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Hybrid nanocomposite from aniline and CeO_2 nanoparticles: Surface protective performance on mild steel in acidic environment

Y. Sasikumar[a], A. Madhan Kumar[b], Zuhair M. Gasem[b,*], Eno E. Ebenso[a]

[a] Material Science Innovation and Modelling (MaSIM) Research Focus Area, Department of Chemistry, North-West University (Mafikeng Campus), Private Bag X 2046, Mmabatho 2735, South Africa
[b] Center of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia

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ABSTRACT

This present work contributes to the development of a new generation of active corrosion inhibitors composed of CeO_2 nanoparticles covered with polyaniline that are able to release entrapped nanoparticles in acidic medium. Nanocomposites of aniline and CeO_2 nanoparticles have been chemically synthesized by in-situ polymerization. The structural evolutions and morphological characteristics of PANI/CeO_2 nanocomposite (PCN) have performed using various techniques such as XRD, IR, XPS, SEM and TEM analysis. It was illustrated from SEM and TEM observation that the PCN has globular particle with core–shell structure. The inhibition properties of synthesized PCN on mild steel (MS) corrosion in 0.5 M HCl were estimated using weight loss and electrochemical techniques. Potentiodynamic polarization results revealed PCN to be a mixed-type inhibitor, while impedance results indicate the adsorption of the PCN film on the MS surface. The inhibition efficiency of PCN was found to increase almost linearly with concentration. Moreover, an increase in the water contact-angle with PCN indicated its adsorption at the MS surface, and ATR-IR, SEM/EDAX and AFM visualization confirmed the formation of a protective film adsorbed on a MS surface. Finally, it was concluded that the PCN is a potential inhibitor for mild steel in HCl medium.

1. Introduction

Due to the potential of merging distinct physical properties of organic and inorganic constituents within a single molecular composite, organic–inorganic hybrid nanocomposites have fascinated considerable attention in recent years. In general, organic materials offer structural flexibility, convenient processing, tunable electronic properties, and the potential for both semiconducting and metallic behavior. On the other hand, inorganic metal nanoparticles provide the potential for high carrier mobilities, a range of magnetic and dielectric properties, and thermal and mechanical stability. Thus, significant effort at organic/inorganic nanocomposite materials has been focused on the ability to acquire the nanoscale structures via innovative synthetic methodologies. Further, the properties of nanocomposite depend not only on the properties of their individual components but also on their morphology and interfacial features. Recent research work has virtually proved that all types and classes of nanocomposite materials deliver novel and improved properties when compared to their macro composite counterparts [1,2]. Hence, nanocomposites promise new applications in many fields such as mechanically reinforced lightweight components, non-linear optics, battery cathodes and ionics, nanowires, sensors and other systems.

Conducting electro-active polymer is a fast growing area in both scientific and technological fields in recent years because of their potential applications in electrochemical displays, sensors, catalysis, redox capacitors, anticorrosion coatings, optical, photoelectrical properties, and secondary batteries [3,4]. Frequently, these polymers are used to prepare organic–inorganic hybrid materials owing to their good stability and controllable thickness and they can be easily united with inorganic materials.

Among organic conducting polymers, polyaniline (PANI) deserves deep interest owing to its good redox reversibility, high conductivity, excellent environmental stability and swift change of color with potential. These properties make it one of the most applied conducting polymers in many fields. Further, it has drawn attention as an effective material for corrosion protection [5,6]. In general, organic compounds particularly those with S, N and O exhibit substantial inhibition efficiency. Thus, PANI is also used as corrosion inhibitor in various environments because of the large availability of π electrons, enables them to function as very effective corrosion inhibitors. However, the poor stability during the charge/discharge process and poor processability due

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* Corresponding author. Tel.: +966 538801789; fax: +966 538604818.
E-mail addresses: madhankumar@kfupm.edu.sa, madhanchem@gmail.com (Z.M. Gasem).

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to the stiffness of its backbone restrict its practical applications. To overcome the drawbacks of PANI, its composites formed with nanomaterial have been widely investigated [7].

To acquire the materials with synergetic or complementary corrosion protection behavior, various nanocomposites of polymer with inorganic nanoparticles have been synthesized in recent years [8]. Amongst the various inorganic nanoparticles, cerium dioxide (CeO_2) nanoparticles have been intensively premeditated due to their unique catalytic, electrical and optic properties, as well as their extensive applications in diverse areas [9,10]. Moreover, cerium ions are recognized for their corrosion protection applications either by coatings [11] or as inhibitors [12]. It has been already reported that the inhibitive performance of PANI increased significantly in the presence of ceric ions [13]. However, to the best of our knowledge, no report is evident for the utility of PANI/CeO_2 nanocomposites as inhibitor for mild steel corrosion in acidic medium. Hence, in this present study, PANI/CeO_2 nanocomposite has been synthesized by in situ polymerization from aniline in the presence of CeO_2 nanoparticles using ammonium per sulphate and the synthesized nanocomposite was well characterized and utilized as corrosion inhibitor on mild steel by various techniques.

2. Experimental procedure

2.1. Materials

Aniline (An), ammonium Ce (IV) nitrate, sodium hydroxide (NaOH) and ammonium per sulphate (APS) were purchased from Sigma–Aldrich. All the analytical grade chemicals were used as received. Aqueous electrolytes used for the synthesis of the nanocomposite were prepared using double distilled water.

Mild steel (MS) substrates with the following chemical composition were used in the experiments (wt.%): C, 0.15; Mn, 1.26; V, 0.017; Si, 0.035; S, 0.008; Cr, 0.036; Ni, 0.03; Al, 0.083; Cu, 0.038; balance Fe. For weight loss and electrochemical measurements, MS substrates were cut into 3 cm × 3 cm × 0.25 cm dimensions. These substrates were abraded with silicon carbide abrasive paper ranging from grit size 320 to 1200, rinsed with distilled water, placed in an ultrasonic acetone bath for about 5 min to remove probable residue of polishing, rinsed with acetone, dried in warm air. Prior to each experiment, MS substrates were treated as described and freshly used with no further storage.

2.2. Synthesis of CeO_2 nanoparticles

To synthesize ceria (CeO_2) nanoparticles, the precursors, ammonium Ce (IV) nitrate and NaOH with 1:4 molar ratio were dissolved completely in de-ionized water and the pH value of the solution was adjusted to be 12. The mixture solution was stirred well using a magnetic stirrer for about 2 h and then, the prepared mixture solution was kept in the microwave oven at a temperature of 60 °C for about 1 h. Synthesized pale-yellow precipitate was filtered and washed with de-ionized water twice. Annealing of the synthesized powder at 130 °C in air for 4 h will result in the formation of CeO_2 nanoparticles.

2.3. Synthesis of polyaniline/CeO_2 nanocomposite

To synthesize PANI/CeO_2 nanocomposite, 5 ml aniline was dropped into 70 ml of 2 M of HCl containing 1 g of CeO_2 nanoparticles under ultrasonic action to reduce the aggregation of nanoparticles. After 12 h, 5 g of APS was dissolved in 20 ml de-ionized water and it was dropped into the solution with constant stirring for about 10 min. The polymerization was allowed to proceed for 12 h at 30 °C. Further, reaction mixture was filtered, and washed with 2 M HCl and de-ionized water, subsequently dried at 90 °C for 12 h in vacuum to obtain a fine tint green powder.

2.4. Characterization of synthesized PANI/CeO_2 nanocomposite

IR spectra for the synthesized nanocomposite were recorded in the range of 400–4000 cm^{-1} using IR reflectance spectrophotometry (PerkinElmer, Spectrum One, with universal ATR attachment with a diamond and ZnSe crystal, The Netherlands) to confirm the formation of nanocomposites. The phase identification of the synthesized nanocomposites was performed using XRD (RINT2500, Japan; CuKα, 40 kV, 20 mA) over a scattering angle range of $20° \leq 2\theta \leq 80°$ at a 2θ step of 0.02°. X-ray photoelectron spectroscopy (XPS) (Thermo Scientific, ESCALAB-250Xi) was employed to find the chemical composition of the nanocomposite. The XPS spectra were recorded using Al Kα radiation (1486.6 eV) as excitation source. The take-off angle θ of the emitted photoelectrons was adjusted to 45° with respect to the normal surface.

The surface morphology of the synthesized products was analyzed using scanning electron microscope (SEM); JSM-6360 (JEOL), at an acceleration voltage of 20 kV and irradiation current of 10 μA. The associated energy dispersive X-ray analyzer (EDAX) has provided qualitative information about the surface elemental composition. TEM measurements were taken using a Hitachi H-600 transmission electron microscope. For TEM observation, synthesized PANI/CeO_2 nanocomposite was suspended in ethanol and a drop of the dispersion was placed onto a carbon film supported by a copper grid.

2.5. Corrosion studies

All electrochemical corrosion investigations were performed in a one-compartment cell with three electrodes connected to Gamry Instrument potentiostat/galvanostat/ZRA (Reference 3000) with a Gamry framework system based on ESA410. The MS substrates were the working electrode; platinum wire was used as the counter electrode and saturated calomel electrode (SCE) as the reference electrode and all the potentials were measured versus the SCE reference electrode. Tafel curves were obtained by changing the electrode potential from −250 to +250 mV versus the open-circuit potential (OCP) at a scan rate of 1 mV s^{-1}. EIS measurements were done under potentiostatic conditions in a frequency range from 100 kHz to 100 mHz, with an amplitude of 10 mV, using an alternating-current signal at OCP. All experiments were measured after immersion for 30 min in 0.5 M HCl with and without the addition of inhibitor.

Weight loss measurements were performed in glass vessels containing 200 ml of 0.5 M HCl solution in the absence and presence of the inhibitor at room temperature. In each experiment, triplicate samples of the precleaned and weighed MS substrates were freely suspended in different test solutions. The test MS substrates were recovered after 24 of immersion, thoroughly cleaned using the chemical method for cleaning rust products as previously reported [14], and reweighed using a digital analytical balance with a sensitivity of 0.1 mg. The standard deviation values among parallel triplicate experiments were found to be smaller than 5%, indicating good reproducibility.

2.6. Surface characterization after immersion

Surface characterization includes SEM/EDAX, AFM, ATR-IR and contact angle analysis were performed on MS surface exposed to 0.5 M HCl solution with and without inhibitor. MS substrates of dimension $3 \times 3 \times 0.25\ cm^3$ were polished successively with silicon carbide abraded paper from 320 to 1200 and with 1 μm diamond paste to get mirror finished surface. The precleaned MS substrates