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# Direct growth of ZnO nanostructures on the Zn electroplated mild steel to create the surface roughness and improve the corrosion protection of the electroless Ni-P coating

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

The disadvantages of some methods applied to deposit or grow ZnO structures led us to conduct experiments on the direct growth of the ZnO through the new and highly applicable procedure. For this purpose, the mild steel surface after the activation was coated with a thin layer of Zn using the electroplating method. This technique eliminated the need of the pure Zn foil as a relatively expensive substrate. The conventional and sonochemical hot water treatment of as-synthesized Zn crystals for the conversion to the ZnO phases offered economic benefits because there was no need for the special pretreatment of the surface before thermal oxidation. As a practical application, as-grown ZnO structures (as the sublayer) were covered with the electroless Ni-P layer and the improvement in corrosion protection of binary Ni-P coatings with and without sublayer of ZnO was studied by the electrochemical method.

## 1. Introduction

Recent advances in the synthesis, modification and practical applications of nanomaterials have led to the development of nanotechnology as a new interdisciplinary area of research in many fields of human life. Modification of various matrixes with nanoparticles (NPs) using several methods such as incorporation, adsorption, deposition, coating and impregnation has offered new solutions in various fields of science [1–6]. Types of nanoparticles have received so much attention in the medical applications (e.g. wound dressing, dental filler and adhesive, drug delivery and cosmetic ingredient) [7–10]. Nano-sized organic and inorganic particles have been also extensively used in a wide range of areas, including electrochemistry, photochemistry, heterogeneous catalysis, supercapacitors and ultracapacitores [11–14]. Besides, the significant improvement in the strength and the corrosion protection of various materials modified by incorporation of nanoparticles has made nanotechnology suitable for a wide variety of engineering applications [15,16]. In spite of the positive aspects, the risks of nanomaterials to health and environmental safety should be carefully considered. Most procedures applied in nanotechnology are involving the dispersion or the production of free nanosized materials. The entry of these particles into the environment may be accompanied by harmful effects due to their increased mobility and reactivity [17]. In this regard, more attention to the preparation of fixed nanoparticles and the procedure applied to obtain them are immediate concerns.

Since in this work, the production of ZnO structures has been targeted, various synthesis methods and applications of this metal oxide have been considered. Due to unique properties of ZnO, a rich variety of physical (vapor-phase process) and chemical (solution phase) methodologies were used to synthesize various ZnO nanostructures (ZnO NSs). Furthermore, the green nanosynthesis approach, which is based on using ecofriendly reagents or biogenic process, was developed to obtain nano-scaled pure ZnO particles [18,19]. Zinc oxide due to nontoxicity and good biocompatibility is developed in biomedical applications [20,21]. Furthermore, this ceramic oxide due to high electron communication feature and near ultraviolet emission, can be used as building blocks for electronic and optoelectronic devices (e.g. solar cells, ultraviolet light emitters, lasers and sensors) [22–24]. Along with solution-based approaches such as hydrothermal, sol-gel and electrochemical deposition developed to grow or deposit ZnO thin films, some other procedures, including pulsed laser deposition (PLD), molecular beam epitaxy (MBE), chemical vapor deposition (CVD), and magnetron sputtering have been extensively used for the ZnO synthesis [25–30]. For instance, Kim et al. suggested the direct growth of vertically aligned

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* Corresponding authors at: Sonochemical Research Center, Department of Chemistry, Ferdowsi University of Mashhad, 91779 Mashhad, Iran (M.H. Entezari)
*E-mail addresses:* z.sharif@um.ac.ir (Z. Sharifalhoseini), entezari@um.ac.ir (M.H. Entezari).

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ZnO nanorods (ZnO NRs) on the window by sputtering a seed layer of the Ga-doped ZnO and the hydrothermal method to get an antireflective, self-cleanable and electrical conductive window layer for the thin film solar cell [31]. Nandi et al. reported the growth of the vertically well aligned and separated ZnO NRs through the reactive magnetron sputtering of zinc target on Si substrate under the argon-oxygen atmosphere (in the range of 300–750 °C). The resulting ZnO thin film/nanorods obtained by their research has potential to use is in light emitting diodes, laser diodes and detectors in the near-UV range [32]. Pulsed laser deposition growth of the 3D ZnO nanowall network as another research carried out in this field for dye- sensitized solar cells (DSSCs) and biosensor applications [33].

Providing sophisticated instruments with high temperature, high vacuum, and thus high cost could be mentioned as technical limitations of these methods. To overcome these limitations, facile methods such as thermal oxidation of metallic Zn has been reported to the direct growth of ZnO NSs [34]. It seems that successful efforts made in the recent years could be useful to produce fixed nanostructures and reduce the production of free nanoparticles. The results of one research conducted on the oxidation of Zn foil at temperatures of 100–400 °C showed that the final morphology of the oxidized Zn foil (including spherical oxide grains, porous nanosheets and ZnO nanorods) is strongly dependent on the oxidation temperature [35]. In another effort, large-scale ZnO nanowire arrays were grown directly on zinc foils using the thermal oxidation in air to investigate the wetting and water adhesion properties [34]. Despite the advantages of the thermal oxidation of metallic Zn film as a simple and cost-effective method, the high crystallization temperature of Zn to ZnO form ($\approx$300 °C), is a limitation of this method. Therefore, it is interesting to investigate the effect of surface oxidation of metallic Zn foils using hot water treatment. Little research conducted into this subject can be addressed [36,37].

In general, the use of the pure Zn foil that is relatively expensive, the need of surface treatment for the activation and the direct growth of ZnO structures, high temperature, and the long time thermal oxidation are still unfavorable factors in the thermal oxidation method. In this regard, the zinc electroplating as a relatively low cost and very popular method has been used to create a thin film of Zn on the mild steel surface in this work. It is well known that the zinc electroplating is widely applied to protect steel from corrosion due to its sacrificial nature of the Zn [38]. Applying this coating method provides a suitable surface that works as the $Zn^{2+}$ source. The use of the resulting surface instead of the pure Zn foil (used in researches as the substrate) could be a cost-effective procedure. After the deposition of a thin layer of Zn, electrogalvanized surfaces have been taken under the hot water treatment to convert Zn to ZnO form. Indeed, the immediate hot water treatment of the as-synthesized Zn crystals created using an electroplating technique eliminates the need of the pretreatment process and surface activation before the ZnO growth. Moreover, to find the effect of the acoustic excitation of the medium on the morphology of the ZnO structures, hot water treatment has been carried out in the presence and absence of ultrasound

The chemical and thermal stability of ZnO make it a good candidate as an anticorrosive pigment in organic coatings [39], whereas its performance of this ceramic oxide in the corrosion protection of metal (and alloy coatings) has been less studied. Thereby, in this research, as a practical application, the influence of as-grown ZnO structures as the sublayer on the improvement in the corrosion protection of the binary Ni-P coating has been investigated. For this purpose, resulting surfaces have been coated by the electroless Ni-P plating (EN plating) and the corrosion resistance of target samples has been evaluated using the electrochemical method (Tafel extrapolation).

## 2. Experimental

### 2.1. Materials

Zinc acetate dehydrate ($Zn(CH_3COO)_2$, $2H_2O$), trisodium citrate ($Na_3C_6H_5O_7$), boric acid, ($H_3BO_3$), sodium chloride (NaCl), nickel sulfate ($NiSO_4$ $(H_2O)_6$), sodium hypophosphite ($NaPO_2H_2$), hydrochloric acid and ammonia solution (all from Merck) were used directly without further purification. The sheet of commercial mild steel was selected as the metal substrate. The chemical composition of the substrate (in wt. %) acquired by a Quantometer, (3460ARLFISONS) as follows: Fe-99.340, Cu-0.043, Sn-0.001, Co-0.007, Al-0.059, Ni-0.031, Mo-0.001, Ti-0.001, P-0.013, S-0.033, Cr-0.028, C-0.024, Si-0.058, Mn-0.387.

### 2.2. Metal surface pretreatment

To prepare test specimens, the steel sheet was cut to the desired dimensions (40 mm × 20 mm × 1 mm) and degreased using a mild detergent solution. Then the surface of plates was grounded with an emery paper (1200 grit, SiC). The plates after rinsing with distilled water and drying were immersed in hydrochloric acid (HCl, 12 M) for 30 s to remove the oxide layer from the metal surface. Afterward, plates were washed with distilled water and immersed into to a basic solution (NaOH, 1 M) for the neutralization of the excess acid on the surface. Finally, the test specimens were soaked into the acid solution (HCl, 0.1 M) for 2 min for the surface activation. It should be noted that the airflow leads to the rapid oxidation of the resulting surface and therefore activated plates should be transferred to the plating bath immediately.

### 2.3. Zn electroplating

To deposit a layer of Zn on the surface of metal substrates, plates were placed in an acid bath. The composition and parameters of the bath used for the electroplating are given in Table 1.

In the applied acid bath, zinc acetate dehydrate and sodium citrate were used as the source of $Zn^{2+}$ ions and the complexing agent, respectively. A complexing agent by controlling the free $Zn^{2+}$ ions improves the quality of the deposit. To enhance the electrical conductivity, sodium chloride as a conductive salt was added to the electrolyte. Additionally, boric acid was used to keep plating operation conditions stable. This component acts as a buffering agent too. After the completion of this step, electroplated samples were treated in the hot water according to the procedure described in the following sections.

### 2.4. Hot water treatment (thermal oxidation)

The thermal oxidation of resulting coatings was carried out for the conversion of the zinc to ZnO structures. The growth of ZnO structures from the Zn were examined in conventional conditions (without ultrasound) and under sonochemical conditions.

**Table 1**
The composition and operating conditions of the used Zn electroplating bath.

| Deposition parameters | Amount |
|---|---|
| Concentration of $Zn(CH_3COO)_2{\cdot}2H_2O$ | 30.0 (g/L) |
| Concentration of $Na_3C_6H_5O_7$ | 7.5 (g/L) |
| Concentration of $H_3BO_3$ | 5.0 (g/L) |
| Concentration of NaCl | 3.0 (g/L) |
| θ (temp.) | 40 (°C) |
| Time | 15 min |
| Current density | 12.5 (mA/cm$^2$) |
| pH | $\approx$ 3 |