

The successful efforts have been made to find the factors affecting the final characteristics of the Ni-P layer. For instance, the role of

Table 1						
The names and	1 synthesis	conditions	for	the	sample	s

Sample	Method	Status	Ultrasonic parameters		Temp. (°C)	Time (min)
			Frequency (kHz)	Intensity <sup>*</sup> (W cm <sup><math>-2</math></sup> )		
I	Conventional	Stirrer	-	-	60 ± 2	20
II	Direct sonication	Horn	20	35	$60 \pm 5$	20
III	Indirect sonication	Bath	40	0.3	$60 \pm 2$	20
IV	Indirect sonication	Cup horn	20	19	$60 \pm 5$	20

\* To measure the ultrasonic intensity, acoustic power was determined by calorimetric method [3].

#### Table 2

Deposition parameters of the used electroless Ni plating 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)		
Temp (θ).	70.00 (°C)		
Time	15 min		
pH	8.0-8.3		

surfactant and the complexing agent on the final property of Ni-P coating has been investigated in the literatures [39,40]. Furthermore, improvement in the structure and corrosion protection of Ni-P by adding some of inert particles or whiskers ceramic reinforcements such as nitrides, carbides, and oxides of aluminum, silicon, titanium, and boron to the nickel bath has been explored in the few past decades [41–43].

Our previous research confirmed that the transfer of the ultrasonic energy to the medium by sweeping the metal surface, agitating the



medium, and producing the effective collisions between the reagents and solid substrate forms the compact and smooth electroless Ni-P layer with few defects, reduced grain size, and higher corrosion resistance [44].

In this paper, the beneficial effects of ultrasound has been used on the dispersion and deagglomeration, metal surface activation, and nanostructure synthesis. In sonosynthesis, the high intensity ultrasonic probe, bath system that has been widely used for the cleaning applications and cup horn system as a high intensity indirect sonicator have been used. In order to study the effect of zinc oxide morphology on the corrosion protection of electroless nickel-phosphorus coatings, the corrosion resistance of the resulting surfaces was evaluated by the electrochemical method (Tafel extrapolation).

# 2. Experimental

#### 2.1. Materials

The chemicals, including zinc acetate dihydrate, sodium hydroxide (used to prepare the  $Zn(OH)_4^{2-}$ ), hydrochloric acid (12 M) (used for

**Fig. 3.** SEM images of the sample I. (B) and (C) are related to the yellow and green areas marked on the image (A), respectively. The micro-sized spherical structures and the zinc oxide nanostructures could be observed in (D) and (E). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** Zinc oxide nanorods with uniform distribution on the surface of sample II. (A) and (B) show the micrographs at the magnification of  $20,000 \times$  and  $50,000 \times$ , respectively.

the surface pretreatment), ammonia solution (to adjust the pH), nickel sulfate, sodium hypophosphite, trisodium citrate, lead acetate (used for the nickel plating), and sodium chloride (as the corrosive medium) were purchased from Merck and used without further purification. In all experiments, mild steel (containing about 99% Fe) was chosen as the substrate. The chemical composition of the substrate acquired by a Quantometer (3460ARLFISONS) is given in the Supplementary data (Table 1S).

# 2.2. Metal surface pretreatment

The metal pretreatment is an essential step to ensure the proper coating process. Metal surface pretreatment was initiated using the detergent and followed by rinsing with distilled water. Then the plate was immersed in the concentrated acid (HCl, 12 M) for 30 s. In this step, releasing the hydrogen bubble from the metal confirms the metal surface activation. After the surface preparation, the plate was immediately used for the next step.

# 2.3. Simultaneous synthesis and deposition of ZnO on the mild steel surface

The dilution of a transparent complex of  $Zn(OH)_4^{2-}$  as an easy, efficient, and eco-friendly method was applied to synthesize the zinc oxide structures on the metal surface. This procedure used to produce the highly pure crystalline ZnO powders in our previous work [45], as follows: the transparent complex of  $Zn(OH)_4^{2-}$  was prepared by dissolving of 5.5 g  $Zn(Ac)_2 \cdot 2H_2O$  in the 50 mL distilled water and adding 8 g NaOH. For each test, 10 ml of the transparent complex was added to the reaction vessel containing the target plates. To sono-synthesize, direct and indirect ultrasonic irradiations have been applied. The details of each procedure are described in the following sections.



**Fig. 5.** Surface morphology of sample III. (B) shows the higher magnification of the area marked with yellow on the image (A), and (C) is related to the higher magnification of blue region on the image (B). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

#### 2.3.1. Conventional method

To prepare the sample under the conventional conditions (without ultrasound), the  $Zn(OH)_4^{2-}$  solution was added dropwise to the 50 mL distilled water in a glass cell equipped with a water circulator. The experiment was carried out under constant stirring (500 rpm) for 20 min at temperature 60 °C. The product prepared by this method was denoted as sample I. The experimental setup designed for this section is presented in the Supplementary data, Fig. 1S.

#### 2.3.2. Sonochemical method

The ultrasound (instead of stirring) was applied with different types of sonication, including direct and indirect sonication. The horn system (as high intensity status) was used for direct sonication, and an ultrasonic bath and cup horn system were used as low and high intensity irradiator for indirect sonication, respectively.



**Fig. 6.** SEM micrographs of the sample IV. (A) and (B) are corresponded to the magnification of  $20,000 \times$  and  $50,000 \times$ . At higher magnification, the formation of an interesting morphology of ZnO network is observed.

2.3.2.1. Direct sonication. To obtain the ZnO structures on the metal surface under high intensity ultrasonic irradiation, during the addition of transparent complex to the distilled water, the reaction medium was irradiated by an ultrasonic status equipped with a horn (20 kHz, model XL 2020). The sample was named as sample II. A water-jacketed cell was used as the reaction container under the same conditions as the conventional one. Water circulation around the cell provided the control of temperature at the desired level (60 °C) during the reaction.

To fix the plate position, a Teflon holder was used. The design of this holder in such a way that at least two plates were fixed in the reaction container. Hence, in addition to higher efficiency in this process, access to the similar samples after each test reduced the experimental errors. Fig. 1 shows schematic details of test setup used in this part.

2.3.2.2. Indirect sonication. For the preparation of ZnO powder in indirect sonication (low intensity irradiation), an ultrasonic bath (40 kHz, Branson 8510E-DTE, internal dimensions:  $49 \text{ cm} \times 29 \text{ cm} \times 16 \text{ cm}$ ) was used. The bath was equipped with the thermostat, which allows adjusting the temperature at 60 °C. Additionally, a beaker was used as the reaction vessel in this experiment (sample III).

For high intensity irradiation, a cup horn system (Misonix) was used. This system has a 5 cm diameter radiating surface and transparent sleeve, which is filled with water. The temperature of circulator attached to this system was set at 60 °C. The plate was placed into a beaker and the beaker was fixed inside the cup horn sleeve.

Fig. 2 shows a schematic representation of cup horn and the experimental setup. The plate covered with the ZnO nanostructures by this sonicator was named as the sample IV.

In this series of experiments, the  $Zn(OH)_4^2$  complex was added to the water at a constant rate (1 mL min<sup>-1</sup>). Beside for a reliable control, the temperature was checked with an external thermometer during the

reaction. The names and the reaction conditions for the all samples are summarized in Table 1.

#### 2.4. Quantity of the deposited ZnO

By weighing the samples before and after 20 min ZnO deposition, the amount of the zinc oxide deposited on the target surfaces was evaluated.

# 2.5. Ni electroless plating

To find the effect of the ZnO deposition on the corrosion resistance of the Ni-P layer, access to the suitable electroless plating bath was inspected. The ZnO dissolution at pH < 6 limits the acid nickel bath to use. Hence, the basic nickel bath was selected and its parameters were optimized. The bath composition and operating conditions applied for electroless Ni plating are given in Table 2.

In the applied bath, nickel sulfate and sodium hypophosphite were used as the source of the  $Ni^{2+}$  ions and the reducing agent, respectively. In addition, sodium citrate was added to the solution as the complexing agent that controls the release of  $Ni^{2+}$  ion in the medium and the pH was adjusted at 8.0–8.3 by ammonia solution during the reaction.

In the plating process, the mild steel was activated according to the protocol described in the Section 2.2, and the other samples (containing zinc oxide) were plated without this step due to the instability of zinc oxide structures in concentrated acidic medium. The reaction vessel was the same water-jacketed cell used for the ZnO deposition in Section 2.3.1. Besides, during Ni plating, the reaction container was kept under constant stirring (rpm = 300). The coating lasted for 15 min at temperature 70 °C. After 15 min Ni plating, the species were removed, washed with distilled water, and dried by a heater.

#### 2.6. Effect of ZnO deposition on the nickel plating rate

To find the influence of the deposited ZnO on the rate of Ni plating, all samples were weighed before and after 15 min electroless plating.

## 2.7. Corrosion study

To evaluate the influence of ZnO morphology on the corrosion inhibition performance of Ni-P, the corrosion resistance of the bare steel surface, the Ni-P coated samples with and without ZnO structures was examined by the electrochemical method. Before any measurement, the samples were left for 10 min at room temperature to stabilize. After measurement of open circuit potential ( $E_{OCP}$ ) and its stabilization, potentiodynamic polarization (PDP) measurements were taken by a potentiostat/galvanostat (SAMA 500; Electro-analysis System) through a three-electrode setup including working electrode (test sample), platinum auxiliary electrode and Ag/AgCl as a reference electrode. For all electrochemical tests, NaCl solution (3.5 wt%) was used as the electrolyte and the exposed area of the test sample to the electrolyte was 1 cm<sup>2</sup> (other parts of the plate were isolated by the epoxy resin from the electrolyte). All experiments were performed at room temperature and repeated in duplicate to provide more accurate results.

# 3. Results and discussion

# 3.1. Characterization of coatings

The morphology of the ZnO deposited surfaces was monitored by 3D microscope (LEO 1450 VP) and the chemical composition of surfaces was determined by the EDS system (attached to the SEM microscope). The morphology of the ZnO structures formed under different conditions are discussed in detail.



3.1.1. SEM analysis

Fig. 3 presents the surface morphology of the sample I. These three-dimensional micrographs, in particular Fig. 3(B) and (C)

indicate the formation of the mountainous structures. An interesting point is the formation of volcanic features on the plate substrate. One of these mountainous structures is shown in the Fig. 3(D).

Apart from these structures (in micro size), at high magnification, Fig. 3(E) shows that the overall surface of the substrate was covered with ZnO nanostructures. The formation of ZnO on the surface is due to proper pretreatment of the metallic surface. Indeed, the activation by the acid solution, though the creation of the active sites on the substrate facilities the synthesis of ZnO.

# Fig. 4 exhibits the surface morphology of the sample II.

The formation of nanorod structures (grown preferentially along the c-axis) with uniform distribution could be assigned to the cavitation. Formation, growth, and implosive collapse of bubbles in the reaction medium follows by the high temperature (~5000 K) and high pressure  $(\sim 20 \text{ MPa})$  [4]. The harsh conditions produced around these hot spots promoted the crystallization of hexagonal nuclei of zinc oxide along the c-axis. Furthermore, the explosive forces, including shock waves and microjets created the strong streams. These streams by propagating Fig. 7. Schematic view of the surface pretreatment and the formation of the various ZnO morphologies on the metal surfaces through the direct and indirect sonication (regardless of the true relative size).

through the reaction medium reduced the nanoparticle agglomeration.

The SEM images of the sample III (Fig. 5) display the synthesis of the flower like structures on the surface.

High magnification  $(50,000 \times, Fig. 5(C))$  confirms the covering of the surface with the ZnO nanostructure. It seems that applying the bath sonicator led to the uniform distribution of the flower-like structures on the target surface. Under sonication, breaking down the agglomerates into the single particles occurred due to shear forces generating from the acoustic cavitation.

As it is well known, the ultrasonic bath is as an environmentally friendly alternative for the cleaning of materials. This significant feature of ultrasound makes it a good candidate for the pretreatment of the metal surface in the industrial processes (e.g. continuous cleaning of wire and cables) [3,46]. The results of our experiments and the other researches confirm that this low power ultrasonic irradiator can also be useful for the synthesis of materials in normal conditions without any further post treatment [3,46-48].

Fig. 6 shows the brilliant performance of cup horn system in the synthesis of the network of the ZnO nanostructures.

From the SEM analysis, it can be concluded that the different types of the ultrasonic irradiation affect the morphology. The results



Fig. 8. The morphology of the sample II after electroless Ni-P coating at the different magnifications.

suggested that the harsh conditions of the direct sonication promote the formation of the elongated ZnO nanorods, while under the continuous indirect sonication (by the ultrasonic bath and the cup horn systems), the nucleation and the crystallization occur in other paths. Indeed, the understanding of how could the employed methods affect the morphology needs to do more research because the simultaneous effect of the some factors, including the applied frequency and the intensity, type of the ultrasonic wave propagation in the medium and even the geometry of the reaction vessel on the morphology should be considered. However, the SEM analysis confirmed that the high intensity sonication methods (direct and indirect) result in the access of the finer nanostructures compared to the sample formed under the low intensity irradiation.

The metal surface pretreatment, simultaneous synthesis and deposition of ZnO, and the morphologies of the resulting structures on the mild steel surfaces (regardless of the true relative size) are summarized schematically in Fig. 7.

Due to higher corrosion resistance of the EN coated sample II

compared to other samples (see the Section 3.5), the SEM images of this sample (as a typical sample deposited with Ni-P coating) were also taken. Fig. 8(A–C) displays the morphology of this sample.

As can be seen, the layer of Ni-P coating with the fine grains is observed (for the chemical composition of the layer, see the Section 3.1.2). An interesting point in these figures (especially Fig. 8(C), which is the higher magnification view of the red part on the Fig. 5(B)), is the formation of the nanoscale dimension of Ni-P structures. By comparison with our previous research [44], the formation of the nanosized EN film could be assigned to the existence of the as-grown ZnO nanoconfiguration as the sublayer. Based on the results gained in the mentioned literature, the Ni-P films directly deposited on the bare steel (in the absence and presence of ultrasound) possessed no nanoscale phase of Ni-P.

# 3.1.2. EDS analysis

The analytical spectra and corresponding EDS analysis of the samples are shown in the Fig. 9.

The elemental analysis confirmed the presence of the expected elements, including zinc and oxygen in the samples I through IV, which can be considered as an evidence for the formation of ZnO phases The detection of iron in the samples I, III and IV is due to the interaction of X-ray beam and base substrate composed mainly of iron. This peak is not observed in the sample II that the existence of the compact ZnO nanorods on its surface may be a reason for this phenomenon. Furthermore, the detection of Au peak in the EDS spectra is due to sputter coating of gold on the surfaces employed in the SEM sample preparation. The position of the Au peaks are marked with the red diamonds on the EDS spectra and its portion is omitted in the reported values. In the case of the sample II after nickel plating, the coating consisted of Ni and P elements. Concerning the mechanism of the electroless plating, this technique results in the formation of the alloy deposition of nickel and phosphorus with different percentage of phosphorus, ranging from 1 to 4 (low phosphorus), 4 to 9 (medium phosphorus), and > 9 (high phosphorus) [49]. The elemental analysis of the selected area (marked on the SEM image) and the measurements on other regions of the surface showed the content of phosphorous in this specimen is about 8 wt%. Therefore, this coating is classified in the medium phosphorus category. This classification has a smaller crystalline size and tends to be semiamorphous compared to the lowphosphorous deposits [49].

#### 3.2. XRD analysis

To ensure the purity of the ZnO NPs, which were synthesized by the mentioned procedures used in this research, the white powders (of ZnO) were collected from the bottom of the cell and separated by centrifugation (at rpm = 5000 for 5 min), washed with distilled water several times, and dried in oven at 80 °C for 18 h. The crystallographic structures were recorded using D8Advanced diffractometer with CuK $\alpha$  radiation ( $\lambda = 0.154$  nm). The crystal structures of the samples characterized by the XRD analysis are shown in the Fig. 10.

The results of this analysis confirmed the formation of the pure ZnO phases. All the diffraction peaks of ZnO attributed to the planes, including (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) can be well indexed to the hexagonal phase ZnO reported in JCPDS card (No. 36-1451, a = b = 3.249 Å and c = 5.206 Å). Moreover, in comparison to the (100)/(002) intensity ratio in the XRD pattern collected for the isotropic ZnO sample (1.17) [50], all the samples showed the typical deviation from the isotropic structure.

#### 3.3. Estimation of the ZnO quantity on the surface

All the samples were weighed before and after ZnO deposition and the results of the measurements were graphed and shown in Fig. 11.



Fig. 9. The EDS spectra and chemical composition of the samples: (A), (B), (C) and (D) are attributed to the samples I, II, III and IV respectively. (E) is referred to the sample II after Ni-P deposition.

According to this figure, the mean value of the ZnO content for the samples I, II, III and IV are 5.2, 1.7, 0.8, and 0.5 mg, respectively. The results also revealed that the sonochemical samples (II, III, and IV) possess lower content of ZnO compared to the conventional one. Additionally, the direct sonication led to the higher ZnO deposition (1.7 mg), in comparison to the indirect ultrasonic irradiations (0.8, and 0.5 mg).

# 3.4. ZnO quantity affects the Ni plating rate

To clarify the effect of the deposited ZnO on the rate of Ni plating, all samples were weighed before and after electroless plating. The test results as a graph are presented in Fig. 12.

According to this graph, the mean value of the nickel deposition rate for the samples I, II, III and IV are 0.0386, 0.0248, 0.0395, and 0.0410, respectively. In comparison to the plating rate of the bare mild steel (0.0422 g/15 min), all the samples containing ZnO have lower rate. On the other word, the presence of ZnO on the surface shows the negative effect on the plating rate. It means that the zinc oxide nanostructure on the surface act as an inhibitor in the Ni deposition rate. Reduction in nickel deposition rate in the presence of ZnO could be illustrated by the mechanism of the Ni electroless deposition. In this technique, metal surface act as a substrate and catalyst too and reduction of sodium hypophosphate  $(P^1 \rightarrow P^0)$  along with the chemical reduction of Ni<sup>2+</sup> ions to the Ni<sup>0</sup> leads to the incorporation of the phosphorus into the nickel matrix and formation of the binary Ni-P coating [44].

By this explanation, the reverse relationship between the ZnO quantity and the plating rate in samples II, III, and VI could be confirmed. It should be noted that the sample I with the highest amount of ZnO didn't show the lowest plating rate. In comparison to the sono-chemical samples, ZnO structures grown on the surface of this sample are larger in size (formation of the micro-sized structures confirmed by the SEM analysis). Less covered metallic surface compared to the other samples containing nanosized ZnO may be a reason of this phenomenon. Therefore, the plating rate can be also influenced by the size of ZnO structures.

# 3.5. Corrosion resistance of the coatings

The electrochemical measurements were performed for the bare mild steel, Ni-P coated surface and the samples of the Ni-P with a sublayer of ZnO. The potentiodynamic polarization curves are shown in Fig. 13.

By extrapolating from the linear regions of anodic and cathodic



**Fig. 10.** The XRD patterns of the ZnO powders; (A), (B), (C) and (D) are attributed to the samples synthesized under the indirect ultrasonic irradiation (low intensity, bath), the conventional conditions, the indirect ultrasonic irradiation (high intensity, cup horn) and under the direct sonication (high intensity, ultrasonic horn), respectively.



Fig. 11. Evaluated amount of the ZnO synthesized in different conditions. Data are shown with mean values and standard error bars.

polarization curves, the electrochemical data, including the anodic and cathodic Tafel slopes ( $\beta_a$ ,  $\beta_c$ ), corrosion current ( $i_{corr}$ ), and corrosion potential ( $E_{corr}$ ) were derived and listed in Table 3. Additionally, by using the Stern–Geary Equation, Rp (polarization resistance) was calculated and this parameter was considered as the corrosion resistance here [44].

The value of the corrosion resistance of the samples I, II, III and IV are about 13, 32, 17, and  $19 \text{ k}\Omega \text{ cm}^2$ , respectively. The electrochemical tests exhibit that the deposition of zinc oxide despite the negative effect on the plating rate result in higher corrosion resistance. According to the extracted data from Tafel extrapolation (Table 3), sample II shows the highest corrosion protection. More positive shift in the potential and the smaller current density for the sample II confirm the lower tendency to corrode.

The enhanced corrosion resistance of the samples containing the sublayer could be illustrated by the physical and the chemical effects of ZnO. The samples containing the nano-configurations of ZnO with finer dimensions, including the elongated ZnO nanorods (sample II) and the ZnO network (sample IV) shaped under the high intensity irradiation possess higher corrosion resistance. This observation can be considered as an evidence for the direct correlation between the average specific surface area of ZnO structures and the corrosion resistance. The



Fig. 12. Estimated Ni-P deposition rate of the target samples. Data are shown with mean values and standard error bars.



Fig. 13. Potentiodynamic polarization curves of the bare mild steel and the samples I through IV.

 Table 3

 The electrochemical parameters excluded from the Tafel plots.

Sample	E <sub>corr</sub> (V vs. Ag/AgCl)	$\beta_{\rm a}$ (V/ dec)	$\beta_{\rm c}$ (V/dec)	В*	i <sub>corr</sub> (μΑ/ cm²)	$R_p^{**}$ (k $\Omega$ cm <sup>2</sup> )
Bare Steel	-0.537	0.29	-0.09	0.0298	47.77	0.626
Ni-P	-0.433	0.23	-0.13	0.0360	4.786	7.531
I	-0.397	0.10	-0.17	0.0273	2.006	13.609
II	-0.377	0.19	-0.07	0.0222	0.686	32.426
III	-0.391	0.17	-0.14	0.0333	1.946	17.131
IV	-0.382	0.11	-0.10	0.0227	1.190	19.083

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

formation of the nanosized ZnO structures by increasing the surface contact improves the adhesion between the Ni-P coating (as the uplayer) and the base substrates. Additionally, based on the scientific reports, the structures with the nanometric dimensions exhibit higher electrical resistivity due to the additional scattering centers. These centers are mainly resulting from the surface and grain boundaries [51]. In the case of the chemical effect of zinc oxide, electron trapping by this semiconductor was proposed as a key factor in the corrosion reduction of the organic coatings modified with ZnO NPs [36]. In a similar way, in our case study, this main characteristic of zinc oxide by the restriction of the electron transfer can reduce the corrosion current.

It should be noted that the formation of an equal amount of ZnO on

the substrates would provide a better understanding of the morphology effect on the anticorrosive performance, but the different efficiency of the conventional, direct and indirect sonication methods on the reaction output limits to make a detailed comparison. However, synthesis of the ZnO as the anticorrosive pigment in the same time discloses the efficiency of the sonication types on the reaction yield. Indeed, a reduction in corrosion current in the presence of the small amount of conventional and sonochemical ZnO nanostructures is as an interesting result. Moreover, the deposition of the different ZnO morphologies (through the applied procedures in this paper) on the various matrixes such as ITO/glass, Si substrate, textile, paper and polymeric films could be useful to search their potential for other applications in the medical, electronic and photoelectronic research fields.

#### 4. Conclusions

In summary, the effect of the amount and morphology of as-synthesized ZnO on the surface of mild steel were examined in the absence and presence of ultrasound (direct and indirect). The samples containing ZnO structures were covered with a Ni-P layer through the electroless method. The effect of synthesized zinc oxide on the anticorrosive performance of Ni-P layer was studied. As a result the both conventional and sonochemical ZnO structures showed the negative effect on the plating rate. Despite the reduction in plating rate, the electrochemical measurements confirmed that the Ni-P films with sublayer of ZnO structures demonstrated higher corrosion resistance than Ni-P layer deposit without ZnO. Additionally the substrate covered with nanorod structures, which formed under horn system possess higher corrosion protection. Based on the obtained results, formation of zinc oxide on the surfaces is accompanied by the beneficial physical and chemical effects on the pretreatment and modification of the surface before plating process. The physical effect could be assigned to the creation of the suitable roughness on the solid substrate that result in the better adhesion of Ni-P. In addition, the restriction on the electron transfer in the presence of this semiconductor that leads to lower corrosion current could be considered the beneficial chemical effect of this ceramic oxide.

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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.2017.10.012.

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