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Generation of Co_3O_4 microparticles by solution combustion method and its Zn–Co_3O_4 composite thin films for corrosion protection

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ABSTRACT

Microcrystalline cobalt oxide (Co_3O_4) powder was successfully synthesized by a simple, fast, economical and eco-friendly solution-combustion method. The as-synthesized powder was calcined for an hour at temperatures ranging from 100 to 900 °C. The crystallite size, morphology, and chemical state of synthesized powders were characterized by powder XRD, TG-DTA, XPS, SEM/EDAX, TEM and FT-IR spectral methods. The as-synthesized Co_3O_4 powder was single-crystalline and Rietveld refinement of calcined samples exhibited cubic structure with space group of *Fm3m* (No. 227). The effect of calcination temperature on crystallite size and morphology was assessed. Scanning electron micrographs show a uniform, randomly oriented pseudo-cubic particle with porous like morphology and EDAX measurement showed its chemical composition. Thermal behavior of as-synthesized compound was examined. The TEM result revealed that, the particles are pseudo-cubic in nature with diameter of 0.2–0.6 μm and a length of 0.9–1.2 μm. The crystallite size increased with increase of calcination temperature. The synthesized Co_3O_4 powder was used to fabricate Zn–Co_3O_4 composite thin films and its corrosion behavior was analyzed by anodic polarization, tafel extrapolation and electrochemical impedance spectroscopy. The results indicate that the Zn–Co_3O_4 composite thin films have potential applications to corrosion protection.

1. Introduction

Over the past decade, a variety of techniques have been functionalized to fabricate nano/microstructures of a broad class of materials, ranging from ceramic dielectrics [1], semiconductors [2], metals [3], and metal oxides [4,5]. Among these materials, transition metal oxides (TiO_2, ZnO, CuO, NiO, SnO_2, Co_3O_4, Fe_2O_3, WO_3, etc.) have been the subjects of scientific and technological interest in different fields of chemistry, physics, and material science, which finds potential applications in microelectronics, photocatalysis, magnetic devices, coatings, biomedical, and powder metallurgy [6–9]. As an important antiferromagnetic p-type semiconductor Co_3O_4 described by a formula unit AB_2O_4 ($A \rightarrow Co^{2+}$, $B \rightarrow Co^{3+}$), is an interesting material that is stable in cubic spinel-type structure which arises due to a cubic close packing array of oxide ions, wherein Co (II) ions occupy the tetrahedral 8a sites and Co (III) ions occupy the octahedral 16d sites [10].

The cobalto-cobaltic oxide (Co_3O_4) material has significant applications in many fields such as electrochromic devices, pigments, heterogeneous catalysis [11], solid-state sensors [12], magnetism, solar energy absorbers, and energy storage [13]. Also Co_3O_4 exhibits diverse abundant nanostructures as nanowires/nanorods [14,15], nanotubes [16], nanocubes [17], nanoflakes [18], nanospheres [19], nanoplates [20], and nanowalls [21] which are obtained from different methods. Co_3O_4 is used in low temperature catalytic converters in fuel-efficient engines [22], solid state gas sensors for carbon monoxide and hydrogen gas monitoring [23], coatings for fuel cells [24], effective catalysis for environmental protection and chemical engineering [11,25], ammonia oxidation [26] and the reduction of NO by methane [27]. One significant characteristic that makes Co_3O_4 is an ideal usage for extreme environmental conditions and excellent anticorrosion properties [28].

Zhang et al. [29] used a mild and inexpensive method to prepare Co_3O_4 microsphere in huge amount, and it possesses large pore volume, which can serve as anode material for lithium-ion batteries; Casella and Gatta [30] have reported electrochemical deposition of cobalt oxide films; Luisetto et al. [31] have used several methods to synthesize Co_3O_4 such as: oxalate decomposition, surfactant-assisted precipitation, sol–gel and polymer combustion; Rahman et al. [32] studied the synthesis of the Co_3O_4 nanoparticles by hydrothermal process under the pulsed magnetic field and examined their electrochemical performances; Azadeh Askarinejad et al. [33] reported the catalytic performance of Co_3O_4 nanocrystals prepared by sonochemical method; Patil et al. [34] have studied the highly sensitive and fast responding sensor characteristics for

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CO of Co_3O_4 nanorods, which were obtained via the chemical co-precipitation/digestion method; Jana et al. [35] have synthesized Co_3O_4 nanocrystals with different sizes by decomposition of Co (II) fatty acid salts above 320 °C; Feng and Zeng [36] have proposed a nitrate salt-mediated route to synthesize Co_3O_4 nanocubes and their sizes were controlled by aging time; Zou et al. [37] prepared Co_3O_4 nanoparticles through a facile solution oxidation route at room temperature and normal pressure. Further, the porous Co_3O_4 nanotubes had been synthesized by microemulsion method [38], its nanorods were prepared by improving the traditional molten salt synthesis [39] and solvothermal method [40].

There are many studies on the synthesis of nanostructured Co_3O_4 material such as chemical impregnation, precipitation, solid state reaction, ion exchange, sodium-nitrate-mediation, microwave irradiation, and sol–gel methods. However, in all the above synthetic routes, an expensive and strict experimental condition, tedious procedures, complex apparatus, low yield, high cost and some unresolved problems. Consequently, it is still a challenge to develop simple methods for the preparation of Co_3O_4 particles for large-scale production. In recent years, an effective, simple, and energy-efficient solution combustion synthesis (SCS) of nano/microsized metal oxide powder has acquired considerable interest because of its simplicity and large scale production. Wen et al. [41] used solution combustion synthesis of cobalt oxide nanoparticles as negative-electrode materials for lithium ion batteries. This method produces more homogeneous and high purity crystalline material [42].

Recently, the fabrication of composite thin films on steel materials exhibited excellent atmospheric corrosion resistance property and thus reducing its chromium passivation. Corrosion resistance property is enhanced by co-deposition of nano/micromaterials such as CNT, MWCNTs, TiO_2, Fe_2O_3, NiO, ZrO_2, MoS_2 and so forth, with metals. In recent times, nano/microsized TiO_2, NiO, ZrO_2, and γ-Al_2O_3 particles are used for the fabrication of Zn-composite thin films for corrosion protection [43–46]. Thus, these materials enhance the mechanical, physical, and tribological properties of the coatings due to their extremely small size typically around 1–100 nm, and are used widely in electrodeposition for corrosion protection. The other important issue of cobalt oxides as negative electrodes for lithium-ion batteries and supercapacitor electrode materials, but the researchers are not yet utilized this Co_3O_4 material in Zn-composite coating by a low cost electrodeposition method for corrosion protection.

However, little work has been performed on the synthesis and corrosion behaviour of Co_3O_4 particles. The present investigation is focused on the bulk synthesis and characterization of Co_3O_4 microparticles by a solution combustion route with cobalt nitrate as oxidizer, dextrose as fuel without using any templates, surfactant, organic dispersant, and capping agent. The sample was dried and calcined at different temperatures. The IR spectra and thermograms of these samples were recorded. The SEM and TEM images, EDAX, XPS and powder XRD patterns were taken to characterize cobalt oxide microparticles. The utilization of Co_3O_4 microparticles was also discussed in detail for the fabrication of Zn–Co_3O_4 composite thin films.

2. Experimental

2.1. Starting materials and synthesis of Co_3O_4 microparticles

$Co(NO_3)_2{\cdot}6H_2O$ (AR grade: 98%) purchased from S. D. Fine chemicals, Mumbai, India and Dextrose (AR grade: 98.5%) from Merck, Mumbai, India, were used as received. Millipore water (specific resistance, 15 MΩ cm at 25 °C, Millipore Elix 3 water purification system, France) was used to prepare the precursor solution. In a typical synthesis, Co_3O_4 nano/microparticles are synthesized using a standard solution combustion technique mentioned in ref [44]. The $Co(NO_3)_2{\cdot}6H_2O$ was used as metal nitrate and dextrose as fuel, respectively. The mixture in the ratio 2:1 (w/w, 10 + 5 g) was dissolved in 25 ml of Millipore water and heated at 80 °C with uniform stirring for 30 min. The resulted homogeneous solution was dehydrated slowly and gradually converted into the viscous before the formation of a gel. The gel was transferred to a silica crucible/alumina bowl and placed in a preheated muffle furnace at 100 °C. The gel boiled and swelled into foam, ignited with a flame which underwent a strong self-propagating combustion reaction with the evolution of a large volume of gases. The entire combustion process which was completed by 5 min gave black powder. The resulting black powder was highly crystalline and the portion of the sample was calcined at different temperatures ranging from as low as 100 °C to a maximum of 900 °C for 1 h in presence of air. Fig. 1 shows the scheme of synthesis of Co_3O_4 using $Co(NO_3)_2{\cdot}6H_2O$ as oxidizer and dextrose (sugar) as fuel.

2.2. Structural characterization

General morphology, structure, crystallite size, oxidation state, and compositional analysis of the nano/microparticles were performed using powder X-ray diffraction (XRD), Thermal analysis (TG-DTA) transmission and scanning electron microscopy, energy dispersive X-ray analyzer (EDAX), X-ray photoelectron spectra (XPS), and Fourier transform infrared spectroscopy (FTIR). X-ray diffraction patterns (X'pert Pro Diffractometer; Phillips, Cu Kα radiation, (λ_{Cu} = 1.5418 Å) working at 30 mA and 40 kV) were recorded in the 2θ range from 10° to 90° at a scanning rate of 1° min^{-1}. For Rietveld refinement analysis, the XRD data were refined using the FullProf Suite-2000 version. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed in the temperature range 25–1000 °C at a heating rate of 5 °C/min under air atmosphere using a SDTA-85 1e from Mettler Toledo. Morphology and compositional analyses were carried out in a scanning electron microscope (SEM; Philips XL 30) fitted with an energy dispersive X-ray analyzer (EDAX) in the voltage range of 200–300 kV. Transmission electron microscope (TEM) images of selected samples were recorded (Model: JEOL 2000 FX-II) with an acceleration voltage of 200 kV and confirmed the size of Co_3O_4 particles in micrometer range. Two microliters of Co_3O_4–ethanol solution was dropped on a Cu grid with a carbon-reinforced plastic film. The X-ray photoelectron spectra (XPS) were recorded by Thermo-Scientific Multilab 2000 equipment employing Al Kα X-rays at 150W, with binding energies in ±0.1 eV. Fourier transform infrared spectra (FT-IR) were obtained on KBr pellets at ambient temperature using a Bruker FT-IR spectrometer (TENSOR 27). The average crystal sizes were estimated using the Scherrer equation [47]:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D is the diameter of the crystal size (nm), K is the shape factor (the typical value is 0.9) λ is the X-ray wavelength (nm) of the incident beam, β is the broadening of the diffraction line measured in radians at half of its maximum intensity (FWHM) and θ is the Bragg's angle.

2.3. Fabrication of Zn and Zn–Co_3O_4 coatings

The plating bath solution was prepared by dissolving 180 g/L $ZnSO_4$, 30 g/L Na_2SO_4, 10 g/L NaCl, 1.5 mM/L sodium lauryl sulphate (SLS) [Himedia AR, India] and 0.5–2.0 g/L Co_3O_4 in Millipore water. The pH of the solution was adjusted to 2.5. The operating parameters and optimum bath composition are shown in Table 1. The bath solution containing 0.5–2.0 g/L Co_3O_4 particles was prepared and stirred for 24 h. The mild steel plates (cathode) were polished mechanically and degreased with trichloroethylene in degreaser plant followed by water wash. These plates were dipped in 10% HCl for few seconds and finally rinsed with water. The zinc plate was used as the anode and its surface was activated by dipping in 5% HCl for few seconds followed by water wash. The electrodeposition was carried out at current density of 3 A/dm^2 for 10 min, while magnetically stirred at a speed of 300 rpm. The coatings were characterized by SEM/EDAX measurement and the corrosion studies were carried out to examine the coatings of Zn and Zn–Co_3O_4.

The electrochemical measurements were performed using the CHI660C electrochemical work station (CH Instruments). For all (polarization, Tafel and EIS) measurements, a conventional three electrode cell with platinum as counter electrode, saturated calomel as reference electrode and specimen under investigation as working electrode was used. The electrolyte was 3.5% NaCl solution. The anodic polarization and the Tafel curves were recorded at a sweep rate of 0.1 mV/s and 0.01 V/s, respectively in 3.5 wt.% NaCl at room temperature using pure Zn and Zn–Co_3O_4 composite coated specimens of 1 cm^2 area. Electrochemical imped-

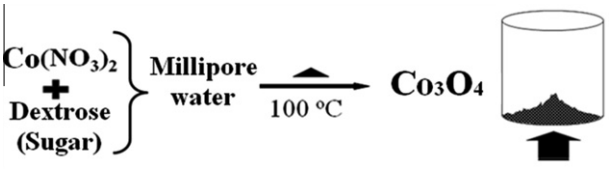

Fig. 1. Schematic diagram of SCS method for synthesis of Co_3O_4 microparticles.