Antibacterial activity of ZnO nanoparticle coatings formed by electrophoretic deposition

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ABSTRACT: The scientific community is focused on the development and use of new nanomaterials to create novel devices and systems that can be useful to solve problems or provide services. Among all nanomaterials, semiconductors allow improving optical, electrical, and catalytic properties of several surfaces, including the corrosion resistance of the materials; corrosion causes several problems and economic losses in the food, pharmaceutical, and hospital industries because the materials selected must be durable, economic, and as innocuous as possible. Zinc oxide (ZnO) is one of the most interesting materials, is a photo-chemically active n-type semiconductor and has particular defects into intrinsic lattices, such as Zn and O vacancies. Herein, we use electrophoretic deposition (EPD) for the synthesis of nanostructured films composed of ZnO nanoparticles (ZnONPs) as a protective coating on low-alloy carbon steel. The electrochemical stability of the coated steel was evaluated and compared with the response of the bare steel. This work used NPs formed in homogeneous media and in reverse micelles (RMs) formed in our previous published report. The coatings were synthesized on the surface of SAE 1020 carbon steel electrodes with 12 mm diameter. As results, two different colloidal systems were formed, by RMs we synthesized high mono-dispersed and spherical 3-5 nm ZnONPs, and by homogeneous media anisotropic 20-100 nm ZnONPs, both systems with excellent fluorescence emission at different excitation wavelengths. The electrochemical evaluation confirms the stability of the coatings obtained, improving the corrosion resistance of the low-alloy carbon steel. We found that the coating obtained with the smallest particles shows better protective properties; the difference between both coatings could be related to the force balance during the electrophoretic deposition, where the friction force, that is against the electrophoretic movement, is proportional to the particle size, reducing the amount of deposited material.

1. INTRODUCTION
The scientific community is focused on the development and use of new nanomaterials to create novel devices and systems that can be useful in solving problems or providing services. In recent years, researchers have increased studies on metallic, polymeric, and semiconducting nanoparticles. Among all nanomaterials, semiconductors allow improving optical, electrical, and catalytic properties of several surfaces, including the corrosion resistance of materials; the corrosion phenomenon causes several problems and economic losses in the food, pharmaceutical, and hospital industries because the materials selected must be durable, economic, and as innocuous as possible. In this sense, by using the properties of materials at nanoscale, it is possible to develop alternatives to solve these issues. Materials at the nanoscale show novel properties typically not observed in bulk scale,1,2 have larger surface areas in comparison to larger-scale, with greater amount of the material that interacts with other surfaces, increasing the reactivity of the system.1,2 Specifically, zinc oxide (ZnO) is one of the most interesting materials to study, with applications in sensor technology,3 optoelectronic devices,4 and transparent photovoltaic applications.5 Zinc oxide (ZnO) is one of many interesting materials; it is a photo-chemically active n-type semiconductor and has particular defects7 into intrinsic lattices, such as Zn and O vacancies.8 Also, it is possible to generate sub-band-gap states that can be studied via electron paramagnetic resonance (EPR) and emission fluorescence.9,10,11,12 Surface modifications, including coatings on metallic materials, represent a common approach to avoid corrosion and improve bioactivity (antibacterial).13 One way is the loading of the surface with biomaterials or molecules with antibiotic and anti-corrosion activity, this can be achieved by forming thin films through simple immersion,14,15 or covalently bonded to the oxidized surface.16 Other ways include magnetron sputtering,17 sol-gel method,18 physical vapor deposition (PVD),19 electrochemical plasma deposition,20 and the approach of our specific interest, electrophoretic deposition (EPD) to grow nanostructured materials.21,22,23 Electrophoretic deposition has some advantages over other methods, eg., work at room temperature24 and possibility to deposit materials on almost any substrate, it is a low-cost methodology and easily scalable. In our case, EPD is a fast method to generate coatings on metallic substrates;25 in fact, it is possible to control the thickness and microstructure of the films deposited by simply changing the applied potential, deposition time, and suspension composition.26 In this sense, EPD is an excellent alternative to modifying metallic surfaces to confront corrosion processes.

As mentioned, in hospital environments there are two main issues over materials, these are caused by corrosion and by microorganisms. The most common pathogen after medical procedures is Staphylococcus aureus.27,28 Therefore, the claim for new alternatives, such as coatings on materials in the industry is increasing.29,30

It is known that ZnO NPs have antimicrobial activity against both Gram-positive and Gram-negative strains.31,32 Zinc oxide NPs are considered nontoxic, biosafe, and biocompatible materials33 used in drug delivery and cosmetics.34 The bioactivity of nanomaterials against several bacteria is strongly discussed. One approach is by generating reactive oxygen species (ROS), causing the destruction of biomolecules, like lipids, proteins, and DNA.35 Also, it is possible that nanoparticles release zinc ions (Zn\(^{2+}\)), affecting the amino acid metabolism and enzyme system disruption.36 Basically, these bioactive properties are enhanced by high surface/volume ratio.32,36 Herein, we evaluate the synthesis and electrophoretic deposition of ZnO nanoparticles on carbon steel, its anti-corrosion protection at different conditions, and antibacterial activity against methicillin-resistant Staphylococcus aureus (MRSA).

2. EXPERIMENTAL

2.1 Materials
The reagents used to prepare nanoparticles were ethanol, Zinc acetate dihydrate (Zn(CH\(_3\)COO)\(_2\).2H\(_2\)O), Sodium hydroxide, and Poly(ethylene glycol) (PEG 12000), which were purchased in Sigma-Aldrich and used as received. Ultrapure water was obtained from Thermo Scientific Smart2Pure equipment.
2.2 Instrumentation

UV/vis spectra were recorded in a spectrophotometer (Shimadzu UV-1800). The emission spectra were obtained with a Photon Technology International QM-40 fluorometer dotted with a xenon lamp. The FTIR spectra were obtained by using a Bruker Tensor 27 spectrometer, the absorption spectra were obtained by co-adding 100 measures with 0.5 cm⁻¹ of resolution, using pure hexane as blank and Platinum ATR.

In dynamic light scattering (DLS), we introduced an apparent hydrodynamic diameter (d_{app}) to compare all our systems. The d_{app} of nanoparticles were determined in a Malvern ZetaSizer Nano-ZS90 with 633 nm He-Ne laser. Thirty independent size measurements were made for each individual sample at scattering angle of 90°. The polydispersity index was always below 0.2.

Transmission Electron Microscopy (TEM) was performed in a FEI TECNAI G2 STWIN at 20 – 200 kV with a camera (Gatan ES100W) and Gatan Digital Micrograph software. For TEM studies, the samples were placed into a formvar-covered copper grid and evaporated slowly.

The electro-analytical measurements were carried out with an Autolab PGSTAT101 (Echo Chemie, Utrecht) controlled by NOVA 1.10.1.9 software (Metrohm, Filderstand).

2.3 Methods

Synthesis of ZnO Nanoparticles

1.10 g of Zn(COOCH₃)₂ · 2H₂O were added to 50 mL of ethanol under stirring and heating. The solution was placed under reflux at 70 °C/1.5 h and cooled to 0 °C; then, the solvent was evaporated. Otherwise, NaOH 6.5 mmol was added drop-wise to solid zinc acetate under stirring at 10 °C to carry out the hydrolysis. Finally, the solution obtained was dried and calcined at 600 °C / 2 h.

Preparation of the carbon steel samples

An SAE 1020 carbon steel bar with 12 mm of diameter and 0.5 cm of length was used to coat and to build the working electrodes. On one of the flat surfaces of bar, a copper wire was welded to make the electrical contact, and in the opposite face it was polished to obtain a homogeneous roughness, this was done with sandpaper from No. 80 to No. 600 grit. Finally, the surface was treated with water and alcohol in an ultrasonic bath to eliminate impurities.

Biological activity

Antibacterial activity was evaluated by halo or inhibition zone in agar media nourished with ideal components for microorganism growth, measured in centimeters at different NP concentrations to determine the percentage of reduction.

3. RESULTS AND DISCUSSION

3.1 Spectroscopic properties

Figure 1 shows some optical properties of the colloidal system formed hydrothermally, the intense absorption band of ZnO nanoparticles at 315 nm, and the IR stretching band at 434 cm⁻¹.
As seen in the UV-vis spectrum, the intensity and location of the absorption band suggest the formation on high concentrated colloidal nanoparticles, results according to some typical characteristics of this type of nanomaterial in solution. The FTIR absorption bands show stretching frequencies at 343 cm⁻¹, corresponding to ZnO formation and 835 and 909 cm⁻¹ to acetate residues from the reaction. Zinc oxide materials are very interesting because they are photo-chemically active n-type semiconductors and have particular defects specifically into intrinsic lattices, such as Zn vacancies, causing fluorescence emission properties (Figure 2).

3.2 Fluorescence emission
Zinc nanoparticles as semiconductors can produce an interesting emission (Figure 2). In our particular case, where are excited at high energy.

As noted in Figure 2, the λ<sub>exc</sub> was varied every 10 nm from 270 to 340 nm. At those wavelengths, the system produces two well-defined emission bands, the first one at 387 nm and the second one at 510 nm (black line) that hypsochromically shift as excitation energy decreases, thus, it is clear to note the red edge excitation shift (REES) phenomena generated in the system. This REES is useful to study the solvation dynamics of several media, such as micro-emulsions. In excited state, the non-viscous and dipolar solvent relaxes around fluorophores on a time scale faster than the fluorescence lifetime. In this sense, the
fluorescence band does not depend on the excitation wavelength, but, if the solvent relaxation in the excited state is slow enough and similar to the fluorescence lifetime, the emission maxima will shift to lower energy as excitation wavelength increases, this is the REES effect.\textsuperscript{46} Thus, these emission spectra suggest two different populations, the first one at high energy (387 nm) that keep unchanged with excitation energy, and the second one that experiences the REES effect $\Delta \text{emi} > 30$ nm. This spectroscopic behavior is product of different sizes and shapes, and product of a slow motion of water dipoles around nanoparticle surface, as consequence of different charge densities. These different shapes were monitored through TEM (Figure 3).

The analysis via TEM and DLS (inset) showed different sizes, around 30 to 90 nm, and, as observed, different shapes were formed that contribute to fluorescence emission. The results suggest that smaller nanoparticles are responsible for the high-energy emission band and larger nanoparticles for low-energy emission. This behavior can be applied in cellular biology using this nanomaterial as molecular marker, a type of emission probe to conduct studies in a fluorescence microscope.

The antibacterial properties of this colloidal solution were tested over MRSA as follows: Small pieces of fabric were cut and submerged in the solution for 15 min under constant stirring, then inoculated with \textit{Escherichia coli} O157:H7 and MRSA as a modified method from the American Association of Textile Chemists and Colorists (AATCC 100).\textsuperscript{47}
Figure 4. Antibacterial assay performed with \textit{E. coli} O157:H7 and MRSA to textile impregnated with ZnONPs.

Figure 4A and B shows the back and front images of the Petri dish, respectively. The image is composed as follows: the left side in Figure 4A called E3 is \textit{E. coli} and the right side, called S3 is MRSA; the top is just a little touch of textile on surface, the center is the textile piece impregnated, and the bottom are droplets of control. The B image is the same assay but from a frontal perspective. The results observed by this study showed not only an interesting growth inhibition of MRSA in the textile, but also no were found UFCs around it. On the other hand, in the top side where the textile first touches the surface before being deposited in the middle of the Petri dish, the bacterial growth was lower in comparison with the control (bottom side). This phenomenon was evaluated at different concentrations.

| Concentration (ppm) | Bacterial reduction (%) |
|---------------------|-------------------------|
| 20                  | 71.43                   |
| 30                  | 99.71                   |
| 40                  | 99.97                   |
| 50                  | 99.97                   |

At low concentration, it is possible to inhibit the natural growth of MRSA, this is the solution used to develop EPD on carbon steel.

3.3 Electrophoretic deposition

To obtain a uniform coating on the steel surface, an electrophoretic deposition of the nanoparticles was evaluated. In this process, the particles suspended in a colloidal system are moved to the electrode surface by applying an external electric field, the particles with negative charge are attracted by the positive electrode and the particles with positive charge are attracted by the negative electrode. Considering that the ZnO nanoparticles obtained in this study do not show a specific surface charge and the steel surface could be damaged by corrosion if a positive potential is applied to it, the surface of the nanoparticles was covered by Polyethylenimine (PEI). This molecule contains a high amount of branched amino groups that generate a positive surface charge, allowing movement of the particles to the negative electrode (steel bar).

To understand the electrochemical behavior of the PEI, the electrode was evaluated in PEI 0.5% solution (Figure 5A). It can be seen that the reduction of the PEI starts at -418 mV Vs. Ag/AgCl, showing a maximum at -830 mV Vs. Ag/AgCl, followed by the hydrogen evolution reaction that starts at -1000 mV Vs. Ag/AgCl. The reverse scan shows that the oxidation reaction starts at the reversible potential (-418 mV Vs. Ag/AgCl), without a maximum, this behavior could be related to the overlap of the PEI and iron oxidation.
Figure 5. A) Cyclic voltammogram of the steel bar in PEI 0.5% solution; B) chrono-amperometric response of PEI (green line) and PEI + ZnO NP, applying -850 mV Vs. Ag/AgCl.

Considering the reduction potential of the PEI, the stability of the steel electrode and the hydrogen evolution reaction, the applied potential for the electrophoretic deposition of the nanoparticles was fixed at -850 mV Vs. Ag/AgCl. The EPD was performed by using both kinds of nanoparticles, those obtained through direct reduction and those obtained by using the reverse micelle system. Figure 5b shows the chrono-amperometric response obtained for the EPD of the ZnO nanoparticles obtained by using the reverse micelle system (blue line) in comparison with the response of the PEI without nanoparticles (green line). Both systems show the same behavior, with a progressive reduction of current during the experiment. This reduction is related to the resistivity of the layer deposited and its consequent increment in the charge transfer resistance; the reduction in current is bigger in the system with nanoparticles because the ZnO nanoparticles act as a barrier on the surface, increasing its resistivity.

The response of the EPD using the particles obtained by direct reduction is not shown because no deposition was observed. The difference in the response using both kinds of particles could be related to the electrophoretic mobility of the nanoparticles. The EPD consist of two consecutive steps, the first one is the transportation of the nanoparticles from the bulk of the solution to the electrode surface and the second one is the deposition. Nanoparticle flux occurs under migration control, when the movement in the solution depends on the applied potential (F_{el}), the electrophoretic mobility of the nanoparticles (F_{ret}), and the viscosity of the media (F_{vis}). The size of the particles obtained by direct reduction is larger than the size of the particles obtained by using the reverse micelle system; this variation could increase friction with the surrounding media, limiting the mobility of the nanoparticles and their deposition.

Figure 6. (A) Schematic representation of the EPD process for the nanoparticles obtained by using reverse micelle, (B) direct reduction, and (C) force balance.
Framed in corrosion phenomena, carbon steel is considered a metal with no more than 2% of carbon in its composition; consequently, it has low resistance to corrosion. The deposition on the electrode surface occurs by assembling charged particles, through action of a specific electric field. It is important to note that EPD is strongly dependent on physicochemical properties of colloidal suspension, as well as on electric field, deposition time, and electrodes.

3.4 Corrosion Studies

In order to verify the electrochemical stability of the coating on the steel surface, the coated electrodes were evaluated in physiological solution by the measure of the open circuit potential, electrochemical spectroscopy impedance, and linear sweep voltammetry. Figure 7a shows the polarization curves of the different materials, the evaluation was performed evaluating the anodic polarization branch to analyze the oxidation process. Bare steel (black line) shows its typical behavior with a corrosion potential ($E_{corr}$) of -517 mV vs Ag/AgCl and corrosion current ($i_{corr}$) of $3.92 \times 10^{-5}$ A/cm$^2$. In this case, the anodic reaction corresponds to the iron oxidation represented with the following reaction:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

According to the Butler-Volmer equation, if the oxidation occurs under kinetic control, the anodic Tafel slope ($\beta_a$) for the transference of two electrons is equal to 69 mV/dec, in this case the calculated $\beta_a$ was 88 mV/dec, the difference between both values could be related to the formation of adherent corrosion products in the electrode surface. The response of the electrode coated with PEI (green line) shows a shift of the $E_{corr}$ to more negative potentials (-536 mV vs Ag/AgCl) and a small reduction in the $i_{corr}$ ($2.5 \times 10^{-5}$). The variation in the potential is related to the thermodynamic equilibrium of the reactions on the electrode surface, this change corresponds to the mixed response of the materials iron+PEI. The change in the corrosion current implies a reduction in the kinetic of the iron oxidation. The response of the electrode coated with PEI+ZnO NPs shows a significative increment in the anodic Tafel slope (104 mV/dec), this variation is related to a change in the reaction control, when the coating acts as a barrier retarding the charge transference. This behavior is confirmed by the electrochemical impedance spectroscopy evaluation (figure 7b), it can be seen than the bare steel (black dots) shows one time constant and have a charge transfer resistance ($R_{ct}$) of 355 Ohm/cm$^2$. The response of the coated electrodes shows a depressed semicircle that corresponds to the overlapped response of the steel and the coating, this behavior could be explained using the equivalent circuit shown in the figure 7b, when the ion transference between the steel and the electrolyte occurs in the pores of the coating ($R_{pore}$). The electrode coated with PEI+ZnO NPs shows a significative increment in the total resistance ($R_{tot}$) confirming the stability of the materials on the steel surface.
Figure 7. A) Tafel plot of the bar steel (black), steel/PEI (green), steel/PEI+ZnO NPs (blue), B) Nyquist plot of the bar steel (black), steel/PEI (green), steel/PEI+ZnO NPs (blue). Insert: equivalent circuit of the steel/PEI+ZnO NPs. Obtained in physiological solution at 25°C.

Table 2. Characteristic values obtained from the electrochemical evaluation of the coated electrodes.

| Material                     | $E_{corr}$ (mV vs Ag/AgCl) | $I_{corr}$ (A/cm²) | $\beta_a$ (mV/dec) | $R_{tot}$ (Ohm/cm²) |
|------------------------------|-----------------------------|---------------------|---------------------|---------------------|
| Steel                        | -517                        | 3.92x10⁻⁵           | 88                  | 355                 |
| Steel/PEI                    | -536                        | 2.51x10⁻⁵           | 88                  | 600                 |
| Steel/PEI+ZnO NPs           | -510                        | 185x10⁻⁵            | 104                 | 730                 |

Conclusions
Zinc nanoparticles with different morphologies were synthesized by hydrothermal method, with better yield compared to those formed by reverse micelles. Nevertheless, variables, like morphology and size are not controlled through this method, obtaining nanoparticles between 20 and 100 nm.

Coatings on SAE 1020 carbon steel with different types of linker molecules and two types of nanoparticles were generated. It was found that smaller nanoparticles are more effective against the corrosion phenomenon than larger ones (anticorrosive coating). Electrophoretic deposition is established as an excellent technique to form coatings on metal surfaces.

The electrochemical evaluation results show the stability of the PEI+ZnONPs coating on the steel surface, this behavior open new possibilities to develop a bifunctional system to stabilize the surface of low alloy steels, avoiding its corrosion and the microbial proliferation.

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