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Synthesis Techniques and Properties of Pure and Doped Fe_2O_3 Nanocrystalline Materials - A Review

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Abstract: Ferric oxide nanoparticles are an environment friendly, non- toxic, stable electrode material having multi functional properties. N-type hematite is an attractive environmental friendly semiconductor material for photoelectrochemical and photo catalytic purposes due to its stability, benign nature and abundance. The thin film of Fe_2O_3 has showed great scientific attention due to its novel structural, optical, electrical and magnetic properties. Various methods of deposition of ferric oxide thin film have been studied including SILAR method etc. This review paper focuses on the pure and doped Fe_2O_3 which is characterized by different techniques such as X-ray diffraction for structural, SEM for morphology, EDX for chemical composition, FTIR, Photo activation and TEM etc. In recent years, many researchers have studied the effect of doping in a-Fe_2O_3 to improve its applicability for electrochemical sensors, solid oxide fuel cell and photo splitting of water etc. Doping of transition metal ions into Fe_2O_3 can improve the properties of nano crystalline materials by narrowing the energy-band gap and inhibiting electron-hole recombination. In addition, several doping species have been introduced into α-Fe_2O_3 in attempts to control materials properties, including Ti, Mn, Al, Zn, F, Co, Ce, Sn, and C etc. This review puts an emphasis on the effect of optical properties for future applications in optoelectronics nano devices, gas sensors, humidity sensors, water splitting and photoelectrochemical applications.

Keywords: Ferric Oxide, water splitting, Photoelectrochemical, gas sensor, solar cell, FTIR.

I. INTRODUCTION

The thin films of Fe_2O_3 have showed great scientific attention due to its novel structural, optical, electrical and magnetic properties. It has different crystalline phases depending on stoichiometry, such as wurtzite (FeO), magnetite (Fe_2O_4), hematite (α- Fe_2O_3) and maghemite (β-Fe_2O_3). N- type hematite (α- Fe_2O_3) is an attractive environmental friendly semiconductor material for photoelectrochemical and photo catalytic purposes due to its stability, benign nature and abundance. Due to its low cost, high resistance to corrosion, good chemical stability, high refractive index and non- toxicity, it has been traditionally used as catalysts, pigments, gas and humidity sensors, solar filters, supercapacitors, as an electrode material, in water treatment, in magnetic storage devices and in solid state lithium batteries, etc. In addition to this, α-Fe_2O_3 shows biomedical applications such as drug delivery system, hyperthermia and magnetic resonance imaging [1]. Hematite (α- Fe_2O_3) have already been studied extensively because of their superior performance as the active electrode materials for the pseudo capacitors compared with the conventional carbon based materials. Moreover, the low cost, good stability, nontoxic, and environmentally friendly nature of the α-Fe_2O_3 and MnO_2 coupled with their high redox activity make them suitable for the extensive applications in pseudo capacitors [2].

Iron (III) oxide has recently attracted a great deal of attention for its promising light-activated functional properties, coupled with its large abundance and low toxicity. In particular, α-Fe_2O_3 (hematite, Eg = 2.1 eV), the most thermodynamically stable Fe_2O_3 polymorph, has emerged as an efficient photocatalyst for solar hydrogen production and as a promising electrode material for dye-sensitized solar cells [3]. nevertheless some associated drawbacks, e.g., it requires working under inert atmosphere, at high reaction temperature and it requires long processing times resulting in high energy and time consumption. More recently, thermal decomposition of iron oleate complexes in presence of oleic acid via heat-up processes has been shown as a convenient method for large scale production of nanoparticles [4].

II. SYNTHESIS OF FE_2O_3 THIN FILMS:

Fe_2O_3 nanomaterial is synthesized by different methods such as - sol-gel technique, Co- precipitation, thermal evaporation deposition, anodic alumina template, biological macromolecular or supramolecular templates, chemical beam epitaxy growth, vapor–liquid–solid deposition, etc [5].

A. SOL-GEL Technique

The sol – gel process is a suitable wet route for the synthesis of nanostructured Fe_2O_3. Sol -gel method is based on the hydroxylation and condensation of molecular precursors in solution, originating a "sol" of nanometric particles. The "sol" is then dried or "gelled" by solvent removal or by chemical reaction to get three-dimensional Fe_2O_3 network. Gel properties are very much dependent upon the structure created during the sol stage of the sol-gel process. These reactions are performed at room temperature; further heat treatments are needed to acquire the final crystalline state [6].

B. Silar Method

SILAR method is one of the simple, nonhazardous and economic chemical solution methods. The growth process in SILAR technique was carried out at room temperature and under ambient pressure utilizing aqueous solutions. The substrate was immersed in separately placed cationic and anionic precursors alternately. This is one of the simple, nonhazardous and economic chemical solution methods. The substrate is rinsed after each immersion to isolates the individual steps. In SILAR method film thickness can be easily controlled directly by adjusting the number of the deposition cycles.

C. CO- Precipitation Method

The co-precipitation process has been used for the preparation of nano or submicro powders in a variety of metal oxides using inorganic salts as precursors. The synthesis of magnetite (γ-Fe_2O_3) nanoparticles with controlled size has long been of scientific and technological interest. However, uniform physical and chemical properties of magnetite nanoparticles greatly depend upon the synthesis route, and how to develop a simplistic and effective way to synthesize magnetite particles with high dispersion and narrow size distribution remains a challenge [7].

III. PURE AND DOPED Fe_2O_3 PURE

The Fe_2O_3 is most common oxide of iron has the important magnetically properties too. From the view - point of the basic research, iron (III) oxide is a convenient compound for the general study of polymorphism and the magnetic and structural phase transitions of nanoparticles. The existence of amorphous Fe_2O_3 and four polymorphs (alpha, beta, gamma and epsilon) is well established.

A. Fluorine Doped Fe_2O_3 Nanostructure

G. Kararo et.al presented a single-stage plasma enhanced chemical vapor deposition (PE-CVD) strategy in the synthesis of the fluorine doped Fe_2O_3 nanometer. The characterization of Fluorine doped Fe_2O_3 was done by X-ray diffraction, field emission-scanning electron microscopy, X-ray electro-spectroscopy, secondary ion mass spectrometry and transmission electron microscopy. An appropriate choice of processing parameters enables the selective formation of α-Fe_2O_3 nanometry, which is characterized by a homogeneous f doping, even 100℃. System nanoscale organization and fluorine content together have been achieved separately by separating temperature growth. The use of materials according to the resulting material, from photocatalysis to photo electronics cells and gas sensing, is used favorably with many technical applications [8].

B. Mn Doped Fe_2O_3 Thin Film

M.R. Belkhedkar et.al found that the SILAR method has been successfully used to grow nanocrystalline Mn doped α-Fe_2O_3 thin films onto glass substrates. The structural investigation revealed that, the films are nanocrystalline in nature with rhombohedral structure. The optical studies showed that α-Fe_2O_3 thin film exhibits 3.02eV band gap energy and it decreases to 2.95eV as the Mn doping % in it was increased from 0 to 8 wt, %. The SILAR grown α-Fe_2O_3 film exhibits antibacterial character against staphylococcus aurous bacteria and it increases remarkably with Mn doping [9].

C. ZnO DOPED Fe_2O_3 Nanotube

K. Krishnaveni et.al found that the biosynthesis of Fe_2O_3 nanoparticles gains attention over the past decades due to its ecofriendly nature and provides nanoparticles with controlled size and shape. In this work, Zinc doped Fe_2O_3 nanoparticles are synthesized by co-precipitation method using pedalim murex leaf extract as reducing agent and capping agent. The resulting nano-particles were characterized by UV-Vis, FTIR techniques. XRD analysis shows that synthesized ZnIONPs are in hematite phase, rhombohedral in structure. The antimicrobial and anti diabetic activities of synthesized ZnIONPs are analyzed by disc diffusion and pancreatic α-amy method and it shows that high level of inhibition [10]. D. Sibera compared two methods of synthesis of nanocrystalline ZnO doped withFe_2O_3.The synthesis was carried out using by microwave assisted hydrothermal synthesis and traditional wet chemistry method followed by calcinations. The phase composition of the samples was determined by X-ray diffraction measurements. Depending on the EDX for chemical composition of the samples, hexagonal ZnO, and/or cubic $ZnFe_2O_4$ were identified. The morphology of the received materials was characterized using scanning electron microscopy. Two different structures of agglomerates were observed: a hexagonal structure and spherical. The effect of the iron oxide concentration on specific surface area and density of the samples was determined [11].

D. Ru Doped Fe_2O_3 Nanostructure

Ceboliyozakha Leonard Ndlangamandla et.al have explored that the α-Fe_2O_3 nanorods doped with ruthenium were successfully deposited on fluorine doped tin oxide (FTO) glass substrates using aqueous chemical growth. Using complementary surface investigation techniques, the Ru incorporation in the Ru-α-Fe_2O_3 nanorods was evidenced. The optical band gap was found to be Ru doping concentration dependent: varying from 2.32 to 2.47eV. These band gap values are well suited for the targeted water splitting process without application of an external bias. [12].

E. La Doped A-Fe_2O_3 Nanoparticles

J.Sharmila Justus et.al found that the rare-earth elements are an attractive class of dopant elements, as they give easily trivalent cations that possibly altering the structure and other properties of the parent nanoparticles and creating multifunctional materials because of their *f*-electronic configurations. lanthanum doped hematite (α-Fe_2O_3) nanoparticles were prepared by a facile solution method using iron (III) chloride ($FeCl_3$) as starting precursor and sodium hydroxide (NaOH) as reducing agent without templates at low temperature. The optical absorption spectrum was recorded in the wavelength range of 200-2000 nm and the optical parameters such as absorption coefficient and optical band gap energy of pure and doped Fe_2O_3 nanoparticles were determined. Obtained results are interpreted by considering the impregnation of trivalent La cations that replaced Fe cations of the host structure [13].

Hao Shan et.al have found that the Pure and La-doped (5 wt%, 7 wt% and 10 wt%) α-Fe_2O_3 nanotubes are synthesized by an electro spinning method and followed by calcinations. Compared with pure α-Fe_2O_3 nanotubes and La-doped α-Fe_2O_3 nanotubes exhibit improved acetone sensing properties. The response of 7wt% La-doped α-Fe_2O_3 nanotubes to 50ppm acetone is about 26, which is 10 times larger than the pure α-Fe_2O_3 nanotubes. Moreover, 7 wt% La-doped α-Fe_2O_3 nanotubes show a good selectivity to acetone [14].

F. Aluminum-Doped Fe_2O_3 FILM

Alan Kleiman- Shwaesctein et.al found that the substitution doping can improve the electronic properties of R-Fe_2O_3 for the solar photoelectrochemical (PEC) applications. Generally speaking, non isovalent substitutional doping helps to enhance the electronic conductivity of R-Fe_2O_3. However, it was found that the introduction of strain in the lattice, which is accomplished by isovalent substitutional doping of Aluminum. The dopant atomic concentrations varying from 0 to 10% were prepared by electro deposition method and their performance for photoelectrochemical hydrogen production was characterized. [15].

G. Li-doped Fe_2O_3 FILM

G. Neri et.al found that the Li-doped iron oxide thin films deposited on a porous ceramic substrate by a liquid-phase method (LPD) were investigated as humidity sensors. Large variations in the distance, up to about 4±5 order of magnitude, were observed by changing the relative humidity (RH) between 10 and 90%. The investigated sensors show a quick and reversible response to cyclic variations in the relative humidity. The role of Li on the response to water vapor of iron oxide (α-Fe_2O_3) thin films is discussed [16].

H. Ti DOPED Fe_2O_3

M. V. Nikolic et.al is proposed that the work analyzed the effects of Ti doping on structural and electrical properties of α-Fe_2O_3. When the amount of added Ti was within the solubility degree and XRD, SEM and EDS analysis revealed a homogenous α-Fe_2O_3 structure, with lattice parameters a= 5.03719(3) Å, c=13.7484(1) Å slightly increased due to incorporation of Ti into the rhombohedral α-Fe_2O_3 lattice. Higher amounts of Ti (10 wt. %TiO2) resulted in the formation of pseudobrookite, besides α-Fe_2O_3, confirmed by SEM and EDS analysis. Studies of electric properties in the temperature range 25-225℃ at different frequencies (100 – 1Mz) showed that Ti doping improved electrical conductivity. Impedance analysis was performed using an equivalent circuit, showing one relaxation process and suggestin g dominant grain boundary contribution. [17].

I. Ce-Doped Fe_2O_3

Dean Cardillo et.al found in this study increase the potential of α-Fe_2O_3 nanoparticles for application in cosmetic products as an inorganic ultraviolet filter with cerium doping, a species whose corresponding oxide CeO_2 has also gained significant interest due to a bandgap (3.2eV) comparable to both ZnO and TiO_2. The co-precipitation method was used to synthesize α-Fe_2O_3 particles with 0, 5, 10, 20 and 30mol% doping concentrations of Ce4+, which were subsequently annealed in air. Calculations following ultraviolet absorption spectroscopy yielded a decreasing band gap with increasing cerium doping concentration (2.42-1.63ev), the 10mol% Ce sample exhibited larger (2.51eV) band gap energy, and a absorption profile with a significant increase in attenuation in the ultraviolet region [18].

J. Sn-Doped Fe_2O_3

Michele Orlandi et.al found that the iron (III) oxide applications as anodic material in electro catalysis and photoelectrochemical cells are currently limited by its poor electric properties. To isolate the effect of doping from those of morphology and crystallinity, a devise fabrication method based on radio-frequency magnetron sputtering yielding crystalline hematite at room temperature, thus enhancing the compatibility towards substrates and the potential for application. Doping in the range 1-12% (atomic) induces lattice distortion with cell volume increase and a substantial extension of the visible absorption range due to a band-gap narrowing of about 0.45 eV for the highest doping level. In this study tin doping leads to improved conductivity and to a decreased (up to 1 order of magnitude) interfacial charge transfer resistance, as revealed by electrochemical impedance spectroscopy. [19].

K. Ni-Doped Fe_2O_3

Ying Guo et.al has reported the high-efficiency planar heterojunction perovskite solar cells (PSCs) employing Ni-doped α-Fe_2O_3 as electron-transporting layer (ETL). Due to the small J-V hysteresis behavior, a higher stabilized PCE up to 11.6% near the maximum power point can be reached for the device fabricated with 4 mol% Ni-doped α-Fe_2O_3 ETL compared with the undoped α-Fe O3 based cell (9.2%). Furthermore, a good stability of devices with exposure to ambient air and high levels of ultraviolet light can be achieved. Overall, their results demonstrate that the simple solution processed Ni-doped α-Fe_2O_3 can be a good candidate of the n-type collection layer for commercialization of PSCs. [20].

L. Co Doped Fe_2O_3

Eman Alzahrani et.al have explored that the ferric oxides have drawn significant interest due to their unique properties, relatively low cost, and due to their potential applications in different fields. In this work, cobalt (Co) doped iron oxide (Fe_2O_3) powder , with ceystallin size 36.97 nm was successfully prepared by microwave- hydrothermal process for the first time and characterized using different teachniques such technique such as fourier transform infrared spectroscopy and ultraviolet- visible spectroscopy. The images show mono dispersed particles with a sharp-edged square morphology. It was found that the average size was about 33.3nm for Fe_2O_3 and 36.97 nm for Co-Fe_2O_3. The Co atomic percentage dopants were approximately 5.73%. [21].

M. Activated C Doped Fe_2O_3

Settakorn Upasen et.al found that the development of an adsorbent material with a high capacity for chlorinated gas treatment on α-Fe_2O_3 nanoparticles deposited activated carbon adsorbent was successfully synthesized. The α-Fe_2O_3 NPs synthesis was done by a facile chemical precipitation method using sodium hydroxide (NaOH) as a precipitant agent. The variation of the molar ratio of the reactant and precipitant (i.e. 1:1, 1:1.5, 1:2 by mole) and of the precipitating temperature (i.e. 50, 70, 90°C) were explored. The physical and chemical characteristics of the synthesized samples were examined using various techniques; Fourier Transform Infra-Red (FT-IR) and Ultraviolet- Visible spectrophotometer. The production yield of the synthesized α-Fe_2O_3 and α- Fe_2O_3/GAC samples was also reported [22]

IV. CONCLUSION

In this report α- Fe_2O_3 is synthesized by different methods sol- gel method, SILAR method, co-precipitate method, thermal evaporation deposition, anodic alumina template, biological macromolecular and the effect of pure doped Fe_2O_3 which is characterized by different techniques such as X-ray diffraction for structural, SEM for morphology, EDX for chemical composition, FTIR, Photo activation and TEM etc. Doping of transition metal ions into Fe_2O_3 can improve the properties of nano crystalline materials by narrowing the energy-band gap and inhibiting electron-hole recombination. In addition, several doping species have been introduced into α-Fe_2O_3 in attempts to control materials properties, including F, Mn, Zn, Ru, La, Al, Li, Ti, Ce, Sn, Ni, Co, C and these applications are water splitting, photoelectrochemical, solar cell, humidity sensors, and gas sensors etc.

REFERENCS

[1] M. Chirita, I. Grozescu (2009) "Fe_2O_3- Nanoparticles, Physical properties and Their Photochemical and Photoelectrochemical Applications" volume 54(68), 1.

[2] Debasish Sarkar, Gobinda Gopal Khan, Ashutosh K. Singh, and Kalyan Mandal "High-Performance Pseudocapacitor Electrodes Based on αFe_2O_3/ MnO_2 Core−Shell Nanowire Heterostructure Arrays"

[3] Davide Barreca, Giorgio Carraro, Alberto Gasparotto, Chiara Maccato, Francesca Rossi, Giancarlo Salviati, Massimo Tallarida, Chittaranjan Das, Fernando Fresno, Dorota Korte, Urska Lavrencic Stangar, Mladen Franko, and Dieter Schmeisser (2013) "Surface Functionalization of Nanostructured Fe_2O_3 Polymorphs: From Design to Light-Activated Applications" journal of Appl. Mater. Interfaces.

[4] Xiumei Feng, Guanqi Hu and Jianqiang Hu (2009) "Solution-phase synthesis of metal and/or semiconductor homojunction/heterojunction nanomaterials" journal of nanoscale, 3,.

[5] Oana Pascu, Elisa Carenza, Martí Gich, Sònia Estradé, Francesca Peiró, Gervasi Herranz, and Anna Roig (2012) "Surface Reactivity of Iron Oxide Nanoparticles by Microwave- Assisted Synthesis; Comparison with the Thermal Decomposition Route" J. Phys. Chem. C, 116, 15108−15116.

[6] S. F. Hasany*, I. Ahmed, Rajan J, A. Rehman , (2012) " Systematic Review of the Preparation Techniques of Iron Oxide Magnetic Nanoparticles" Journal of Nanoscience and Nanotechnology , 2(6): 148-158

[7] M. Farahmandjou and F. Soflaee, (2015) "Synthesis and Characterization of α-Fe_2O_3 Nanoparticles by Simple Co-Precipitation Method" Journal of Phys. Chem. Res., Vol. 3, No. 3, 193-198.

[8] G. Carraro, A. Gasparotto, C. Maccato, E. Bontempi, O. I. Lebedev, S. Turner, C. Sada, L. E. Depero, G. Van Tendelood and D. Barreca (2015) "Fluorine doped Fe2O3 nanostructures by a one-pot plasma-assisted strategy" journal is a the royal society of chemistry , 3, 23762 .

[9] M.R. Belkhedkar, A.U. Ubale, Y.S. Sakhare, Naushad Zubair, M. Musaddique,(2015) "Characterization and antibacterial activity of nanocrystalline Mn doped Fe_2O_3 thin films grown by successive ionic layer adsorption and reaction method" j.jaubas. 03.001.

[10] K.Krishnaveni, A.S. Sakthi athithan, J.Jeyasundari, Y.Brightson Arul Jacob, D.Renuga (2018) "Biosynthesis and characterization of zinc doped iron oxide nanoparticles from pedalium murex and its new avenues in pharmacological applications" Journal of Pharmacy and Biological Sciences 13, 6 , PP 67-74.

[11] D. Siberaa, R. Jedrzejewskia, J. Mizerackib, A. Preszb, U. Narkiewicza and W. Łojkowskib (2009) "Synthesis and Characterization of ZnO Doped with Fe2O3- Hydrothermal Synthesis and Calcinations Process" Journal of Nanotechnology Vol. 116.

[12] Ceboliyozakha Leonard Ndlangamandla, Krish Bharuth-Ram, Osman Muzi Ndwandwe, Balla Diop Ngom, and Malik Maaza (2015)"Aqueous Synthesis of Ru Doped Hematite Nanostructures: A Morphological, Structural, Optical, and Magnetic Study" Journal of Nanoparticles Volume, Article ID 654587, 7.

[13] J. Sharmila Justus, S. Dawn Dharma Roy, A. Moses Ezhil Raj (2016) " Influence of Lanthanum Doping on the Structural and Optical Properties of Hematite Nanopowders" Journal of Applied Science and Engineering Methodologies Volume.2, No.3,Page.272-277.

[14] Hao Shana, Changbai Liub, Li Liua, Shouchun Li a, Lianyuan Wanga, Xiaobo Zhanga, Xiaoqing Boa, Xiao Chia (2013)"Highly sensitive acetone sensors based on La-doped α-Fe_2O_3 nanotubes" journal of Sensors and Actuators B 184, 243–247.

[15] Alan Kleiman- Shwarsctein, Muhammad N. Huda, Aron Walsh, Yanfa Yan, Galen D. Stucky, Yong-Sheng Hu, Mowafak M. Al-Jassim, and Eric W. McFarland,(2010) "Electrodeposited Aluminum-Doped Fe_2O_3 Photoelectrode: Experiment and Theory" journal of Chem. Mater, 22, 510–517.

[16] G. Neria, A. Bonavitaa, S. Galvagnoa, C. Paceb, S. Patane, A. Arenab (2001)"Humidity sensing properties of Li iron oxide based thin flms" journal of Sensors and Actuators B 73, 89 94.

[17] M. V. Nikolic, D. L. Sekulic, N. Nikolic, M. P. Slankamenac, O. S. Aleksic, H. Danninger, E. Halwax, V. B. Pavlovic, P. M. Nikolic, (2013) "Structural and Electrical Properties of Ti Doped α-Fe_2O_3" Science of Sintering, 45, 281-292

[18] Dean Cardillo,Konstantin Konstantinov, Thierry Devers (2012) "Synthesis and Characterization of Ce-doped α-Fe2O3 Nanoparticles for Ultraviolet Protection in Cosmetic Products" Research Gate.

[19] Michele Orlandia, Alberto Mazzia,1, Giacomo Arbana, Nicola Bazzanellaa, Paolo Rudatisb, Stefano Caramorib, Nainesh Patelc, Rohan Fernandesc, Carlo A. Bignozzib, Antonio Miotelloa (2016) "On the effect of Sn-doping in hematite anodes for oxygen evolution" journal of Electrochimica Acta 214 345–353.

[20] Ying Guoa,Tao Liua, Ning Wanga, Qiang Luoa, Hong Linc, Jianbao Lib, Qinglong Jiangd, Lili Wue, Zhanhu Guoe, (2017) "Ni-doped α-Fe_2O_3 as electron transporting material for planar heterojunction perovskite solar cells with improved efficiency, reduced hysteresis and ultraviolet stability" journal of nano energy 38, 193–200.

[21] R. Suresh, L. Vijayalakshmi, A. Stephen and V. Narayanan (2010). "Hydrothermal Synthesis and characterization of Cobalt doped α-Fe_2O_3." research gate

[22] Settakorn Upasen (2018) "Activated carbon-doped with iron oxide nanoparticles (α-Fe_2O_3 NPs) preparation: particle size, shape, and impurity" Vol.11 No.10, pp 33-40,