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Research Article

Comparative Analysis among Different ZnO Nanoparticles Synthesized by Different Techniques

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Abstract

Semiconductor oxides were synthesized and systematically examined on 100 % cotton fabric to optimize the properties. Nano-technology is employed in this research work to form nanoparticles of semi-conductor oxides. Four samples were synthesized by using different methods and dyed to find the effective one. Different characterization techniques are used to characterize nanoparticles e.g. X-ray powder diffractometer, Energy dispersive X-ray spectroscope (EDS, EDX or EDXRF) and SEM images. By examining diffraction pattern and SEM images homogeneity, crystalline phase, transparent finishing process and unit cell dimensions are found. ZnO-3 (sample 3) (TEA 0.025M) treated cotton is revealed to have unique properties and implied a transparent finishing process.

Keywords: Energy dispersive X-ray spectroscope (EDS, EDX or EDXRF); cotton fabric; X-ray powder diffraction (XRD); Triethanolmine (TEA)

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1. Introduction

Nanotechnology is an evolving world-shattering technology occupying many disciplines like mechanics, plastics, medicines, optics, energy, electronic, aerospace and material science. The basics of nanotechnology lie in the fact that properties of substances intensely alter when their size is reduced to the nanometer ranges. Whenever any bulk material is distributed into small size particles with one or more dimension length, width or thickness, in the nanometer range or even smaller, the individual particles exhibit entirely different properties, different from the bulk material. Atoms and molecules that make the bulk material having totally different characteristics from that bulk material. Properties of atoms and molecules are determined by quantum mechanics while classic mechanics state the properties of bulk material. Nanotechnology is also playing its role in textile industry. Textile industry is now focusing towards the new notion of Shift in Functionality and performance and this new technology make it possible by using nanosize substances by generating nanostructures during manufacturing and finishing processes. To alter surface properties and impart textile functions nanoparticles such as ceramics and metal oxides are also used in textile finishing [1, 2]. They have a larger surface area and hence higher efficiency than larger size particles. In addition, nanosize particles are transparent, and do not blur colour and brightness of the textile substrates. Though, avoiding nanoparticles from clump is vital to accomplish a preferred performance. Nanoparticles such as MgO and TiO_2 used as biological and chemical protective materials. When used as composite nanoparticle, they also provide self-sterilizing function. Basically their photolytic activity is the key to destroy toxic and harmful biological and chemical agents. Fabric turned into sensor based materials after finishing with nanoparticles. In addition to Mg and Ti nanoparticles of Ag, Pt, Pd (Palladium) and Fe are used on textiles to provide heating, antibacterial and conductive magnetic properties [3]. Nanoparticles of metal oxides Al_2O_3, $Ti0_2$, MgO and ZnO provides electrical conductivity, UV absorption, catalytic ability, and photo-oxidizing capacity against biological and chemical agents. UV shielding and reduction of static electricity is now possible in nylon fiber by filling it with ZnO particles [4-6]. Semiconductor oxides are used as UV blockers i.e. ZnO, Al_2O, TiO_2, and SiO_2 by scattering and absorbing UV radiations [7-11]. There is a strong focus on metal oxide particles for UV protection because of intensive degradation of natural fibres i.e. cotton. Silk and wool etc. on exposure to sunlight [12, 13]. Besides causing degradation to textile materials UV radiation can cause serious human health problem i.e. sunburn, skin cancer, premature wrinkling and eye damage etc. [14].

ZnO most commonly known for its wide range of applications like field-emission displays, high-efficiency vacuum fluorescent displays, acoustic wave device solar-cell windows and transparent conductive films. Nano-coating of these oxides on textile materials can be carried out by many ways e.g. sol-gel method, electrochemical deposition, microwave heating method, vacuum evaporation, spin coating, dip coating and electro deposition etc. [15-18]. From most of nanocoating techniques, mostly require plane substrate, which may be a ceramic, polymer or metal. Some techniques may use a precursor for coating [11]. The possible force between the material being coated and the coating material are covalent bonding, electrostatic or hydrogen bonding [14].

Sol-gel method produces very small size nanoparticles i.e. 20-40nm, that can't be achieved by the previous method of grinding. This technique is used specifically for optical coating where optical clarity is required. Owing to weak bonding, difficulty in controlling porosity and high permeability this method nor arrives to the industrial potential. Dip coating is a well-known method for producing thin film coating by spin coating method. Electro deposition is a technique by which metal alloys deposition on textile material is possible. Fabrication of oxide film of desired thickness can be formed by electrochemical method [19].

2. Materials and Methods

In this research work, fabric used is plain weave 100 % cotton, warp count 60s, weft count is 55s, whiteness CIELAB

65, absorbency 3 sec, picks per inch and ends per inch are 86 and 108 respectively.
MLR for electrochemical reduction process 1:20, dye use Navacron, dyeing temperature 60-80 ℃, sample weight 150g.

Scoured and bleached woven fabric was used in this work for dyeing. The fabrics were dyed using the exhaust dyeing technique on hank dyeing machine with hot brand reactive dyes. Cotton is dyed by dyes. Mostly red, black, yellow, blue shade colours are used in this research because it gives more UPF rating. Finishing is applied by the electroplating method, micro wave heating method and sol gel method. Also referred as electro-deposition, electroplating coats electrically conductive textile materials with a layer of metal particles by means of electrical current. It produces a thick, stiff and heavy coat of metal on textiles.

5 oxides are synthesized by different techniques.

2.1. Synthesis and application of ZnO-1

The solution was synthesized from zinc acetate 6.12gm, 2-methoxyethanol 50ml, Triethanolamine 0.72gm.

For the preparation of nanosol ZnO-1, the amount of 6.12gm of Zn. acetate dihydrate was added to 50ml of 2-methoxyethanol under vigorous stirring at about 105 ℃ for 30 min. subsequently, Triethanolamine was added drop wise into above solution it forms a transparent homogeneous solution. The reaction mixture was stirred at 105 ℃ for 10min and then stored at ambient temp overnight. The prepared sol was quite sensitive to water.

The as-prepared solution might be applied onto substrate by various techniques as dip-pad-cure, dip-coating and spraying processes. In this study, the dip-pad-cure process was employed to form a thick layer of seeds. The cleaned substrate were dipped in the ZnO solution for one minute and then padded with an automatic padder at a nip pressure of 2.75 kg/cm2. The padded substrate were air-dried for 30min and finally cured at 130 ℃ for 5-10min.

2.2. Synthesis and application of ZnO-2

The sol was synthesized from a zinc acetate 13.16gm, dimethyl formamide solvent 100 ml and manganese acetate 7.35 gm. ZnO-2 is synthesized by sol gel method.

For the preparation of nanosol ZnO-2, the amount of 13.16gm of Zinc (Zn) acetate and dopant salts were completely dissolved in 100ml of DMF by stirring at room temperature for 5hrs. The sols were stable and homogeneous, no particulates were visible to eye and their appearance was unchanged for several months. Solution were usually stirred overnight at room temperature before use.

The dip-pad-cure process was employed to form a thick layer of seeds. The cleaned substrate were dipped in the ZnO-2 sol for one minute and then padded with an automatic padder at a nip pressure of 2.75 kg/cm2. The padded substrate were air-dried for 30min and finally cured at 130 ℃ for 5-10min.

2.3. Synthesis of ZnO-3

The solution was synthesized from zinc sulphate 1.24gm, double distilled water 120ml, sodium hydroxide 24ml (1.5M). ZnO-3 is synthesized by microwave heating method.
First 120ml of double distilled water was taken and 1.2gm of zinc sulphate was weighed and dissolved by aid of magnetic stirring at room temp for 10min.Then 24ml of 1.5M sodium hydroxide was mixed with the above solution to get pH-12 and stirring for 10min with dyed sample (10×4cm), after stirring a homogeneously turbid, curdy white solution was obtained which is transferred into a Pyrex glass bottle. Set the microwave temp at 100 ℃, 300 watt for 810min.

Air-dry the sample for 30min and Cure at 130 ℃ for 30min.

2.4. Synthesis of ZnO

The solution was prepared by using zinc chloride 0.05M and tartaric acid 0.01M, water 200ml and Current density - 0.5 mA/cm ² ZnO is synthesized by electrochemical deposition.

The electrochemical deposition of ZnO thin films was carried out in 0.05 M $ZnCl_2$ aqueous solutions. In order to control the surface shapes of ZnO films, tartaric acid was added to the deposition bath. Before electrodeposition, the stainless steel was cleaned ultrasonically in 0.1 M HCl, distilled water, and acetone and then rinsed in distilled water again. All the electrochemical deposition experiments were carried out in a configured glass cell at 90 ℃, in which a stainless steel plate, a graphite rod, textile substrate. Galvanostatic electrolysis was utilized in all electrochemical depositions with a current density of 0.50 mA/cm2 and deposition time of 60 min.

Dry the sample in air and cure the sample for 10 min at 130 ℃. The surface morphology and the phase identification of the deposited ZnO films were characterized by atomic force microscopy (AFM, SPM-9500J3), and field emission scanning electron microscope (FE-SEM, JSM-6330F) and power X-ray diffractometer (D/MAX 2200 VPC with Cu Ka radiation), respectively.

2.5. Dyeing procedure on treated samples

After synthesis of four samples, dyeing with H (hot) brand dyes are performed. For dyeing dye bath temperature was set at 50 ℃, pH just below 7, put the material and run it in the bath for 5 minutes, added pre dissolved dyes and continued dyeing for 10 minutes, added the salt in two portions during the period of raising the temperature to 80-85 ℃ in 30 minutes, dyed for 20 minutes at 85 ℃ after the last salt addition, poured alkali in two portions at the interval of 10 minutes, dyed for a further 30-60 minutes at 85 ℃ , dropped the bath and washed-off.

3. Characterization techniques

Four samples were synthesized and passed through different characterization techniques for phase identification, homogeneity and chemical characterization.

3.1. X-ray diffractometer

X-ray powder diffraction (XRD) is an analytical tool that provide information regarding unit cell dimensions, phase identification of a crystalline material. To study atomic spacing and crystal structure, diffraction grating is used. XRD is centred on a crystalline samples and constructive interference of monochromatic X-rays. X-rays are caused by a cathode ray tube and then filtered to yield monochromatic radiations, collimated to focus and engaged towards the sample. Constructive interference (and a diffracted ray) is produced when incident rays interact with the sample, hence at that time Bragg's Law conditions are satisfied.

$$n\lambda = 2d\sin\theta \qquad (1)$$

This equation stated that electromagnetic radiations' wavelength relates with lattice spacing and diffraction angle. After diffraction, the X-rays are identified, managed and counted. All possible directions of diffraction can be obtained by scanning the testing material (sample) through 20 angles owing to unsystematic orientation of the powdered materials.

3.2. Energy dispersive X-ray spectroscope

This is an analytical tool to assess chemical characterization and elemental analysis of a sample. Woking principle of Energy dispersive X-ray spectroscope (EDS, EDX or EDXRF) is an analysing of X-ray coming out from the matter through the interaction of electromagnetic radiations. As each element has its own specific atomic structure that allows the specific x-rays which are the characteristic of its atomic structure. EDS setup has four main components analyser, beam source, pulse processor and X-ray detector. This system is found mostly on electron microprobes and electron microscopes.

4. Results and discussions

4.1. Energy dispersive X-ray spectroscope analysis

The EDX of the nano structure of ZnO-3 is shown in the following Figure 1. This was the direct evidence to have the conclusion that expected for Zn and O (elements of ZnO).

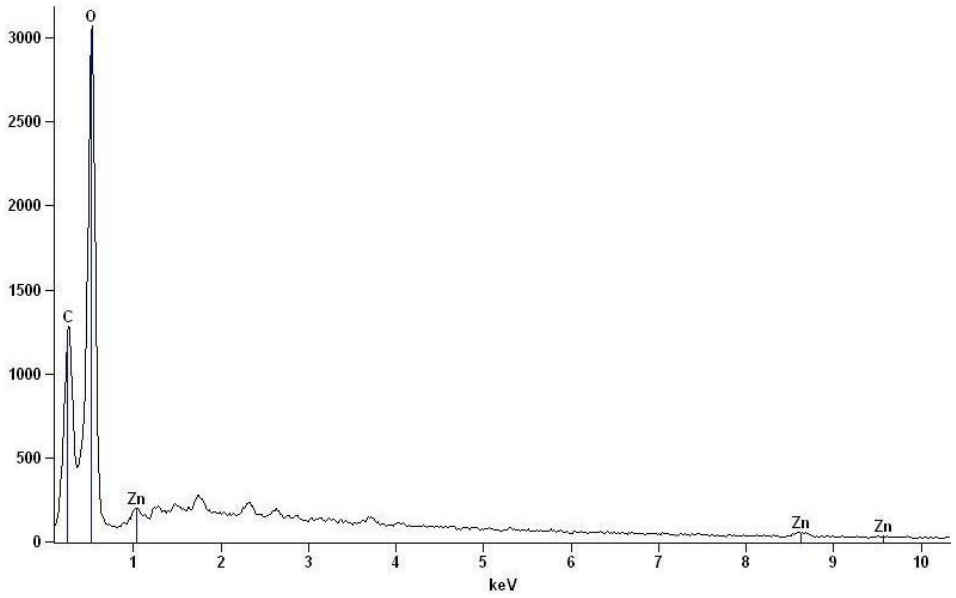

Figure 1 EDX of the nano structure of ZnO-3

4.2. X-ray diffraction analysis

X-ray diffraction pattern of four prepared samples are carefully observed to get information about unit cell dimensions, homogeneity and crystalline phase. From the XRD pattern (Figure 2) it can be seen that well defined peaks of Zinc oxide oriented in the (100), (002), (101), (110), (103), (200), (112), (201), (202) and (004) planes with maximum intensity in the (002) plane. Results shows that obtained ZnO nanostructures possess the hexagonal wurzite structure (space group $P6_3me$) with good crystallinity and no diffraction peaks of any other minerals were detected. Especially the diffraction peaks are higher and narrower at 002 showing that the ZnO-3 crystallizes well.

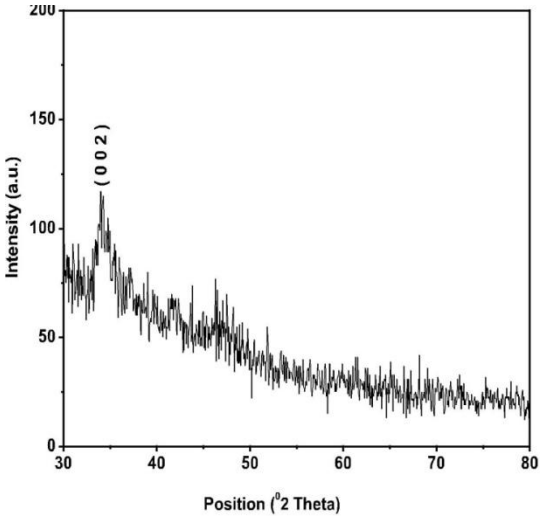

Figure 2 XRD pattern of nano-structure ZnO-3

4.3. SEM results

The surface of the treated fabric were observed by scanning electron microscopy as shown in Figure 3. SEM image shows the nanoscale Zinc oxide particles on cotton. The nano particles are well dispersed on the fibre surface, although some aggregated nano particles still visible. The particle size plays a primary role determining their adhesion to this fiber, it is responsible to expect that largest particle agglomerates will be easily removed fiber surface, will the small particles will penetrate deeper and adhere strongly into the fabric matrix. Following SEM image confirm that the large agglomerates are removed from textile surface after washing. Instead although nanoparticles are not covalently grafted to the fabric materials preliminary gravimetric essays show that more than 50% of there initial amount remains there bound to the fiber surface after washing in case of ZnO-3 nanoparticles.

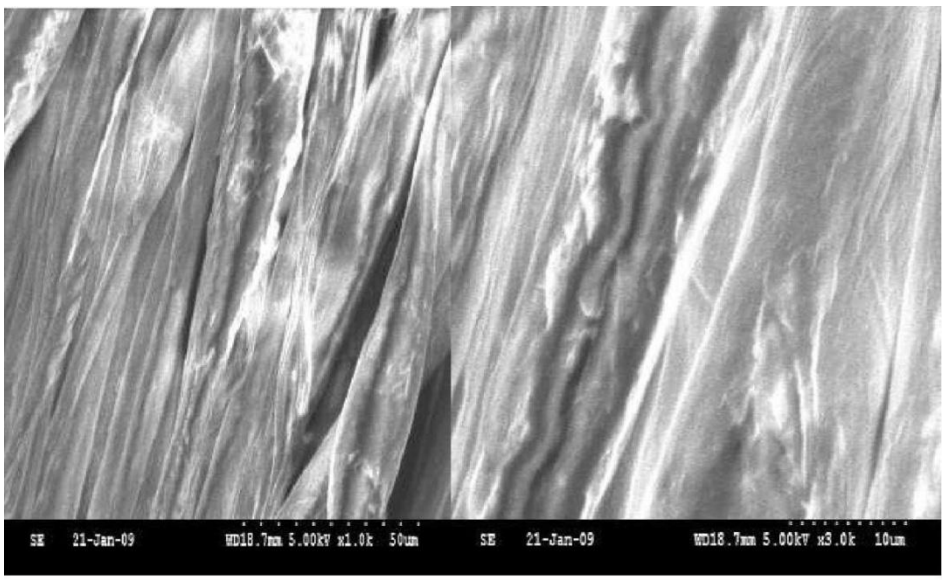

Figure 3 SEM image of ZnO-3 nanoparticle before and after washing.

5. Conclusion

The detailed testing procedure based on the vivo method is given in an Australian/New Zealand standard AS/NZS 2604. This finishing process is suitable for textile, apparel and delivers a continual wash The cotton fabric treated with semi-conductor oxide ZnO^{-3} demonstrated a unique UPF of 800+ in visible region, the transmission of the treated substrate was about 10% lower than that cotton fabric sample and implied a transparent finishing process. Semi-conductor oxides are produced by different synthetic techniques. After dyeing they are carefully examined to find out optimal properties. Standardized characterization techniques are applied to inspect and test the samples. Energy dispersive X-ray spectroscope analysis, SEM and x-ray diffraction analysis showed the new high peaks for ZnO^{-3} as compared with other three samples ZnO, ZnO^{-2} and ZnO^{-1}

The results obtained suggest that among different synthetic techniques, micro wave heating method nano sol coated fabric was found to exhibit comparatively better properties than other four methods. This technique is of sufficient generally for various nano sols and substrates, and open new doors for nano structured materials with varied functional properties. Further research work are being carried out to enhance UV protection activity of ZnO loaded textile fabrics.

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