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Ultrasound assisted synthesis of calcium zinc phosphate pigment and its application in nanocontainer for active anticorrosion coatings

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HIGHLIGHTS

- Ultrasound assisted synthesis of calcium zinc phosphate nano pigment demonstrated.
- LbL assembly of calcium zinc phosphate nanocontainers have been achieved.
- Improvement in the anticorrosion properties of coatings due to the nanocontainers.

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ABSTRACT

The present work deals with the loading and responsive release of corrosion inhibitor (benzotriazole) on polyelectrolyte layer in the case of anticorrosive nano pigment calcium zinc phosphate [$CaZn_2(PO_4)_2$] prepared by layer-by-layer (LbL) method. Synthesis of $CaZn_2(PO_4)_2$ and the encapsulation of polyaniline (PANI) on nano $CaZn_2(PO_4)_2$ and LbL assembly of nanocontainers has been achieved using ultrasonic irradiation. Formation of small/uniform particle size of nanopigment and complete encapsulation of polyelectrolyte on the pigment has been observed mainly due to the presence of ultrasonic irradiations during the preparation process. The release of benzotriazole from $CaZn_2(PO_4)_2$ nanocontainer have been quantitatively evaluated in water at different pH. With an increase in the percent loading of $CaZn_2(PO_4)_2$ nanocontainer from 0 to 4%, the corrosion rate has been found to be decreased from 2.2 to 0.15 mm/y respectively in 5% HCl. Corrosion potential values are found to be shifted to positive side from −0.62 to −0.485 V with the addition of 4 wt.% of $CaZn_2(PO_4)_2$ nanocontainers in the alkyd resin. Results of corrosion rate analysis, Tafel and Bode plots of nanocontainer coatings on mild steel panel showed significant improvement in the anticorrosion performance of the nanocontainer/alkyd resin coatings.

1. Introduction

Pigments such as lead and chromates are not preferred in the surface coating formulations due to the environmental reasons and are now being replaced by the eco friendly pigments. Such pigments include phosphate based pigments among which zinc phosphate has been found to have wide range of application due to its non-toxic nature, excellent anticorrosive properties and can be readily used in the coatings [1–4]. Recently, the pigments containing the basic phosphates and its modifications with cations and anions such as Zn, Si, Ca, Fe, K have been depicted as modified eco-friendly pigments. This modification can enhance the corrosion inhibition efficiency and make water insoluble complex leading to an enhancement in the anticorrosion property. Few literature illustrations also report modified phosphate pigments using organic moieties such as long chain organic modifiers on organo-clay or nanoclay. Functionalization of phosphate compounds by addition of organic moieties is a recent technology in anticorrosion coatings; however, the important requisite is that the surface of metal should be compatible for silane coupling. Recent works also report the additions of ions such as cation like calcium, potassium, aluminum etc. during preparation of nanopigments, which are being used as anticorrosion pigments in the surface coating industry ranging in the micrometer size [5–9]. Only few reports illustrate the synthesis of calcium zinc phosphate in nanosize range [10]. Inherently, zinc phosphate pigment has low anticorrosion property due to low solubility. Anticorrosion performance of zinc phopshate pigment can be intensified by modifying the zinc phosphate pigment by an addition of cations such as calcium, potassium, aluminum or anions such as SiO_4 and MoO_4^{3-} [10,11].

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Use of ultrasonic irradiations has been proved to be a useful tool for intensification of the synthesis of nanoparticles [12]. The chemical effects of ultrasonic irradiation arise from acoustic cavitation, which can be described as the formation, growth and implosive collapse of bubbles in a liquid medium resulting in the generation of high temperature and pressure pulse and intense turbulence associated with liquid circulation currents [13,14]. These extreme conditions of high temperature, pressure and local intense micromixing helps in the formation of nanoparticles with near-uniform size distribution [12,15]. With this background, the synthesis of calcium zinc phosphate is investigated in the presence of ultrasound, which is expected to assist the dissolution of precursor of zinc phosphate and generate final particles with smaller size with narrow size distribution. Further, if the calcium zinc phosphate particle size is reduced to nanosize range, it is expected to show a better effect on the anticorrosion properties of coatings based on calcium zinc phosphate [10].

Encapsulation of active materials loaded on the inorganic core is one of recent technique, for the storage and release of liquid corrosion inhibitor on the demand, described as "nanocontainers" which could be loaded on the organic coating formulations [16–23]. The important advantages offered by the incorporation of these containers into organic coatings are as follows, (1) responsive and sustainable release of inhibitor as a function of pH or temperature (2) if the liquid inhibitors cannot be used directly in the coatings formulation due to possible reaction of these inhibitors with the coating, encapsulation method can be used to prepare the reservoir of inhibitors in micro or nano-container. In order to achieve the dual advantage of the anticorrosive pigment (core of nanocontainer) and inhibitor loaded on the inorganic core, calcium zinc phosphate has been used as a core of the nanocontainer formulation, which works as a cathodic inhibitor controlling the cathodic reactions as well as a good nano-filler. Nanosize calcium zinc phosphate may significantly inhibit the corrosion of the bare steel by a cathodic protection mechanism, which is also enhanced due to an increase in its surface area (due to the reduction in the size to nano-range). Also the protection of metal substrate is given by cathodic inhibition properties of Zn^{2+} by precipitation at cathode (reduction of O_2 to HO^-) and thereby preventing the direct contact between the metal surface and potentially aggressive species such as O_2, H_2O, Cl^- etc. and hence metal surface is protected.

The current work reports an innovative attempt to prepare nanocontainer using calcium zinc phosphate. The main aim of this study was to intensify the synthesis of nano-pigment in the form of layer by layer assembly using ultrasound and to evaluate the anticorrosive properties of calcium zinc phosphate nanocontainer. The calcium zinc phosphate pigment was innovatively prepared through ultrasound assisted co-precipitation technique. Further studies involved the preparation of nanocontainers using the calcium zinc phosphate pigment as a core and loading these containers into the alkyd resin at different concentrations. The release of the benzotriozole inhibitor from the Layer by Layer (LbL) assembly of calcium zinc phosphate nanocontainers incorporated in alkyd resin has also been investigated. One of the prospective applications of these nanocontainers could be for the corrosion protection in the oil and gas field and marine equipment applications.

2. Experimental

2.1. Materials

Analytical grade chemicals such as zinc oxide (ZnO), calcium hydroxide ($Ca(OH)_2$), phosphoric acid (H_3PO_4), ammonium persulphate (APS, $(NH_4)_2S_2O_8$, inhibitor) and sodium dodecyl sulfate (SDS, $NaC_{12}H_{25}SO_4$, surfactant) were procured from S.D. Fine Chem. and used as received without further purification. Analytical grade chemicals such as sodium hydroxide, benzotriazole, HCl, NaOH, NaCl and ethanol, polyacrylic acid (PAA, $M_w = 50{,}000\ g\ mol^{-1}$) were procured from Sigma Aldrich. The monomer aniline (analytical grade, M/s Fluka) was distilled two times prior to the use. Demineralized water prepared using Millipore apparatus was used during all the experimental runs.

2.2. Concept of preparation of $CaZn_2(PO_4)_2$ nanocontainer

Fig. 1 depicts the mechanism of $CaZn_2(PO_4)_2$ nanocontainer synthesis process. As shown in Fig. 1, initially the $CaZn_2(PO_4)_2$ nanoparticles are functionalized with Myristic acid (MA), which improves the hydrophobicity of the $CaZn_2(PO_4)_2$ nanoparticles and subsequently, negatively charged $C_{13}H_{27}COO^-$ ions gets adsorbed on the surface of $CaZn_2(PO_4)_2$ nanoparticles. Due to the hydrophobicity of MA coated $CaZn_2(PO_4)_2$ nanoparticles and developed negative charge on $CaZn_2(PO_4)_2$ nanoparticles, the deposition of PANI layer on $CaZn_2(PO_4)_2$ nanoparticles is successfully accomplished in the next step. Further, adsorption of second layer of benzotriazole molecules is obtained on the PANI encapsulated calcium zinc phosphate nanoparticles. Finally, adsorption of the negatively charged PAA layer is accomplished after the formation of the layer of benzotriazole. Use of ultrasonic irradiations in all the depositions of PANI, benzotriazole and PAA layer results in the distinct formation of $CaZn_2(PO_4)_2$ nanocontainer particles with an increased component diffusivity meeting the requirements of the particle size and uniform coating/layer formation.

2.3. Ultrasound assisted preparation of $CaZn_2(PO_4)_2$ and nanocontainers

Synthesis of $CaZn_2(PO4)_2$ has been carried out by using ultrasound assisted chemical precipitation method. Initially, aqueous solution of calcium zincate was prepared by chemical reaction between 2.2 g zinc oxide and 4.8 g calcium hydroxide prepared in 250 mL deionized water in the presence ultrasonic irradiation (ultrasonic horn operating at frequency of 22 kHz and power as 240 W) and magnetic stirring for 20 min. The reaction mass was then heated to 60 °C and reaction temperature was maintained throughout the experimentation. Drop-wise addition of stoichiometric amount of dilute H_3PO_4 to the above prepared mixture was accomplished within 30 min in the presence of ultrasound irradiation and further reaction was continued for additional 30 min (total reaction time being 60 min). Synthesis of $CaZn_2(PO4)_2$ nanocontainers have been carried out in a stepwise manner as described below:

2.3.1. Preparation of PANI encapsulated nano $CaZn_2(PO_4)_2$

During the synthesis of $CaZn_2(PO_4)_2$ nanocontainer by LbL method, $CaZn_2(PO_4)_2$ was used as core because of its excellent anticorrosion properties due to the presence of Zn and phosphate moieties. $CaZn_2(PO_4)_2$ nanoparticles were initially functionalized using the myristic acid by adding 0.2 g myristic acid (MA) in 10 mL methanol and then adding it subsequently in the aqueous solution containing $CaZn_2(PO_4)_2$ (1 g in 100 mL water) at 60 °C. The mixture was then irradiated using ultrasonic horn for 60 min. Myristic acid functionalization generates negative charges on the surface of $CaZn_2(PO4)_2$. Encapsulation of MA functionalized $CaZn_2(PO_4)_2$ (core) by positively charged PANI layer has been accomplished by ultrasound assisted in situ emulsion polymerization [24]. Initially, surfactant solution was prepared by adding 3 g of SDS and 0.2 g of MA modified $CaZn_2(PO_4)_2$ in 50 mL water, which was subsequently transferred to an ultra-