



Synthesis and characterization of layer-by-layer assembled magnesium zinc molybdate nanocontainer for anticorrosive application



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HIGHLIGHTS

- Synthesis of magnesium zinc molybdate nanoparticles for core of nanocontainers.
- Dual corrosion inhibition mechanism with combination of magnesium, zinc and molybdate.
- Loading of benzotriazole inhibitor using LbL technique resulting in a nanocontainers.
- Enhancement in anticorrosive performance due to inorganic core.
- Significant improvement in the anticorrosive performance of nanocontainers.

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ABSTRACT

Magnesium zinc molybdate nanoparticles which has been synthesised by conventional method, used as core of nanocontainer. In the present work, a novel approach for the loading and responsive release of corrosion inhibitor (benzotriazole) on the magnesium zinc molybdate nanocontainer by layer by layer (LbL) assembly has been presented. The synthesized nano particle coated with corrosion inhibitor i.e. benzotriazole and polyelectrolyte layer, provides enhanced corrosion protection. The thickness of the layer, surface charge and functional groups present on each layer has been achieved by using particle size distribution (PSD), zeta potential and Fourier transform infrared spectroscopy (FTIR) analysis respectively. The X-ray diffractograms (XRD) and thermogravimetric analysis (TGA) gives the development of nanoparticle as well as nanocontainer. The morphological studies shows the variation in the size of magnesium zinc molybdate nanoparticles and the nanocontainer. The release of benzotriazole from the magnesium zinc molybdate nanocontainer has been quantitatively evaluated in water at different pH. The anticorrosive performance of nanocontainers has been studied by incorporating it in epoxy based coating and evaluating by DC polarization measurement. The current density has been found to be decrease significantly with the addition of 1 wt.% of magnesium zinc molybdate nanocontainers in neat epoxy-polyamide resin. Additionally, corrosion potential values are shifted to positive side with the addition of 1 wt.% of magnesium zinc molybdate nanocontainers. The corrosion results from Bode plots and Salt spray test shows the significant improvement in anticorrosive performance for epoxy-polyamide-nanocontainer coatings. The results shows the successful application of magnesium zinc molybdate nanoparticles as a core of nanocontainers by giving rise to dual corrosion inhibition mechanism due to combination of magnesium, zinc, molybdate ions and inhibitor loaded on inorganic core.

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1. Introduction

The corrosion of metals is one of the main detrimental processes that lead to huge economic losses to the industries. The

annual costs related to corrosion and corrosion preclusion has been estimated to a significant part of the gross national product in the developed countries. Along with economic losses, corrosion can give rise to failure of structures that have notable consequences for humans and the surrounding environment [1]. Throughout the last decades two main approaches namely an active and a passive corrosion protection are used for corrosion protection. The passive corrosion protection is gained by deposition of the barrier

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layer preventing contact of the material with the corrosive environment [2]. As a barrier layer, both organic and inorganic coatings viz. cerium, chromium, molybdates, vanadates and phosphates have been extensively applied for the protection of metals against corrosion [3]. The disadvantage of these inhibitors is the toxicity; chromium containing anticorrosion pigments has been extensively used for a long time. Undoubtedly, they belong to the group of inhibitors showing excellent corrosion inhibitive performance [4]. But by virtue of increasing strict regulations and concerns for environmental protection and potential health hazard related with chromates, their use is being restricted. And also if this barrier layer is partially disrupted, the coating itself cannot stop the corrosion process. Hence, in the hope of providing effective replacement of harmful anti-corrosive species with the environmental and user-friendly materials, corrosion inhibition properties of numerous compounds have been examined. Benzotriazole and its derivatives are among the most effective inhibitors used for the protection of metals, especially aluminium, copper and iron [5].

The main argument of active corrosion protection is decrease the corrosion rate when main barrier is damaged and corrosive species come in contact with the substrate. For such purpose, an active protection of metals is done by introduction of corrosion inhibitors in the system. But, only the combination of both approaches can give reliable long-term corrosion protection of metallic structures which are making contact with electrolytes or a humid environment. If the inhibiting species are directly incorporated into coating, causes detrimental interactions between the matrix and the active species, namely the loss of the inhibition capability, coating degradation or both. Effectiveness of inhibiting agents is achieved only if their solubility in the corrosive surroundings is in the precise range. Lack of active agent at the metal interface takes place owing to very low solubility, which gives rise to weak inhibition. And if the solubility is too high, the substrate will be protected comparatively only for a short time due to the rapid leaching of inhibitor from the coating. Hence, in this context, the development of a new approach to introduce environmentally friendly corrosion inhibitors, which can provide lasting and even “smart” release of the inhibiting species on demand, becomes an important issue for many industries [2,6,7].

The encapsulation of active species within inert host structures of dimensions having an average diameter ranging from 1 μm to several hundred micro meters are referred as microsphere or microcapsules [8,9] and structures with those having diameter in nanometer range referred hereafter as nanocontainers [10,11] has been found as a promising strategy of encapsulation. This encapsulation or trapping technique for nanocontainers has opened its applications in various field viz. pharmaceutical and biomedical for drug delivery vehicle [12–14] food technology for encapsulating various food ingredients viz. flavoring agents, preservatives [15,16] diagnostics [17] agriculture, catalyst, textile etc. In recent years, successful applications of nanocontainers have been found in field of corrosion by encapsulating the corrosion inhibitor on nanosize anticorrosive pigments [7,18–25]. Several approaches have been developed to fabricate micro or nanocontainers where inhibiting molecules are loaded into micro or nanocontainers and the release process is mainly diffusion-controlled [2,26]. One of the approach is layer-by-layer (LbL) technique, which involves an assembly of alternating layers of oppositely charged polyelectrolytes and inhibitor onto the outermost surface of dense template nanoparticles [6,27–30].

In 1966, Iler first proposed LbL assembly of oppositely charged species. However, the breakthrough was achieved decades later, in the 1990s, when Mallouk et al. and Decher et al. extended the technique to polyelectrolytes. In this they implemented polycations,

polyanions and charged nanoparticles as the constituents of the container shell. Post 1990 this technique got impressive popularization due to its use to assemble almost all classes of materials, including polymers, organic dyes, colloidal particles, proteins, carbon nanotubes etc. The LbL process is simple, robust and employs mild, environmentally friendly reagents and conditions. The unique advantage of the method is that a wide variety of materials, both organic and inorganic, can be incorporated into LbL thin films and the ability to control film thickness with nanometer precision [31–33].

The LbL technique is extremely versatile due to the fact that is possible to form thin films with a wide range of properties onto various substrates viz; colloidal particles and porous membranes. Due to possibility of control the nanocontainer shell properties, it opens perspectives for further applications of these nanocontainers in many research and industrial fields such as pharmaceutical, cosmetic and food industries. Further, any restriction is not there on the type of the charged species used for shell construction due to universal character of the method [8,34].

In the current work an attempt to prepare nanocontainer using novel magnesium zinc molybdate has been made. Magnesium zinc molybdate has been used as a core of the nanocontainer formulation, in order to get the dual advantage for the anticorrosive pigment and inhibitor loaded on the inorganic core. The main aim of study was to encourage the synthesis of nanopigment by LbL technique using conventional method and to assess the anticorrosive properties of magnesium zinc molybdate nanocontainers. In case the electrolyte shell containing inhibitor becomes inactive, magnesium zinc molybdate core will still remain active against the corrosive species by virtue of dual inhibition principle of magnesium, molybdate and zinc combination against water and salt. Researchers have proposed that magnesium can provide sacrificial protection and also form a protective oxide layer at the alloy surface by pore blocking mechanism, where the Mg^{2+} and similarly Zn^{2+} ions present in the coating form insoluble precipitates, most likely hydroxides and oxides, thereby further preventing the potentially aggressive species such as O_2 , H_2O , Cl^- and hence enhancing barrier protection [35–38]. Whereas molybdate has found to be good corrosion inhibiting pigment when it is combined with a suitable carrier or substrate like sodium, potassium and ammonium [39–42]. Further studies involved the attempt to demonstrate the possibility to employ magnesium zinc molybdate nanoparticles coated with polypyrrole/benzotriazole/polyacrylic acid layers. The release of the benzotriazole inhibitor have been investigated using UV spectroscopy in aqueous media at different pH. One of the prospective applications of these nanocontainer could be for the corrosion protection in various field such as manufacturing, chemical and petrochemical industries.

2. Materials and methods

2.1. Materials

Zinc oxide (Analytical Grade, 99%), sodium molybdate dihydrate (Analytical Grade, 99%), Magnesium nitrate hexahydrate (Analytical Grade, 99%) and nitric acid were procured from S.D.Fine chemicals Ltd., Mumbai and used for preparation of magnesium zinc molybdate nanoparticles. Pyrrole, benzotriazole, polyacrylic acid (PAA, $M_w = 50,000 \text{ g mol}^{-1}$) were procured from Sigma Aldrich, Mumbai and used for preparation of nanocontainer. Deionized water (DI water) with conductivity of $<0.2 \mu\text{S/cm}$ has been used throughout the experimentation. Epoxy resin having E.E.W. 450 g/eq, was obtained from Grand Polycot, Mumbai, India. Polyamide resin having A.V. 300 mg KOH/g was obtained from Grand Polycot, India.

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