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Synthesis and surface modification of zinc oxide nanoparticles to prepare corrosion resistant coatings

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Abstract: Zinc oxide is an active, inorganic material for a number of important applications. Zinc Oxide have wide properties for industrial applications which has been further increased by making the use of it in nanoscale size that fit in the corrosion resistant coatings. Nanoparticles have unique properties such as large surface area and nanoscale size due to which it possess various application in coatings and paints. Coating is a covering which when applied to the surface forms a layer and act as a protective barrier to the surface based on the property of the coating. Nanocomposite coatings are comparatively low cost and have more applications like dealing with the corrosion and radiation resistivity. Incorporation of nanoparticles in coating enhance its property by reducing the void and expected to induce barrier property for corrosion.

For this purpose, zinc oxide nanoparticles were synthesized using wet chemical method. The effect of reactants (base) used in ZnO synthesis was studied from pH 9 to 11 and was characterized using XRD, SEM-EDX. To increase the hydrophobicity and to make them suitable to disperse in polymeric binder, synthesized ZnO nanoparticles, have been surface modified with different silanes such as aminopropyl triethoxy silane (APTES), hexadecyl trimethoxy silane (HDTMS) and vinyltriethoxy silane (VTES). Surface modification was examined by FTIR, SEM-EDX and Contact angle analysis and VTES was found suitable for surface modification. Surface modified ZnO nanoparticles have been dispersed in polymeric binder (liquid EPDM) with other additives to form coating formulations. These coating formulations were applied on MS panels and it was observed that developed coating formulations have good mechanical and physical properties and high corrosion resistance.

Keywords: Zinc oxide, nanoparticles, surface modification, coatings, corrosion resistant

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1. Introduction:

Zinc Oxide nanoparticles are commonly used in many areas due to their properties and low cost. They provide wear proof property, high toughness and anti-ageing performance when used in the coating. Hence, investigations on the synthesis and modification of ZnO nanoparticles have tremendous attention. There are various methods for the synthesis including sol-gel technique[1], hydrothermal processing[2], direct precipitation[3], wet chemical method etc.

However, ZnO nanoparticles agglomerate due to Zn-O-Zn bond formation, high surface energy and large surface area. Therefore, it is necessary to modify its surface for better performance[4]. Surface modification is basically the physical adsorption or grafting depending on the particle surface. Surface modification can inprove the inherent characteristics of nanoparticles. Silane compound have been widely used for the purpose to enhance the surface chemical and physical properties.

A lot of development work has been done on various coatings but we are trying to fill the gap to develop flexible polymer nano-composite coating for radioactive waste storage containers having both corrosion and radiation resistent property. So, we are starting with the corrossion property using spherical shape synthesized and surface modified zinc oxide.

In the present study, ZnO nanoparticles have been synthesized at pH-9, 10, 11 and was characterized using XRD, SEM- EDX, FT-IR. Synthesized pH-11 nanoparticles, based on the study, was finalized for the surface modification and use of it in coating to induce corrosion barrier property. Also, VTES was selected as the promising silane agent out of VTES, APTES & HDTMS for Zinc Oxide nanoparticle modification examined by contact angle, FT-IR, SEM.

The SEM study shows shperical shape synthesized zinc oxide nanoparticles while the market zinc oxide nanoparticles are like flakes. We will study the shape effect on the corrosive property in the next series of paper. Also, the study shows the successful surface modification of zinc oxide nanoparticles using VTES, it showed super hydrophobic behavior with contact angle greater than 150°. Study of synthesized spherical zinc oxide nanoparticles at different pH and surface modification using vinyltriethoxysilane for corrosion barrier property is novel. The synthesized and surface modified zinc oxide will be used as a filler in coating which will impart exceptional corrosion resistance, impermeability towards moisture and good mechanical properties.

1. Methods:

1.1. Synthesis of zinc oxide nanoparticles

ZnO nanoparticles were synthesized by wet chemical method. Firstly, 0.1M solution of zinc acetate was made in high purity water in round bottom flask. The solution was allowed to stir vigorously at 80°C for an hour. Then, 2M NaOH aquous solution was added drop by drop untill the desired pH was reached. The precipitate was centrifuged at 4,000rpm followed by washing it 2 times with high purity water. Then, it was calcinated at 500°C for 4hrs. The obtained powder was characterised for various properties like XRD, SEM-EDX.

1.1. Surface modification of zinc oxide nanoparticles

Zinc oxide nanoparticles were surface modified with APTES, HDTMS and VTES. To carry out surface modification, mixture of 200ml toluene and 5 gm Zinc Oxide nanoparticles was made and sonicated for 15 minutes at room temperature. The mixture was added in the round bottom flask and allowed to stir for 30 minutes at 80°C. 15% of VTES was added [5] and the reaction mixture was refluxed for further 3 hours. The mixture was centrifuged at 4,000 rpm for 10 minutes followed by 2 washing with toluene. Surface modified nanoparticles were dried at 60°C in vacuum oven for 6-8 hours. The same procedure was followed for modification with APTES and HDTMS. Surface modification of Zinc Oxide nanoparticles was examined by FTIR, SEM and Contact angle.

1.1. Scanning electron microscopy (SEM)

The morphology of synthesized & surface modified zinc oxide nanoparticles was studied by SEM using SNE-4500M Plus of SEC. The ZnO nanoparticles were mounted on aluminum stub using double-sided carbon adhesive tape. Samples were gold coated to make it conductive at 20mA for 120 second by Sputter coater MCM-100P of SEC. The magnification of the microscope was selected as required for the detailed morphological studies.

1.1. Energy-dispersive X-ray spectroscopy (EDX)

The elemental analysis of ZnO nanoparticles was done by Bruker XFlash® 630 EDS with a spectrum resolving power less than 129.0 eV and 30 mm detector area.

1.1. X-ray diffraction (XRD)

X-ray Diffraction Analysis (XRD) was done in the range of 10–90°, using Rigaku MiniFlex X-ray diffractometer with Cu Kα radiation of wavelength, λ=1.54 Å and Scherrer constan-t, K=0.94.

1.1. Contact angle analysis

To determine the wettability of synthesized and surface modified ZnO nanoparticles, the Contact angle analysis was carried out using instrument drop shape analyzer DSA 100S of Kruss by drop method. In this method water droplet is put on the surface of the sample by a syringe, a high-resolution camera captures the image from side view and the angle between water droplet, and sample surface is measured. High value of contact angle against water shows hydrophobic nature of sample.

1. Results and Discussion:

1.1. Synthesis of zinc oxide nanoparticles

1.1.1. XRD

The XRD patterns of ZnO nanoparticles of pH 9, pH 10 and pH 11 are shown in figure 1. XRD data determines crystalline structure and phase formation of zinc oxide nanoparticles. It was performed to determine the crystallite size of zinc oxide nanoparticles which was calculated using debyl-scherrer equation. Crystallite size calculated was >80nm of every pH.

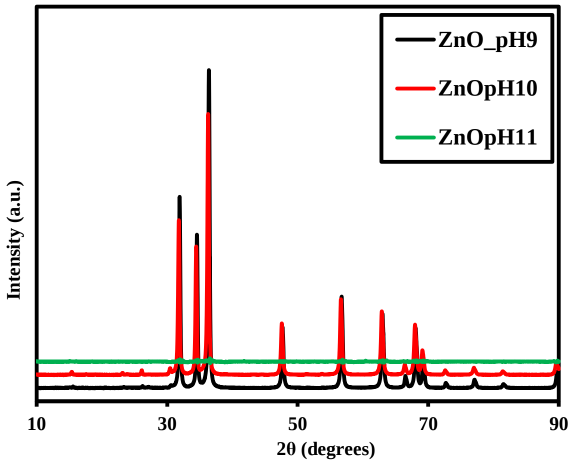
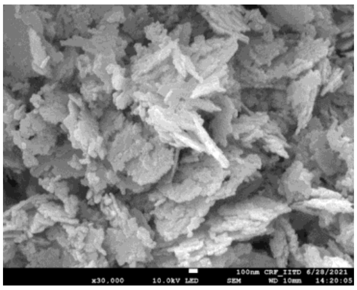


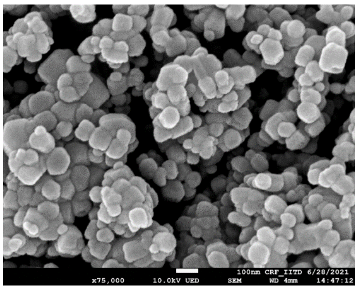
Figure 1. XRD of Synthesized pH-9, pH-10 and pH-11 zinc oxide.

1.1.1. SEM-EDX

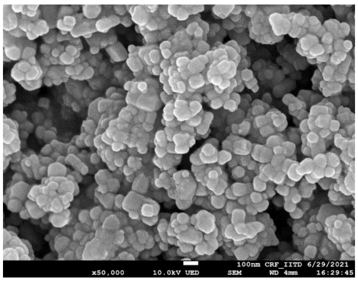
SEM images of market procured zinc oxide, ZnO with pH-9, pH-10 and pH-11 are shown in figure 2a-2d respectively. The synthesized nano-crystals are spherical in shape with diameter 78 nm, 75 nm and 65 nm for pH-9, pH-10 and pH-11 respectively while market procured ZnO are like flakes. At pH-9, the nano crystal size is bigger as compared to pH-11. It seems that with increase in pH, size decreases.



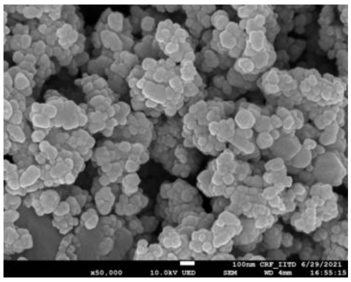
(a)Market ZnO



(b)Synthesised ZnO (pH-9).



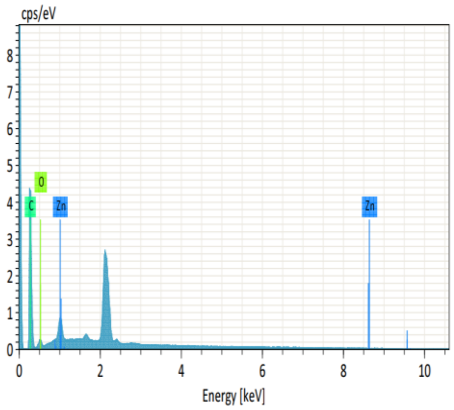
(c)Synthesised ZnO (pH- 10)



(d)Synthesised ZnO (pH- 11).

Figure 2. Scanning electron micrograph of market and synthesised zinc oxide nanoparticles of pH-9, pH-10 and pH-11.

The chemical composition of Zinc Oxide nanoparticles was studied using EDX and drawn in figure 3.



Spectrum	C	O	Zn
ZnO nanoparticles 1127	13.30	9.95	76.75

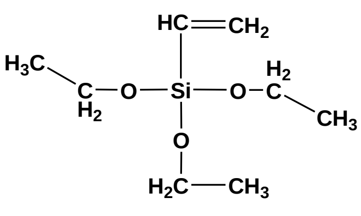
Figure 3. EDX of zinc oxide nanoparticles.

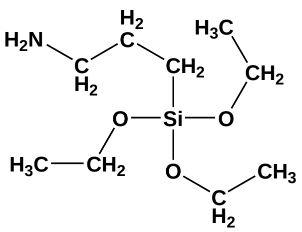
XRD spectra determines the crystalline structure. Debyl scherrer equation indicates the size decrease with increase in pH of samples. SEM images have shown the surface images and size of the crystal which also shows the decrease in crystallite size with increase in pH. EDX represented that nanoparticles contain only Zn and O elements.

Based on the characterization, pH-11 was selected as the suitable one for surface modification because of less crystallite size.

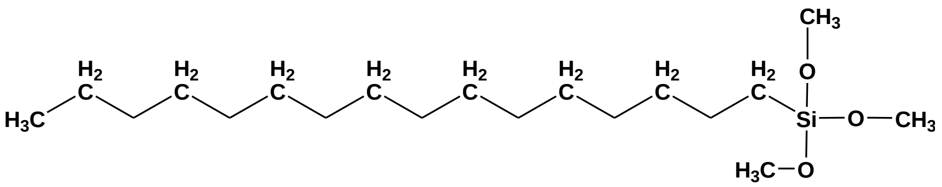
1.1. Surface modification of zinc oxide nanoparticles

Surface modification of zinc oxide nanoparticles was carried out with different surface modifying agents: Vinyltriethoxy silane (VTES), 3-Aminopropyltriethoxy silane (APTES) and hexadecyltrimethoxy silane (HDTMS).





Vinyltriethoxy silane (VTES) **3-Aminopropyltriethoxy silane (APTES)**



Hexadecyltrimethoxy silane (HDTMS)

Figure-4: Chemical structure of silanes used for surface modification of zinc oxide nano-particles

1.1.1. FT-IR

The FTIR analysis of surface modified zinc oxide nanoparticles was carried out to identify the change in functionality of the surface modified ZnO nanoparticle with unmodified ZnO and to establish interactions between functional silanes with ZnO nanoparticles.

The FTIR spectra of surface modified ZnO as well as unmodified ZnO are shown as Figure 5. The broad peak at 3431-3454 cm^{-1} in all IR spectra relates to O-H stretching of hydroxyl groups. No change in functional groups was observed in case of ZnO nanoparticles modified with APTES. The peak at 1450 cm^{-1} , 974 cm^{-1}, 1016 cm^{-1} and 488 cm^{-1} indicates the C=C, Si-C, Zn-O-Si and Si-O bonding respectively in ZnO nanoparticles modified with VTES. The peak at 1724 cm^{-1}, 1450 cm^{-1}, 1269 cm^{-1}, 737 cm^{-1} and 471 cm^{-1} indicate the C-O stretching, CH_3 stretching, Zn-O-Si bonding, Si-O-C, Si-O bonding respectively. On the basis of results it was observed that the functional groups of surface modifying agent (silane) are attached with ZnO nanoparticles in case of VTES and HDTMS whereas not much effect was observed with APTES surface modifying agent.

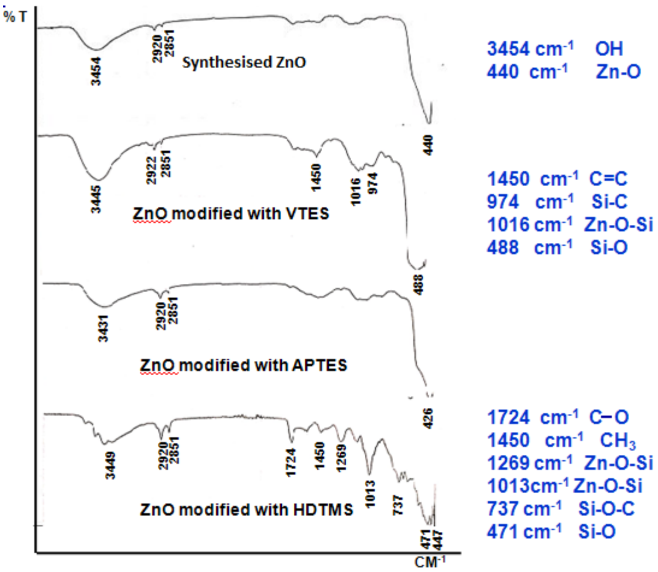


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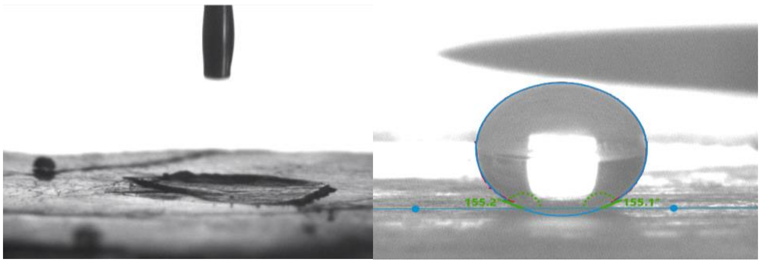
Figure 5. FTIR analysis of synthesized (pH-11) and surface modified zinc oxide nanoparticles.

1.1.1. Contact Angle

During the contact angle analysis, when water drops on synthesized unmodified ZnO surface, it collapses within seconds due to zinc oxide highly hydrophilic nature. Same observations were found in case of APTES modified ZnO nanoparticles. In case of VTES and HDTMS modified ZnO nanoparticles; the water drops were very stable on these surface for longer period (> 2 hour) and contact angle was 155.3 and 124.1 respectively which can be attributed to hydrophobic nature of modified ZnO nanoparticles. As EPDM is also hydrophobic in nature, hence the surface modified ZnO nanoparticles with VTES and HDTMS will be compatible to EPDM coatings.



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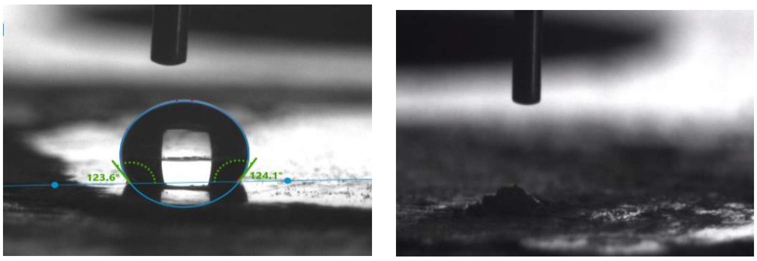
(a)Synthesised ZnO (pH-11) **(b)ZnO modified with VTES.**

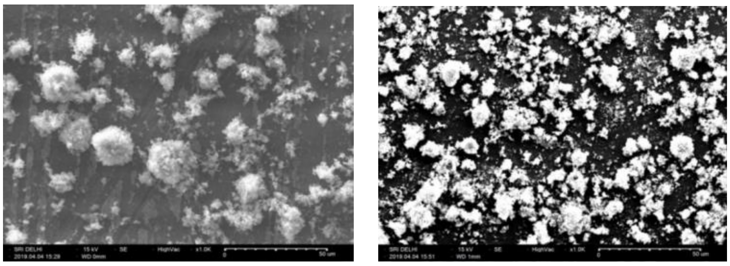


(c)ZnO modified with HDTMS **(d)ZnO modified with APTES.**

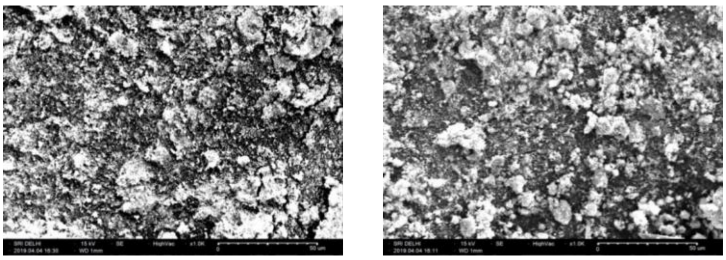
Figure 6. Contact angle analysis of synthesized ZnO (pH-11) and modified zinc oxide nanoparticles with VTES, APTES and HDTMS.

1.1.1. SEM

The SEM images of synthesized pH-11 ZnO nanoparticles show the agglomeration, whereas the SEM images of zinc oxide nanoparticles modified with VTES and HDTMS showed improved dispersibility as compare to unmodified and modified ZnO NPs with APTES. To prepare coating formulations, homogeneous distribution of zinc oxide nanoparticles in polymer matrix (EPDM) is necessary to prevent corrosion. SEM results revealed that ZnO nano-particles modified with VTES shows non-agglomerated behaviour which will improve the dispersion of ZnO nano-particles in EPDM polymer matrix.



(a) Synthesised ZnO (pH 11) **(b) ZnO modified with VTES.**



(c) ZnO modified with HDTMS **(d) ZnO modified with APTES.**

Figure 7. Scanning electron micrograph of synthesized and modified zinc oxide nanoparticles with VTES, APTES and HDTMS.

Conclusions:

The zinc oxide nanoparticles with pH-9, 10 and 11 was synthesized by wet chemical method at 500°C. The XRD spectra of nanoparticles determine the crystalline structure of zinc oxide. Debye-Scherrer equation indicates the crystallite size decrease with increase in pH of samples. SEM images also show the decrease in crystal size with increase in pH. EDX represented nanoparticles contains Zn and O elements. From all the observations, pH-11 was selected for surface modification.

For surface modification, VTES, HDTMS and APTES was used. SEM images show that the agglomeration decreases after modification. During contact angle analysis, unmodified zinc oxide and modified zinc oxide with APTES had zero contact angle i.e. the water droplet collapsed within seconds which indicates the hydrophilic nature while modified zinc oxide with VTES and HDTMS had contact angle 155.3 and 124.1 respectively which shows the hydrophobic nature. FT-IR peaks also show the interaction between functional silanes and zinc oxide nanoparticles. Therefore, VTES was selected as the promising agent for modification.

Surface modified pH-11 zinc oxide nanoparticles can easily be dispersed in EPDM based coating for corrosion resistant property.

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