Analysis of Synthesis and Magnetic Characterization of Iron Oxide

H. G. Kale

Lecturer & Research Student – M.S.S. Arts, Commerce & Science College, Jalna

Abstract – In the context of the diminishing fossil energy resources and global warming, much research is focused on sustainable energy sources. The research that is presented in this category as it contributes to the development of a device that stores solar energy into a chemical fuel. This device is based on the photoelectrolysis of water in a tandem-cell that produces hydrogen and oxygen under illumination of sunlight.literature The aim of this paper is to improve the photooxidation activity of iron oxide photoanodes in order to improve the practical conversion efficiency of the tandem-cell. For this purpose we have prepared thin films of nano-structured iron oxide with various deposition methods and characterized their performance on the photooxidation of water.

Keywords: Development, Chemical, Improve, Iron Oxides, Performance, Technique, Synthesis

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INTRODUCTION :

Materials based on the assembly of nanoparticles, nanotubes, and nanofibrils exhibit different electrical, magnetic, electro optical, and chemical properties. In the case of nanoparticles, their behavior arises from the large fraction of atoms which reside on their surface and from the finite number of atoms in each crystalline core. It was in magnetic materials that such finite-size effects were first evidenced. Later, they were also noted in nonmagnetic materials such as semiconductors. the ability to assemble such materials with uniform and specified internal diameters into well-ordered superstructures is crucial for further developments. To this purpose, anodically grown alumina nanoporous membranes were used by Martin for preparing nanoscale tubes and fibrils. Solid or hollow microcylinders of desired materials, such as polymers, metals, and carbons, semiconductors, and metal oxides, have been obtained in the membrane pores, showing a number of interesting features. Particles too can be inserted easily into the pores, filling them and forming particle nanowires. Among the most interesting new aspects of monodimensional superstructures are their magnetic properties. Perpendicular magnetic media (with preferred magnetization perpendicular to the recording plane) is a field of great investigation. Magnetic media with perpendicular anisotropy allow a smaller bit size, and therefore, greater recording densities can be achieved. We report on the preparation, structure, morphology, and magnetic properties of magnetite particle nanowires and iron oxide tubes and fibrils obtained in the pores of alumina and polycarbonate nanoporous membranes.[1,2]

Iron oxides are one of the most important transition metal oxides of technological importance. Sixteen pure phases of iron oxides, i.e., oxides, hydroxides or oxy-hydroxides are known to date. These are Fe(OH)3, Fe(OH)2, Fe5HO84H2O, Fe3O4, FeO, five polymorphs of FeOOH and four of Fe2O3. Characteristics of these oxide compounds include mostly the trivalent state of the iron, low solubility and brilliant colors.

REVIEW OF LITERATURE:

Synthesis of iron oxides in the nano range for various applications has been an active and challenging area of research during the last two decades. The processes include careful choice of pH, concentration of the reactants, temperature, method of mixing, and rate of oxidation. The morphology of the iron oxide particles depends on the competition between several processes like nucleation, growth, aggregation and adsorption of impurities. However, in many cases it is not possible to precipitate specific iron oxide particles directly in the desired size and shape. Instead, the synthesis must be done by the transformation of another iron oxide precursor particle. The sensitivity of the preparative method complicates both the reproducibility and scale up of the process. Recently, several colloidal chemical synthetic procedures have been developed to produce mono-

disperse nanoparticles of various materials. These oxides find applications as catalysts, sorbents, pigments, flocculants, coatings, gas sensors, ion exchangers and for lubrication. Iron oxide nano-composites have potential applications in areas such as magnetic recording, magnetic data storage devices, toners and inks for xerography, and magnetic resonance imaging, wastewater treatment, bioseparation, and medicine. Below a critical size, Fe2O3 nanoparticles can be used for niche applications like transparent iron oxide pigments, due to their durability, shade, UV absorption and added value. Careful control of the preparation process of transparent iron oxide pigments results in the formation of pigments with very small primary particle sizes. When fully dispersed, they do not scatter light and are hence completely transparent. A brief literature scan is reported in the present review considering the application of various forms of nano iron oxides in the above fields.[3,4].

CHEMICAL PRECIPITATION:

The precipitation technique is probably the simplest and most efficient chemical pathway to obtain iron oxide particles. Iron oxides (FeOOH, Fe3O4 or γ-Fe2O3) are usually prepared by addition of alkali to iron salt solutions and keeping the suspensions for ageing. The main advantage of the precipitation process is that a large amount of nanoparticles can be synthesized. However, the control of particle size distribution is limited, because only kinetic factors are controlling the growth of the crystal. In the precipitation process, two stages are involved i.e., a short burst of nucleation occurs when the concentration of the species reaches critical super saturation, and then, there is a slow growth of the nuclei by diffusion of the solutes to the surface of the crystal. To produce mono disperse iron oxide nanoparticles, these two stages should be separated; i.e., nucleation should be avoided during the period of growth. Size control of mono dispersed particles must normally be performed during the very short nucleation period, because the final particle number is determined by the end of the nucleation and it does not change during particle growth. A wide variety of factors can be adjusted in the synthesis of iron oxide nanoparticles to control size, magnetic characteristics, or surface properties. A number of studies have dealt with the influence of these different factors. The size and shape of the nanoparticles can be tailored with relative success by adjusting pH, ionic strength, temperature, nature of the salts (perchlorates, chlorides, sulfates, and nitrates), or the Fe(II/Fe(III) concentration ratio. Pure goethite was synthesized using 1 M ferric nitrate solution and 10 M sodium hydroxide solutions under controlled conditions. Ferric nitrate solution was vigorously stirred at room temperature with the simultaneous addition of 10 M sodium hydroxide solution until the pH of the solution reached 12–12.5. In order to obtain Cu, Ni or Co doped goethites, the respective sulphate solutions were mixed with ferric nitrate solution prior to alkali addition. Further studies were carried out to convert the goethite to primarily magnetite. Cerium-doped goethite samples in the nano range were prepared through aqueous precipitation by varying Ce(IV)/Fe(III) atomic ratio in the range of 0.015 to 0.07. Irrespective of the amount of cerium oping, all the samples showed only goethite as the crystalline phase. Doping of cerium in goethite affected the peak positions (positive shift 0.02–0.04), crystallinity and lattice parameters of goethite and perturbed the particle structure of α-Fe2O3 during transformation process. The lattice image of a typical sample with Ce(IV)/Fe(III) atomic ratio 0.035:1, indicated that the goethite grew along (1 1 0) plane and there was no separate plane of cerium phases present in goethite structure. On heating the samples to 400oC, goethite was completely transformed to hematite while the crystallization of CeO2 was only partial. Further calcination to 800oC resulted in the formation of two distinct phases of CeO2 and α-Fe2O3 as observed from XRD pattern. Lattice image of the same sample revealed intergrowth of (1 1 1) plane of CeO2 along (0 1 2) plane of α-Fe2O3. However, CeO2 crystallites did not separate from α-Fe2O3. Nano-structures of CeO2–α Fe2O3 oxides were retained even on calcination at 800oC. The first controlled preparation of superparamagnetic iron oxide particles using alkaline precipitation of FeCl3 and FeCl2 was performed by [9].The process engineered by rapid synthesis of homogeneous γ-Fe2O3 nanoparticles allowed for coating by a wide range of monomeric species, such as amino acids, R-hydroxyacids (citric, tartaric, and gluconic acids) hydroxamate (arginine hydroxamate), dimercaptosuccinic acid (DMSA),or phosphoryl choline. Adding increasing amounts of citrate ions in the Massart process allowed for a decrease in the diameter of citrate-coated nanoparticles from 8 to 3 nm. Through such a process of size selection using NaCl as an extra electrolyte, the size distribution of the 7 nm citrate nanoparticles obtained by the Massart process could be reduced. studied the influence of the Fe2+/Fe3+ ratio on the composition, size, morphology, and magnetic properties of co-precipitated nanoscale particles. also studied the influence of different parameters, including the iron media and the iron concentration. In their setup, the most important factor is the Fe2+/Fe3+ molar ratio. The mean size increased with the Fe2+/Fe3+ ratio, whereas the preparation yield decreased. These results were corroborated by literature data. The dependence of particle mean size of magnetite upon the acidity and the ionic strength of the precipitation medium has been reported. The higher the pH and ionic strength, the smaller the particle size and size distribution width will be, because these parameters determine the chemical composition of the crystal surface and consequently the electrostatic surface charge of the particles investigated the

dependence of the ionic strength of the reaction solution on the formation of magnetite. The magnetite prepared with the addition of 1 M NaCl aqueous solution created iron oxide nanoparticles 1.5 nm smaller than those formed without its presence. In addition, these smaller nanoparticles formed in the higher ionic strength solutions displayed lower saturation magnetization (63emu/g) than those prepared in NaCl-free solutions (71 emu/g). Many factors may influence the size of the nanoparticles. For example, an increase of the mixing rate tends to decrease the particle size. On the contrary, injection flux rates did not seem to have a preponderant influence on the nanoparticle synthesis. Several researchers report the use of an elevated reaction temperature and suggest its significance in optimal crystal formation. Bubbling nitrogen gas through the solution not only protected against critical oxidation of the magnetite but also reduced the particle size when compared to methods without oxygen removal[10].

1-Sol-Gel and forced hydrolysis techniques- Solgel processing route is a wet chemical process for the synthesis of colloidal dispersion of inorganic and organic inorganic hybrid materials. The synthesis of metal oxides by sol-gel synthesis has proven extremely versatile since it allows the formation of a large variety of metal oxides at relatively low temperatures via the processing of metal salt or metal alkoxide precursors. The structure and composition of nano oxides formed by sol-gel method depend on the preparation condition, the nature of the precursors, the ion source and pH. It offers advantages such as:

(i) Tailor-made materials due to good process control,

(ii) Homogeneous multicomponent systems due to mixing in liquid medium,

(iii) Low temperature for materials processing. This process is based on the hydroxylation and condensation of molecular precursors in solution, originating a bsolQ of nanometric particles.

Further condensation and inorganic polymerization leads to a three dimensional metal oxide network denominated wet gel. The main parameters that influence the kinetics, growth reactions, hydrolysis, condensation reactions, and consequently, the structure and properties of the gel have been reported. The Sol-Gel synthesis of iron oxide particles was carried out from condensed ferric hydroxide gels, obtained from $FeCl_3$ solutions in NaOH. After aging the gel at 100°C for 8 days, mono-disperse pseudo-cubic α-Fe_2O_3 particles were obtained. The particles were poly-crystals composed of much smaller subunits. The reaction proceeded through a two-step phase transformation from precipitated $Fe(OH)_3$ gel to a fibrous β-FeOOH and finally to α-Fe_2O_3. The widely used method to synthesize iron oxy-hydroxide consists of the hydrolysis of Fe^{3+} cations. However, aging of the sol prepared by pouring fresh ferric solutions into concentrated NaOH or KOH solutions has to take place at 60–80°C for a period of time ranging from a few days to several weeks. As referred by Cornell and Schwertmann (1996), particles formed by the oxidation of Fe^{2+} solutions at neutral conditions are usually much less developed and the crystals are smaller than those obtained in alkaline Fe^{3+} solutions. Moreover, oxidation of the ferrous salt solutions by air bubbling yields one or several of the following products: goethite (α-FeOOH), lepidocrocite (γ-FeOOH), magnetite (Fe_3O_4) and hematite (α-Fe_2O_3). The crystallization of Fe-oxides are strongly affected by the anions or cations adsorbed by ligand exchange. Furthermore, various phases formed during the oxidation of aqueous ferrous systems suggest that the oxidation rate, which can be influenced by pH, temperature and other additives (anions or cations) present in the system, is the dominant factor in determining the hydrolysis product. For the advanced particulate materials, size and shape are often as crucial as crystal structure in determining the performance. Using the forced hydrolysis technique α-FeOOH, γ-FeOOH, and Fe_3O_4 with different morphological properties were produced under a wide variety of synthesis conditions. Acicular goethite particles were obtained after aerial oxidation of iron(II) solutions at 20°C – 80°C in acidic conditions. Depending on the temperature, the length of the particles varied between 0.1 – 0.5 μm and the aspect ratio lay between 5 and 10. Polydisperse magnetite micro crystals were prepared in neutral or basic pH at 90°C by the addition of KNO_3 to $FeCl_2$ and KOH solution. Spindle-type colloidal hematite particles of narrow size distribution were prepared in a similar way by forced hydrolysis of ferric chloride solution in the presence of phosphate and hypophosphate at 100°C for 2 to 7 days. These hematite particles can easily be converted in maghemite particles of the same size and shape by heating under hydrogen gas flow followed by re-oxidation with air. Plate-like hematite particles of about 5 – 10 μm in diameter were obtained by aging basic ferric salt solutions in the presence of either EDTA or KNO_3 or triethanolamine and hydrazine or hydrogen peroxide.

2-Electrochemical methods - In this method electrons act as reactant. It is an environmental friendly process with no pollution. However, the costly platinum is used as an electrode and not for reuse in aqueous solution. The electrochemical synthesis of nanosized particles of γ-Fe_2O_3 of about 20 nm in non-aqueous medium was reported by [5]. They used stainless steel plate as anode and cathode respectively, the solvent used can be re-used. prepared 3-8 nm maghemite particles by electrochemical method from an iron electrode in an aqueous solution of DMF and cationic surfactants. Here current density

controlled the particle size. Electrochemical deposition under oxidizing conditions has been used to prepare nanowires of by [6-8].

3-Hydrothermal technique - Hydrothermal technique is defined as any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions. Hydrothermal treatment of iron salt could generate iron oxides when the applied conditions are appropriate. The hydrothermal preparation of goethite and hematite from amorphous iron(III) hydroxide was studied at various pH values in the temperature range 100–200oC. In the pH range 8.0–10.0, goethite and hematite were formed. In the range 10.5– 10.8 only goethite was formed, and in the pH range 0.8–2.6 hematite was the only reaction product. The decomposition of α-FeOOH to α -Fe2O3 in neutral and weakly alkaline hydrothermal solution was observed at 150oC+ 200C, and this temperature was suggested to be the upper temperature for the formation of the α-FeOOH minerals. However, the transformation is also strongly pH dependent so that the transformation temperature increased by 25K per pH unit. The first in situ investigation of the rate of crystallization of amorphous iron(III) hydroxide to α-Fe2O3 and α - FeOOH was made at hydrothermal conditions using neutron powder diffraction. reported a facile and environmental friendly ultrasonic-assisted hydrothermal route for preparation of goethite flower structures using Fe nano-powders at low temperature (850C). The flower structure consisted of tens of hundreds of nano wires and such structures could further selfassemble with the flake with micro size area. Structural, morphological, and elemental analysis revealed that the products consisted of flower-like structures with high structural uniformity, good crystal quality, and high yields. Magnetic measurements showed that the as-obtained goethite flowers exhibited weakly ferromagnetic characteristics at room temperature, which were quite different from those of the corresponding bulk materials.

4-Surfactant mediated /template synthesis - Supramolecular surfactant-controlled method for the synthesis of mesostructured iron oxides has acquired more importance in recent scenario, which uses neutral or charged template molecules. Hexa-decylsulfonic acid mixed at room temperature with an aqueous solution of FeCl2 yielded a hexagonal structured iron oxide with a d-spacing of 3.75 nm. In a similar approach, lamellar iron oxide/surfactant composites were produced by the controlled precipitation and hydrolysis of aqueous iron cations into self-assembled iron/surfactant arrays. These composites were obtained by mixing iron(II) or iron(III) salt solutions with diluted aqueous solutions of sodium n-alkyl sulfates at room temperature. Lamellar iron(hydro) oxyhydroxide-surfactant composites were also prepared by adding ammonia to a FeCl3 solution followed by mixing with the sodium n-alkyl sulfate template. By adjusting the reaction conditions, composites with inorganic walls from about 10 – 26 Å were produced in a controllable manner. Not only long-chain surfactant templates can influence the morphology of the iron oxide particles, it is well known that inorganic anions like chloride, phosphate or sulfate have a strong influence on particle size and shape. α-Fe2O3 nanorods and nanotubes have been synthesized using different surfactant i.e., polyisobutylene bissuccinimide (L113B) or surfactant Span80. Highquality one dimensional products were obtained with aqueous butanol solution as the solvent and carbamide as the base, giving rise to single-crystalline products at 150°C.

5-Flow injection syntheses - Reaction zone confinement in different “matrices”, such as emulsions, etc., has been used to produce particles with narrow size distributions and, in some cases, to tailor the particle morphology. However, a specific design of the reactor can serve as an alternative to the “matrix” confinement. developed a novel synthesis of magnetite nanoparticles based on a flow injection synthesis (FIS) technique. The technique consisted of continuous or segmented mixing of reagents under laminar flow regime in a capillary reactor. The FIS technique has some advantages, such as a high reproducibility because of the plug-flow and laminar conditions, a high mixing homogeneity, and an opportunity for a precise external control of the process. The influence of chemical parameters and conditions on the properties of the material was investigated. The obtained magnetite nanoparticles had a narrow size distribution in the range of 2-7 nm.

CONCLUSION:

In this paper we explored novel materials set and structures, silicon photoanode catalyzed by iron-oxide thin film to efficiently split water molecules into oxygen and hydrogen. Thin iron-oxide film was deposited on silicon substrate by low temperature atmospheric pressure CVD to catalyze oxygen evolution reaction. When iron-oxide film was sufficiently thin, around 10 nm or less, otherwise nonresponsive silicon photoanode showed a high photocurrent at a decent overpotential. Parametric studies revealed that the photoresponses become effective iron-oxide film is thin, titanium content is high and operation pH is high.

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