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Research Article

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Simple and Direct Synthesis of Zinc Vanadate (ZnV_2O_5) Nanocrystals for its Electrocatalytic and Antimicrobial Activity

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ABSTRACT

Zinc Vanadate (ZnV_2O_5) Nanocrystals were prepared by two steps, ceramic route process. Optimization of the ceramic route processing conditions enhances the Electrocatalytic and Antimicrobial performance of the prepared nanoparticles. The thermally treated material was subjected to XRD, FTIR, UV-Visible spectroscopy, SEM and EDS, which confirmed the formation of Zinc Vanadate (ZnV_2O_5) Nanocrystals. The electrochemical detection of Anthracene by Zinc Vanadate nanoparticles was investigated by Cyclic Voltammetry. The result concludes that the ZnV_2O_5 NPs have higher activity for detection and oxidation of Anthracene. The as synthesized ZnV_2O_5 NPs were found to exhibit strong antimicrobial activity against both Escherichia coli (E.coli) gram negative and Staphylococcus aureus (S. aureus) gram positive microorganisms implying their strong potential as antimicrobial agent.

Keywords: ZnV_2O_5 Nanocrystals; Antimicrobial activity; *Escherichia coli*; *Staphylococcus aureus*; Thermal decomposition; Electrocatalytic activity; Anthracene

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INTRODUCTION

Nanostructured materials have been widely investigated for the fundamental scientific and technological interests in accessing new classes of functional materials with unprecedented properties and applications [1-3]. In recent years, there has been an increasing interest in the synthesis of nanosized crystalline metal-metal oxides because of their large surface areas, unusual adsorptive properties, surface defects and fast diffusivities. ZnV_2O_5 is a very important material extensively used in catalysis, gas sensors, electrochromic films, battery cathodes, heterogeneous catalytic materials and magnetic materials [4,5]. Due to their small size, nanoparticles exhibit novel material properties that are significantly different from those of their bulk counterparts.

The metal-metal oxide semiconductors have been extensively explored by researchers in pure and doped form. Doping introduces remarkable changes in the structural, optical, electrical, magnetic, and semiconducting properties which encourage their use in various applications, namely, sensors and piezoelectric, photovoltaic, electro-optic, and micro-electromechanical devices [6-10]. Zinc Vanadate (ZnV_2O_5) is a multifunctional material with wide band gap (3.23 eV), n-type hexagonal structured, high electron mobility, large piezoelectric constants, high nonlinear optical coefficients, radiation hardness, biocompatibility, and large 60 meV exciton binding energy characteristics. It is suitable for small wavelength optoelectronic devices. The anti-microbial activity of nanoaparticles has been correlated to their ability to interact or penetrate the cell wall of bacteria and generation of reactive oxygen species (ROS) [11-13].The antimicrobial activity of ZnV_2O_5 has been studied by various research groups on variety of micro-organisms. ZnV_2O_5 have been found to be effective against gram positive, gram negative and some of the multi-resistant strains such as *Staphylococcus aureus, Escherichia coli, Salmonella enteric,* methicillin-resistant *Staphylococcus aureus* [14-18].

In the present study, we have investigated a simple and rapid route to synthesize Zinc Vanadate nanocrystals using Zinc Oxide and Ammonium meta-Vanadate. The whole process takes only a few hours to yield Zinc Vanadate nanoparticles. The structure, morphology and optical properties of the synthesized Zinc Vanadate nanoparticles have been investigated by XRD, FT-IR, UV- Visible spectroscopy and SEM with EDS. In addition, the electrocatalytic oxidation ability of zinc vanadate in the Cyclic Voltammeter has been investigated, for the Oxidation of Anthracene to Anthraquinone. It's anti-microbial activity on gram negative *Escherichia coli (E.coli)* gram negative and *Staphylococcus aureus (S. aureus)* gram positive microorganisms. The anti-microbial experiments were carried out using Kirby-Bauer disc diffusion method.

EXPERIMENTAL SECTION

Synthesis of ZnV_2O_5 Nanocrystals

0.008 mole of Ammonium meta-Vanadate (NH_4VO_3) and 0.004 mole of Zinc Oxide (ZnO) were weighed and mixed in an agate mortar and pestle for 1 hr initially. The obtained powder was ball milled in agate grinding jar using agate ball for 2 hr to achieve better homogeneity. After milling the mixed powder was dried in an oven at 80°C for 20mins and was transferred to Quartz crucible for calcination. The powder was calcined at 550°C in an horizontal furnace for 6 hrs. Then obtained material was subjected to further Structural characterization, Electrocatalysis and Antimicrobial activity [19-23].

Materials and Structural Characterization

Synthesizing ZnV_2O_5 nanostructure in this research includes the use of several materials such as Zinc Oxide (ZnO) ≥ 99% purity (Sigma aldrich) and Ammonium meta-Vanadate (NH_4VO_3) ≥ 99% purity (Sigma aldrich). The crystal structure of ZnV_2O_5 nanoparticles was analyzed by a PANalytical Empyrean 300TT X-ray diffractometer with Cu-Kα1 radiation (λ=1.5406 Å). FT-IR spectrum of the ZnV_2O_5 was recorded on Perkin Elmer FT-IR 8300 series instrument by using potassium bromide pellets. The morphology of the materials was analyzed by SEM HITACHI SU6600 scanning electron microscopy and energy dispersive spectroscopy respectively. UV-Vis spectral analysis was done by using UV-Visible spectrophotometer (UV-1100, India). UV-Visible absorption spectrophotometer with a resolution of 5 nm between 200 and 600 nm was used. The electrochemical experiments were performed on a CHI 600A electrochemical instrument using the as-modified electrode and bare GCE as working electrode, a platinum wire was the counter electrode, and saturated calomel electrode (SCE) was the reference electrode [23].

Antimicrobial Activity of Zinc Vanadate Nanoparticles

The anti-microbial activity of ZnV_2O_5 NPs was studied using Kirby-Bauer disc diffusion method. The anti-bacterial activity of ZnV_2O_5 NPs was studied against gram negative *E.coli* and gram positive *S. aureus* bacteria. The plates containing Luria Bertani (LB) agar medium were sterilized and solidified. Approximately 106 colony forming units (CFU) were spread on LB agar plates to cultivate the bacteria. The sterilized filter paper discs of 5 mm diameter were dipped in ZnV_2O_5 NPs solutions of varying concentrations (1–3 μg/ml) and placed in agar plates. One disc was dipped in 1 mM ZnO solution and considered as control. The plates were then incubated at 37°C for 24 hours. The zones of inhibition for control and ZnV_2O_5 NPs were measured. The experiments were repeated thrice and the average was taken.

Electrode Modification

Ultrasonically dispersed ZnV_2O_5 nanopowder in 5 mL of water was drop coated onto the GCE and dried at room temperature. The ZnV_2O_5 coated electrode prepared by electrochemical deposition techniques and used for electrocatalytic reduction of Anthracene. CV's were run in electrochemical cell containing 50 mL DD water and 0.1 M KOH in presence of SCE reference electrode and Platinum wire as counter electrode.

RESULTS AND DISCUSSION

Synthesis of ZnV_2O_5 Nanocrystals

The probable mechanism for the synthesis of prepared ZnV_2O_5 nanocrystals is as follows:

$$ZnO + 2NH_4VO_3 \xrightarrow[24hrs]{\triangle} ZnV_2O_5 + 2NH_2\uparrow + 2H_2O\uparrow$$

The Synthesis of ZnV_2O_5 nanocrystals was carried out by taking 0.04 moles of Zinc Oxide powder and 0.008 moles of Ammonium meta-Vanadate in mortar pestle and was grinded for 2 hrs which results in formation of white colored precursor. Then the obtained material was calcined at 500°C for 24hrs and it was noticed that after 2 hrs the white colored precursor starts turning dark red in color. This change in color was due to reduction of ZnO and NH_4VO_3 to ZnV_2O_5 nanoparticle as one of the properties of Nanoparticles [19] and the smell of ammonia was observed during calcination and grinding which was considered as the evaporation of ammonium group from the reaction system.

XRD Analysis

XRD pattern of synthesized ZnV_2O_5 nanoparticles by ceramic route method is shown in Figure 1. The XRD pattern shows a high crystallinity of ZnV_2O_5 sample level with diffraction angles of 12.3°, 27.4°, 28.3° and 51.8°, which correspond to the characteristic face centered cubic (FCC) of ZnV_2O_5 lines indexed at (111), (200), (210) and (222), respectively. The size of the nanoparticles obtained were estimated to be 77 nm using Debye-Scherrer Equation, which may indicate a high surface area, and surface area to volume ratio of the nano-crystals. The equation is written below:

$$d = \frac{K\lambda}{\beta \,Cos(\upsilon)}$$

Where K, known as Scherer's constant (shape factor), ranges from 0.9 to 1.0, λ is 1.5418 Å, which is the wavelength of the X-Ray radiation source, β1/2 is the width of the XRD peak at half height and υ is the Bragg angle.

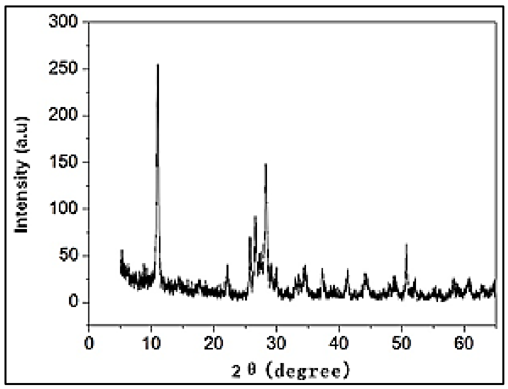

Figure 1: XRD analysis of ZnV_2O_5 nanocrystals

FTIR Analysis

FT-IR spectrum of ZnV_2O_5 nanoparticles (Figure 2) showed significant absorption peaks at 1607, 3480, 647, 1635 and 1428 cm^{-1}. The absorption band at 1607 cm^{-1} was assigned to M-O stretching vibration mode [20] and 647 cm^{-1} was assigned to the bridging vibration of O-M-O bond [21]. The weak band near 1635 cm^{-1} is assigned to H-O-H bending vibration mode were presented due to the adsorption of moisture, when FTIR sample disks were prepared in an open air atmosphere. These observations provided the evidence for the presence of hydration in the structure [22] band near 3480 cm^{-1} due to the OH-stretching vibrations of free and hydrogen-bonded hydroxyl groups. The formation of ZnO phase present in tetrahedron unit of vanadates is characterized by an intense and very broad IR band with poor resolved shoulders at 1428 cm^{-1} [23].

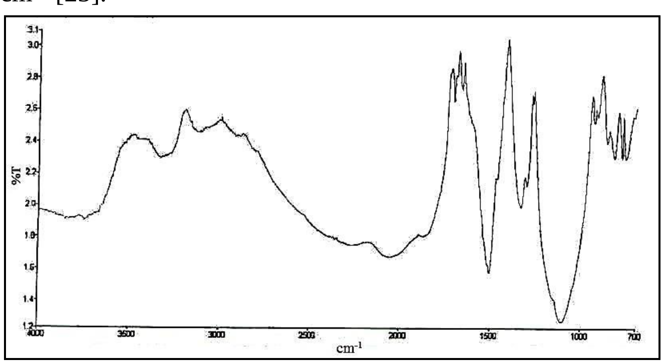

Figure 2: FTIR Analysis of ZnV_2O_5 nanocrystals

UV-Visible Spectroscopy Analysis

The energy band gap of nanocrystalline zinc vanadate nanocrystals was obtained from the UV-Visible spectroscopy at room temperature and is shown in Figure 3. It displays an absorption inflection point at around 385 nm, which should be assigned to the excitonic absorption feature of ZnV_2O_5. The direct band gap calculated from diffused reflectance spectra is 3.23 eV, which is higher for nano Zinc Vanadate than that for bulk Zinc Vanadate. The increment of the values of optical band gap arises due to improvement in the crystallinity of during annealing treatment [9]. The energy band gap value is reflected in the inset of (Figure 3) which comes out to be 3.21 eV, that is, less than pure ZnO (3.37 eV). The band gap energy of V_2O_5 is 2.3 eV and ZnO is 3.37 eV; when V_2O_5 is doped in ZnO, alloy is formed which causes decrease in band gap.

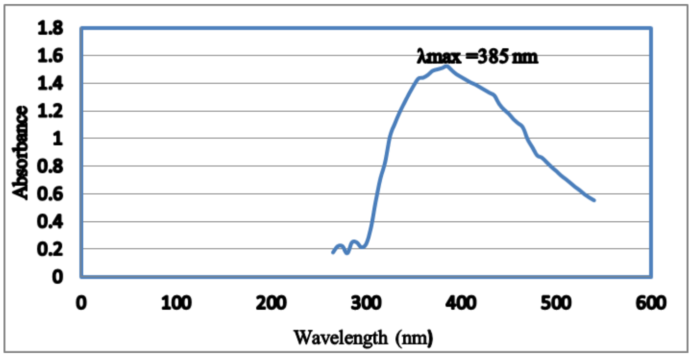

Figure 3: UV-visible spectroscopy analysis of ZnV_2O_5 nanocrystals

SEM and EDS Analysis

Scanning electron microscopy (SEM) has been used to identify the size, shape and morphology of nanoparticles. The SEM micrograph of the ZnV_2O_5 calcined at 500°C is shown in Figure 4. It can be seen that the particles adopt irregular morphology with different sized particle. In addition, ZnV_2O_5 nanoparticles show cube shape with smooth surface. It clearly indicates the fine crystal like particles adsorbed on the surface due to the aggregation. It shows the crystal like agglomerates were purely due to the magnetic induction between the particles. The Energy Dispersive X-ray Spectroscopy (EDS) spectrum of the synthesised ZnV_2O_5 nanoparticles Figure 5. shows strong Zinc signal along with vanadium and weak peaks of oxygen and oxides analysis by EDS confirms the formation of pentavalent Vanadium(V_2O_5) and Zinc Ions (Zn^{+2}) i.e., ZnV_2O_5.

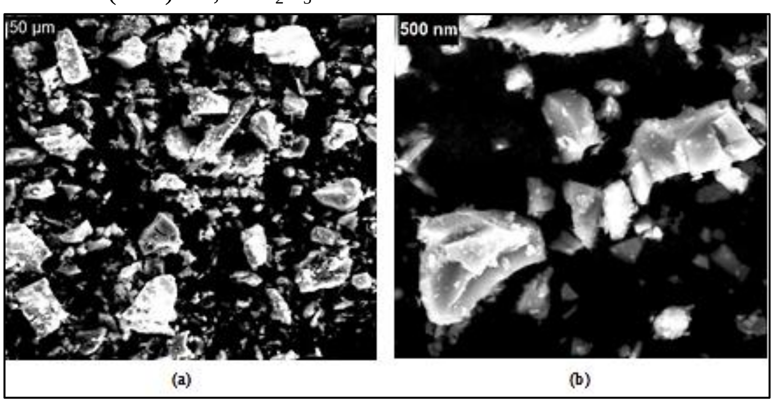

Figure 4: SEM images of ZnV_2O_5 nanocrystals

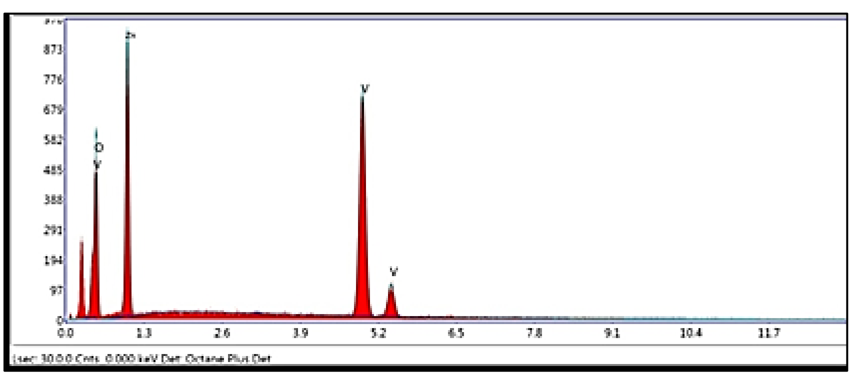

Figure 5: EDS analysis of ZnV2O5 nanocrystals

Electrochemical Property

The electrochemical behaviour of 1 mM Anthracene at ZnV_2O_5/GCE was tested with cyclic voltammetric (CV) measurements in 0.1 M KOH. Figure 6 shows the CV of ZnV_2O_5/GCE in KOH electrolyte. It can be seen that the ZnV_2O_5 is non-electroactive in the selected potential region. Figure 6 shows broad peaks in the potential range from −0.4 to -0.6 V. Figure 7 shows oxidation of Anthracene at ZnV_2O_5/GCE. It shows the cathodic peak at -0.8 V with enhanced current response relative to that of ZnV_2O_5/GCE. At the same time, we have noticed that the ZnV_2O_5/GCE shows higher current response at the positive potential region 0 to 0.2 V, which was indicative of the electron transport property of Anthracene. It indicated that the ZnV_2O_5 were catalytically more active toward electrochemical oxidation of Anthracene to Anthraquinone.

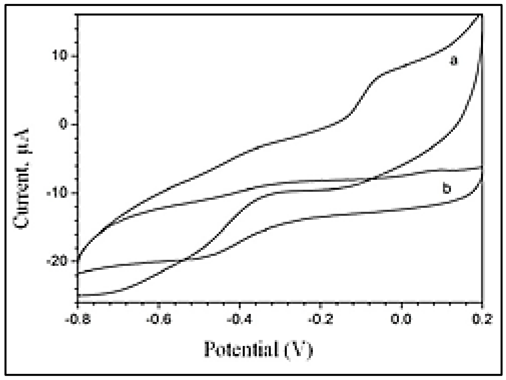

Figure 6: Cyclic voltammograms (CV) of (a) ZnV_2O_5modified GCE (b) Bare GCE forthe reduction of 0.001 M anthracene in 0.1 M KOH electrolyte at 50 mVs^{-1}

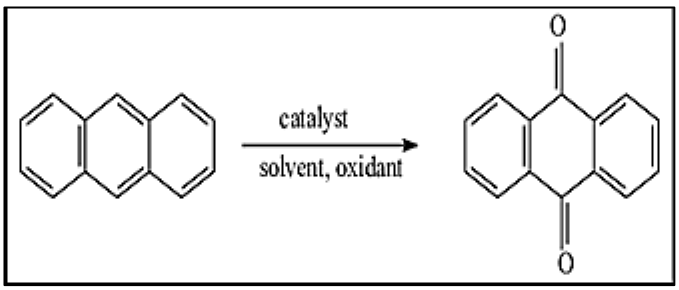

Figure 7: Oxidation of anthracene to anthraquinone

Anti-Microbial Activity of Zinc Vanadate (ZnV_2O_5) nanoparticles

Zinc nanoparticles, due to their antimicrobial properties have been used most widely in the health industry, medicine, textile coatings, food storage, dye reduction, wound dressing, antiseptic creams and a number of environmental applications. Since ancient times, elemental Zinc and its compounds have been used as antimicrobial agents. We have examined Zinc Vanadate (ZnV_2O_5) nanoparticles as possible antibacterial agents. The Zinc Vanadate (ZnV_2O_5) nanoparticles were immediately tested for respective antimicrobial activities towards both gram positive (*S. aureus*) and gram negative (*E. coli*) bacterial strains showing the zones of inhibition. Based on the zone of inhibition produced, synthesized Zinc Vanadate (ZnV_2O_5) nanoparticles prove to exhibit good antibacterial activity against *E. coli* and *S. aureus*. On the other hand, control exhibit minimum antibacterial activity. The results of antibacterial activities of prepared Zinc Vanadate (ZnV_2O_5) nanoparticles evaluated from the Kirby-Bauer disc diffusion method are given in Table 1. The Zinc Vanadate (ZnV_2O_5) nanoparticles showed efficient antimicrobial property compared to other due to their extremely large surface area providing better contact with cell wall of microorganisms (Figure 8).

Table 1: Size of the inhibition zones for ZnV_2O_5 against the tested microorganisms

Escherichia coli			*Staphylococcus aureus*		
Disc	**Sample**	**Inhibition zone (mm)**	**Disc**	**Sample**	**Inhibition zone (mm)**
1	Control 1.0 µg/ml	5	1	Control	5
2	2.0 µg/ml	6	2	1.0 µg/ml	9
3	3.0 µg/ml	12	3	2.0 µg/ml	10
4		24	4	3.0 µg/ml	13

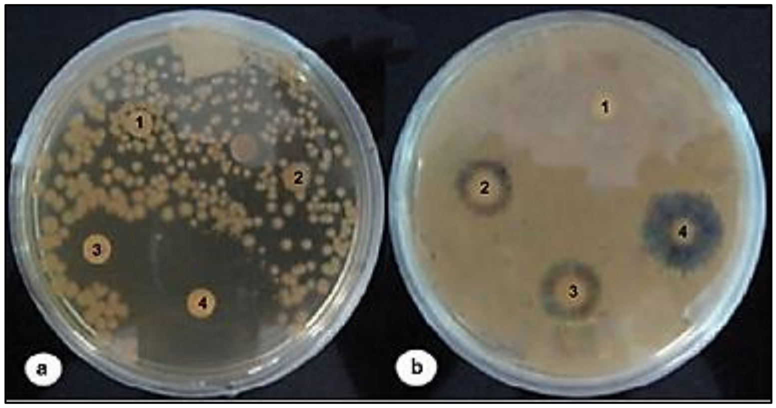

Figure 8: Anti-microbial activity of ZnV_2O_5 NPs in terms of zone of inhibition created by ZnV_2O_5 NPs. (a) Anti-bacterial activity of ZnV_2O_5 NPs against *E.coli* bacteria (b) Anti-bacterial activity of ZnV_2O_5 NPs against *S. aureus* bacteria

CONCLUSION

The Zinc Vanadate (ZnV_2O_5) nanoparticles were prepared by thermal decomposition method. FT-IR analysis confirms the formation of the Zinc Vanadate (ZnV_2O_5) nanoparticles. The calcined Zinc Vanadate (ZnV_2O_5) nanoparticles at 500°C were characterized by using XRD. The XRD confirms the crystal structure of the samples. The SEM of Zinc Vanadate (ZnV_2O_5) nanoparticle shows the crystal agglomerated particles. The optical absorption spectrum of Zinc Vanadate (ZnV_2O_5) sample was studied by UV-Visible spectroscopy. The electrochemical detection of Anthracene by Zinc Vanadate (ZnV_2O_5) nanoparticles was investigated by cyclic voltammetry. The results conclude that the Zinc Vanadate (ZnV_2O_5) nanoparticles have higher activity for the detection of Anthracene. The anti-microbial activity measurements suggest that the ZnV_2O_5 NPs have strong toxic potential towards bacteria *E.coli and S. aureus.* The two step process makes this method easy, economically viable and useful for large scale production.

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Conflict of Interest

The author Arvind Singh K Heer states that there is no conflict of interests regarding the publication of this paper.

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