

Fe₂O₃ – Nanoparticles, Physical Properties and Their Photochemical And Photoelectrochemical Applications

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Abstract: This paper outlines the main properties of iron oxide nanoparticles and their various applications. Many novel approaches are described in the use of photoelectrochemistry such as solar energy conversion, water splitting, photocatalysts for the removal of organic and inorganic species from aqueous or gas phase. The nanocrystalline semiconductor thin films are shortly described. Also, we describe briefly the core shell and core-shell-shell structures. Nnanocomposites structures with particularly interesting architectures in photocatalysts is presented. Extremely modern various shapes and dimensions of iron oxide nanomaterials are reminded, such as nanowires, nanorods, nanotubes, hollow fibers, snowflake-like, and ring-like.

Keywords: photoelectrochemical, photocatalyst, antiferromagnetic, core-shell, core-shell-shell, transparent conducting substrate (TCO)

1. Introduction

The iron with his 26 protons in nucleus is a component of *transition elements* group. Isotopes like ⁵⁴Fe, ⁵⁶Fe, ⁵⁷Fe and ⁵⁸Fe are extremely stable. It is the last element produced in the nucleus of stars (only in the stars bigger than five solar mass) through nuclear fusion, so that the iron is the heaviest element created outside the cataclysmic supernova processes. In abundance, is the tenth in the Universe and the forth on the Earth (the second metal after aluminum). The Earth comprises 80% Iron in a 2160 miles radius sphere. Iron is widely spread in the nature in different chemical compounds. The interesting question about transition metals is that their valence electrons or the electrons they use to combine with other elements are to be found in more than one shell. This is the reason why, they often exhibit several common oxidation states. Normally, the iron has eight electrons on valence shield and due to oxygen's electronegativity it can form bivalent and trivalent combinations. The iron oxide (Fe₂O₃), the most common oxide of iron has the important magnetically properties too. From the viewpoint 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 Fe₂O₃ and four polymorphs (alpha, beta, gamma and epsilon) is well established [1]. The most frequent polymorphs structure "alpha" (hematite) having a rhombohedral-hexagonal, prototype corundum structures and cubic spinel structure "gamma" (maghemite) have been found in nature. At a temperature of 650 °C, hematite turns into Fe₃O₄ with a high energy loss. Hematite has strongly antiferromagnetic properties. Gamma Fe₂O₃ (maghemite) is the ferrimagnetic cubic form of Fe(III) oxide and it differs from the inverse spinel structure of

magnetite through vacancies on the cation sublattice. In time, at room-temperature, the maghemite turns into hematite crystalline structure. Maghemite has the same crystalline structure like Fe₃O₄ (magnetite). Main distinct features of maghemite are the presence of vacancies in Fe position with symmetry reduction. The other polymorphs, the cubic bixbyite structure "beta" and orthorhombic structure "epsilon", as well as nanoparticles of all forms, have been synthesized and extensively investigated in recent years [1,2]. Epsilon is a transition phase between hematite and maghemite. The first scientific reports about epsilon Fe₂O₃ was published in 1934 (Forestier and Guiot-Guillain). The detailed structural characterization of epsilon phase was published by Tranc in 1998 and by Klemm and Mader later. Until now, the way to produce epsilon Fe₂O₃ is gamma->epsilon->alpha Fe₂O₃. Beta Fe₂O₃ with his cubic bixbyite structure has paramagnetic properties. Gamma and epsilon type Fe₂O₃ are ferromagnetic; alpha Fe₂O₃ is a canted antiferromagnetic while beta type Fe₂O₃ is a paramagnetic material. Maghemite Fe₂O₃ is biocompatible and therefore is one of the most extensively used biomaterials for different applications like cell separation, drug delivery in cancer therapy, magnetic induced hyperthermia, MRI contrast agent, immunomagnetic separation IMC and others. Generally, the semiconductor properties of the hematite are extremely useful in solar energy conversion, photocatalyse, water splitting and the magnetic properties of maghemite play an important role in different applications of health care. For this purpose, a large number of materials in bulk as well as in the form of nanoparticles have been created for a variety of photochemical and photoelectrochemical applications.

In this paper, we summarize the main features of photochemical photoelectrochemical applications, where

semiconductor properties of iron oxide nanoparticles are in use.

2. AlfaFe₂O₃-Hematite, physical properties

Hematite has the same crystallographic structure like (6:4) alpha Al₂O₃ - corundum. The anions have a hexagonal closed packed structure (characterized by the regular alternation of two layers; the atoms in each layer lie at the vertices of a series of equilateral triangles, and the atoms in one layer lie directly above the centers of the triangles in neighboring layers) and the cations occupy 2/3 of the octahedral sites [3]. In other words, the oxygen ions occupy hexagonal sites and the iron ions are situated only in the surrounding octahedral sites.

As distances between atoms are rising with temperature, hematite magnetization depends strongly on this parameter. Therefore antiferromagnetic hematite nanoparticle deserves a special attention, due to the fact that is not a typical ferromagnet [4].

Below 260 K the magnetic arrangement has Fe³⁺ spins directed along the [111] axis and paired across the shared octahedral 260 K, the spins become essentially localized in (111) sheets face. However, the spins have canted slightly out of the plane, generating a weak ferromagnetic moment along the [111] axis. In addition to the antiferromagnetism below 260 K the hematite exhibits weak ferromagnetism above 260 K. This low temperature transition is called the Morin transition-T_M. The Morin temperature has been found to be strongly dependent on the size of the particles, generally decreasing with it and tending to disappear below a diameter of ~8 (nm) for spherical particles [7]. Under 8 (nm), the hematite nanoparticle has superparamagnetic properties but these dimensions are strongly dependent of the synthesis methods. Superparamagnetic hematites with 20 (nm) radius have been reported.

The hematite photoelectrochemical properties were intensively studied in the last years, especially in water splitting, photovoltaic effects, photocatalytic effects. The biggest challenge is to produce cheap semiconductors with a low band gap and large absorption capacity from solar spectrum. Hematite has an absorption spectrum in visible between 600 and 295(nm) [4]. Undoped nFe₂O₃ was intensively studied [4] and the efficiency in water electrolyze was 2%. In [4] an efficient coupling between n and p-hematite is presented. Type p-hematite was obtained by spray-pyrolysis method. In literature, the magnesium is the most studied p-dopant for hematite, as well as Ca and Ti which can be used for p-doping hematite obtaining. New dopants like Cu, Ca, Mg, Ni, Zr, Zn, are described in the literature lately. Photocurrent generation in nanostructured thin films was presented by many [5, 6, 9, 10]. The main differences between magnetite and maghemite are the presence of Fe II in magnetite and the presence of cation vacancies in maghemite [14]. The ionic radius of Fe (II) is larger than of Fe (III) so that the Fe(II)-O bond is longer and weaker than Fe(III)-O bond. Since the acid dissolution involves the breakdown of the Fe-O bond, the dissolution of magnetite is faster than the maghemite one [14].

Fe₂O₃ has ten percent lower magnetic properties than magnetite Fe₃O₄ and a lower density than hematite. Cherepy [13] carried out ultra fast studies of photoexcited electron dynamics in both maghemite and hematite semiconductor nanoparticles. They found that hematite had an absorption spectra with 200, 230, 285 and 340, extending to 560 (nm) corresponding to 6.2; 5.4; 4.4; 3.6 and 2.2 (eV) respectively [5].

Maghemite has a similar crystalline structure to magnetite and the same chemical composition as hematite being a metastable phase between magnetite and hematite. In the crystalline structure of magnetite and maghemite, oxygen ions are cubic close packed with both octahedral and tetrahedral sites occupied by iron, whereas in hematite, oxygen ions are hexagonally close packed, and iron is present only in octahedral sites. The main distinct feature of maghemite is the presence of vacancies in Fe sites paralleled with crystal symmetry loss confirmed by RX diffraction. At room temperature, the magnetic moment of bulk gamma type Fe₂O₃ is ~430 (emu/cc) and the magnetic moment of alpha type Fe₂O₃ is very small (~1emu/cc) [3]. Under 15nm [15], gamma Fe₂O₃ nanoparticles become superparamagnetic. Due to special magnetic properties, maghemite can be used with success for a variety of medical purposes: cell separation, drug delivery in cancer therapy, magnetic induced hyperthermia, MRI contrast agent, immunomagnetic separation IMC as well as other applications. The absorption spectra for maghemite has been identified at 200 and 285 (nm), corresponding to 6.2 and 5.4 (eV) respectively. The optic value of maghemite band gap is 2.3 (eV) [6]. The photodissolution process of maghemite, constitutes a powerful limit in use of this material in photoelectrochemical applications.

2.1 Photochemistry and Fermi level

An important concept in discussion of solid state materials is the Fermi level. This concept is presented very clear by Adrian W. Bott in [17] and we transcribe here. *Fermi level* is defined as the energy level at which the probability of occupation by an electron is 1/2; for example, for an intrinsic semiconductor the Fermi level lies at the mid-point of the band gap. Doping changes the distribution of electrons within the solid, and hence changes the Fermi level. For a *n*-type semiconductor, the Fermi level lies just below the conduction band, whereas for a *p*-type semiconductor it lies just above the valence band. We now need to consider what happens at the (idealized) interface between a semiconductor electrode and an electrolyte solution. In order for the two phases to be in equilibrium, their electrochemical potential must be the same. The electrochemical potential of the solution is determined by the redox potential of the electrolyte solution, and the redox potential of the semiconductor is determined by the Fermi level. If the redox potential of the solution and the Fermi level do not lie at the same energy, a movement of charge between the semiconductor and the solution is required in order to equilibrate the two phases. The excess charge that is now located on the semiconductor does not lie at the

surface, as it would for a metallic electrode, but extends into the electrode for a significant distance (10^2 - 10^3 Å). This region is referred to as the *space charge region*, and has an associated electrical field. Hence, there are two double layers to consider: the interfacial (electrode/electrolyte) double layer, and the space charge double layer. For an *n*-type semiconductor electrode at open circuit, the Fermi level is typically higher than the redox potential of the electrolyte, and hence electrons will be transferred from the electrode into the solution. Therefore, there is a positive charge associated with the space charge region, and this is reflected in an upward bending of the band edges. Since the majority charge carrier of the semiconductor has been removed from this region, this region is also referred to as a *depletion layer*. For a *p*-type semiconductor, the Fermi level is generally lower than the redox potential, and hence electrons must transfer from the solution to the electrode to attain equilibrium. This generates a negative charge in the space charge region, which causes a downward bending in the band edges. Since the holes in the space charge region are removed by this process, this region is again a depletion layer. As for metallic electrodes, changing the potential applied to the electrode shifts the Fermi level. The band edges in the interior of the semiconductor (i.e., away from the depletion region) also vary with the applied potential in the same way as the Fermi level. However, the energies of the band edges at the interface are not affected by changes in the applied potential. Therefore, the change in the energies of the band edges on going from the interior of the semiconductor to the interface, and hence the magnitude and direction of band bending, varies with the applied potential. There are three different situations to be considered:

a) At a certain potential, the Fermi energy lies at the same energy as the solution redox potential. There is no net transfer of charge, and hence there is no band bending. This potential is therefore referred to as the *flatband potential*.

b) Depletion regions arise at potentials positive of the flatband potential for an *n*-type semiconductor and at potentials negative of the flatband potential for a *p*-type semiconductor.

c) At potentials negative of the flatband potential for an *n*-type semiconductor, there is now an excess of the majority charge carrier (electrons) in this space charge region, which is referred to as an *accumulation region*. An accumulation region arises in a *p*-type semiconductor at potentials more positive than the flatband potential. The charge transfer abilities of a semiconductor electrode depend on whether there is an accumulation layer or a depletion layer. If there is an accumulation layer, the behavior of a semiconductor electrode is similar to that of a metallic electrode, since there is an excess of the majority of charge carrier available for charge transfer. In contrast, if there is a depletion layer, then there are few charge carriers available for charge transfer, and electron transfer reactions occur slowly, if at all. However, if the electrode is exposed to radiation of sufficient energy, electrons can now be promoted to the conduction band. If this process occurs in the interior of the semiconductor, recombination of the

promoted electron and the resulting hole typically occurs, together with the production of heat. However, if it occurs in the space charge region, the electric field in this region will cause the separation of the charge. For example, for an *n*-type semiconductor at positive potentials, the band edges curve upwards, and hence the hole moves towards the interface, and the electron moves to the interior of the semiconductor. The hole is a high energy species that can extract an electron from a solution species; that is, the *n*-type semiconductor electrode acts as a photoanode. At the flatband potential, there is no current, either in the dark or upon irradiation, since there is no electric field to separate any generated charge carriers. At potentials negative of the flatband potential, an accumulation layer exists, and the electrode can act as a cathode, both in the dark and upon irradiation (the electrode is referred to as a dark cathode under these conditions). At potentials positive of the flatband potential, a depletion layer exists, so there can be no oxidative current in the dark. However, upon irradiation, a photocurrent can be observed at potentials negative of the redox potential of the analyte, since some of the energy required for the oxidation is provided by the radiation (via the high energy hole). Using similar reasoning, it can be shown that *p*-type semiconductor electrodes are dark anodes and photocathodes.

3. Photocatalytic and photoelectric process

A number of major disciplines have separately developed as distinct fields of energy research utilizing nanostructure materials: i. Heterogeneous photocatalysis; ii. Photoelectrochemistry - including electrochemical photovoltaic cells; iii. Photochemistry in zeolites and intercalated materials; iv. Photochemistry of thin films and membranes-including self assembled structures; and v. Supramolecular photochemistry [17].

According to IUPAC (*International Union of Pure and Applied Chemistry*) compendium of chemical terminology, photocatalysis is defined as a catalytic reaction involving light absorption by a catalyst or by a substrate [18]. Significant research efforts were made to search for new oxide materials with smaller bandgaps to enhance visible light absorption. Fe_2O_3 stands out with its nearly ideal bandgap of 2.2 (eV) and its high-photochemical stability in aqueous solutions. Faust et al. [19] examined the suitability of Fe_2O_3 as a photocatalyst by studying the kinetics and mechanisms of the photocatalytic oxidation of sulfur dioxide in aqueous colloidal suspensions of 3–25 (nm) Fe_2O_3 . The results showed that the small hematite crystals possessed photocatalytic activity for the oxidation of sulfite (S(IV)), which readily depleted when the colloidal solutions containing 1 (mM) S(IV) , and 0.1 (mM) of the nano- Fe_2O_3 particles were illuminated with light, of 320 (nm), in the presence of air. Kormann et al. [20] also examined the suitability of Fe_2O_3 (3–20 nm) in size as photocatalysts. They also compared the photocatalytic activity of hematite to the activities of colloids and suspensions of ZnO and TiO_2 . While ZnO and TiO_2 were found to be quite active photo-oxidation catalysts in the formation of hydrogen peroxide and in the degradation of

chlorinated hydrocarbon molecules, only negligible photocatalytic activity was found for Fe₂O₃. Bahnemann [21] has also carried out several tests to compare the efficiencies of several semiconductors as photocatalysts.

In recent years, environmental cleanup and water splitting applications have been one of the most active areas in heterogeneous photocatalysis. An ideal photocatalyst should be stable, inexpensive, non-toxic and, of course, highly photoactive [22]. Another primary criteria for the degradation of organic compounds is that the redox potential of the H₂O/•OH couple (OH⁻ → •OH + e⁻; E⁰ = -2.8V) lies within the bandgap of the semiconductor [23]. Several semiconductors have bandgap energies sufficient for catalysing a wide range of chemical reactions. Thus, understanding of the fundamental nature of Fe₂O₃ for photoelectric and photochemical properties is necessary. The properties are related to the atomic structure presented above. Only hematite (α-Fe₂O₃) plays any role in the applications and is of interest here. Photocatalysis is attributed to the electrical characteristics of hematite.

Like in photoelectric process, photons need certain energy to penetrate the band gap to generate the electron dislocation towards conduction level. After recombination, the electrons can react with donors or acceptors situated on the photocatalyst surface in two directions:

- a) The holes react with water or OH group for radical-hydroxyl production responsible for organic substances degradation
- b) The electrons react with dissolved oxygen to form superoxid ions with strongly effects. Much more, the superoxid ions can react furthermore evolving into hydroxyl ions.

An excellent description of this process is presented in [24]. Recombination of the photoexcited electron-hole pair needs to be retarded for an efficient charge transfer process to occur on the photocatalyst surface. The efficiency of the photocatalytic process can be measured as a quantum yield, which is defined as the number of defined events occurring per photon absorbed by the system or as the amount (mol) of reactant consumed or product formed per amount of photons (Einstein) absorbed [18]. The ability to measure the actual absorbed light is practically not feasible in heterogeneous systems due to scattering of light by the semiconductor surface and the recombination. It is usually assumed that all the light is absorbed and the capacity is quoted as an apparent quantum yield. If several products are formed from the photocatalytic reaction, then the efficiency is sometimes measured as the yield of a particular product. The quantum yield for an ideal system (ϕ) can be given by the simple relationship [25]:

$$\phi \approx \frac{k_{CT}}{k_{CT} + k_R}$$

where k_{CT} is the charge transfer process rate and k_R is the electron-hole recombination rate.

Assuming that diffusion of the products occurs quickly without the reverse reaction, ϕ is proportional to the rate of the charge transfer processes and inversely proportional to

the sum of the charge transfer rate and the electron-hole recombination rate. Without recombination the quantum yield would take on the ideal value of 1 for the photocatalytic process. Charge carrier trapping would suppress recombination and increase the lifetime of the separated electron and hole. Surface and bulk defects naturally occur during the synthesis and they may help suppress the recombination by trapping charge carriers. The hole produced by irradiation reacts with water or surface-bound hydroxyl ion producing hydroxyl radical. Electron released by irradiation of photocatalyst combines with dissolved molecular oxygen, producing the superoxide radical, O₂^{•-}. Hydrogen peroxide possibly added acts as an oxidant, but also as an e scavenger instead of dissolved molecular oxygen. H₂O₂[•] dissociates to hydroxyl radical and hydroxide ion even easier than H₂O₂, due to an extra electron. The photocatalyst can be used for the photodegradation of organic molecules denotes the conversion of organic compounds to CO₂, H₂O, NO₃, or other oxides, halide ion, phosphate, *etc.* for environmental remediation. Often degradation begins with partial oxidation, and mechanistic studies relevant to oxidative photocatalytic degradation frequently focus on early stages involving photooxygenation, photooxidative cleavages, or other oxidative conversions. Environmental decontamination by photocatalysis can be more appealing than conventional chemical oxidation methods because semiconductors are inexpensive, nontoxic, and capable of extended use without substantial loss of photocatalytic activity.

4. New Fe₂O₃ architectures

4.1 The core-shell, core-shell-shell and nanocomposites structures

It is often necessary to coat the nanoparticle surface with an organic or inorganic shell, in order to protect them from chemical degradation or agglomeration according to the environments in which they will be used [26]. The coating can also be performed in order to add new functionalities to the magnetic core, such as biological stealth, optical properties, catalytic or adsorbing capacity. The core-shell and core-shell-shell structures and nanocomposites structures are particularly interesting architectures in photocatalysts. Charge separation mechanism in core-shell, involve the electrons photogeneration in the first (shell) and their injections in conduction level of the second (core) in n-p structures and vice versa in p-n structures. Development of these semiconductor systems is very promising and has the potential to contribute significantly to the area of photocatalysis. By changing parameters, such as the thickness of the shell or the particle radius of the core, we can improve the photocatalytic, optical and magnetic properties of the photocatalyst. It is the d orbital of the Fe (III) ions which is very important for photocatalysis applications. The carrier mobility in maghemite and magnetite are relatively low because of the narrowness of the d bands. This has been explained by Wait in [11], who

suggested that narrow bands arise from orbitals which do not appreciably overlap, therefore electrons or holes do not move as freely, that is, they have lower mobility. The band structure of hematite has been reported to involve a conduction band composed of empty Fe (III) orbitals. The valence band edge is made up of mixture of Fe^{3d} orbital and O^{2p} orbital [12]. The reported optical absorption of 2.2 (eV) is the result of weak transitions between d-d orbitals. The band gap which is important in photocatalytic applications has a value of 3 (eV), and involves a strong charge transition between O^{2p} and the empty Fe^{3d} orbitals [12]. Others have reported that the direct transitions from O^{2p} valence band orbital to the conduction band orbital occur within the 3-4.7 (eV) range [13].

One of the best methods for photocatalytic process improvement is the hematite deposition on the SiO₂ surface microsphere, making a nanocomposite structure. They are special because SiO₂ granules have a low reactivity and a very good optical transmission.

Numerous papers describe the modification of magnetic nanoparticles with an organic polymer [27,28,29] or a silica shell [30,31,32]. In contrary, relatively few works have been performed on magnetic nanoparticles coated with titanium dioxide (TiO₂) [33,34,35,36,37,38,39,40,41,42].

However, TiO₂-based particles are largely used owing to their widespread applications as pigment [43], in light-assisted environmental cleanup (photocatalysis) [44], or in solar energy conversion [45]. Therefore, the addition of a TiO₂ shell to a magnetic core at the nanometer scale may lead to bifunctional nanoparticles which could be applied for example as magnetic photocatalyst. Papers reporting TiO₂ coating onto magnetite (Fe₃O₄), maghemite (Fe₂O₃), or ferrite (MFe₂O₄) where M is a divalent cation) cores [33,37,46,40], describe rather large or aggregated particles. When used as magnetic photocatalysts [33, 37,46,40], the activities of these materials are generally low. This was explained by an unfavorable electronic interaction between the TiO₂ shell and the magnetic core, leading to an increase in electron-hole recombination [33]. To avoid this problem, several authors [34,35,36,37,42] synthesized Fe₃O₄/SiO₂/TiO₂ and BaFe₂O₄/SiO₂/TiO₂ particles, in order to isolate TiO₂ from the magnetic core by a passive silica layer. Although activities of the magnetic photocatalysts were increased, they remain lower than that of the commercial TiO₂ photocatalyst. This can be explained by a reduced accessibility to the catalytic sites since large particles or aggregates having diameters of more than 500 (nm) were obtained. The difficulty of obtaining very small magnetic- TiO₂ core-shell nanoparticles is probably due to the fact that hydrolysis and condensation of the TiO₂ precursors—usually titanium tetraalkoxides Ti(OR)₄— is very fast and difficult to control [47]. A possibility consists in preparing core-shell colloids by hydrolysis and condensation of Ti(OR)₄ around seed nanoparticles in an ethanolic solution with a small amount of water. Indeed, some works have described the preparation of monodisperse spherical core-shell SiO₂/TiO₂ nanoparticles in these conditions [48,49]. Therefore, we propose here to extend the procedure using magnetic cores that are

previously coated with a SiO₂ shell in order to obtain core-shell-shell Fe₂O₃/SiO₂/TiO₂ nanoparticles of few tens nanometers.

An interesting study is presented in [50] The authors focused on spray pyrolytic synthesis of p-Fe₂O₃. Magnesium has been the most studied p-type dopant for Fe₂O₃. Also, calcium and titanium were used for p-type doping in prior studies [10]. Other dopants that will be included in this present work will be manganese, copper, cobalt, nickel, tin, zirconium and zinc. In [50], a novel kind of loaded photocatalyst TiO₂/SiO₂/-Fe₂O₃ (TSF), which can photodegrade effectively organic pollutants in the dispersion system and can be recycled easily by a magnetic field, is reported. The photocatalyst is made up of Fe₂O₃ core, a SiO₂ membrane, and a TiO₂ shell. In this photocatalyst, the TiO₂ shell is the photocatalyst, the Fe₂O₃ core is for separation by the magnetic field and the SiO₂ membrane between titania shell and Fe₂O₃ core is used to weaken the bad influence of the Fe₂O₃ core on the photocatalysis of the TiO₂ shell. The photodegradation of dyes on TSF under UV irradiation is also examined compared with that under visible irradiation. Another interesting and very new study is presented by Valerie Cabuil and coworkers who prepared core-shell-shell Fe₂O₃/SiO₂/TiO₂ nanoparticles of few tens nanometers performed by successively coating onto magnetic nanoparticles a SiO₂ layer and a TiO₂ layer, using sol-gel methods. The thickness of the two layers and the aggregation state of the particles can be controlled by the experimental conditions used for the two coatings. These composite nanoparticles may find application as magnetic photocatalysts, since they are characterized by their small diameters which allow a good accessibility to the TiO₂ shell.

4.2 Nanowires, nanorods, nanotubes, hollow fibers, snowflake-like, and ring-like

Various shapes and dimensions of iron oxide nanomaterials [51] are experimentally available, such as nanowires [52], nanorods [53], nanotubes [54], hollow fibers [55], snowflake-like [56], and ring-like [11]. The performance of iron oxide is strictly influenced by its morphology, size and porosity. Very recently (2008), a short historic in this field is presented by Dan Zheng and coworkers in [51]. Wu et al. have synthesized hematite nanorods with different BET surface (Brunauer, Emmett, and Teller area) and proved that there are superior sensing properties for HCHO gas with larger surface areas due to its porous structure [57]. Qiang Liu et al. have demonstrated that the iron oxide catalysts have different activities in CO disproportionation for different morphologies [68]. The quantumconfinement effect of the α -Fe₂O₃ nanorod array has been studied by the RIXS (Resonant inelastic X-ray scattering) method in a previous research [59]. Hematite (α -Fe₂O₃) nanocrystals with small size on the surface of monodispersed silica microsphere exhibit a quantum size effect on surface photovoltage (SPV) and the relationship between the size and photogenerated charge separation has been studied [60].

Therefore, it is of great interest to study the photoelectric properties of iron oxide with different nanostructures for their promising application in photocatalysis or photoelectric conversion device [51]. Nanomaterials grown on substrates with the structure of ordered array assembly of one-dimensional (1D) material (including nanorods, nanowires and nanobelts) have large surface areas and high surface-to-volume ratios. Possible quantum-confinement effect could still remain for the composite quantum-sized nanocrystal in the array. Besides, the directional channel for the electron transport along the ordered nanocrystals makes the assembly of 1D nanomaterials very attractive on photonics and electronics. For example, vertically oriented Ti-Fe-O nanotube array films have been fabricated for solar spectrum water photoelectrolysis, which show enhanced photocurrent compared to the pure hematite (α -Fe₂O₃) nanoporous film [61]. Vertically aligned ZnO nanorod arrays as low-cost and high performance gas sensors synthesized by hydrothermal method exhibit excellent gas sensing properties to NH₃, CO and H₂ [62]. Co₃O₄ nanowire arrays [63], SnO₂ nanorod arrays [64], TiO₂ nanotube arrays [65], CdS nanowire arrays [66], and Cu-ferrite nanorod arrays [67] etc. have also been prepared by different methods with attractive performances in electronic devices, heterojunction dye-sensitized solar cells, photocatalysis, sensing devices and so on. Uniform, vertically aligned arrays of α -Fe₂O₃ nanorods [53], nanowires [52] and nanobelts [68] have been already synthesized by simple aqueous chemical route or gas-solid reaction process etc. Up to now, the α -Fe₂O₃ nanorod array structure has found its potential value on photocatalysis owing to its efficient harvesting of visible light, shortened distance for the photogenerated holes to reach the surface/interface before recombining with conduction band electrons [69], and enhancement of the band gap [59]. The oriented nanorod array structure has been demonstrated to own higher incident photon-to-current conversion efficiency than the film with spherical particles [53], which can be further improved by doping with Zn and surface modification [70]. It has promising potential in the generation of H₂ from direct photo-oxidation of water by solar irradiation without external bias, which has not been realized yet experimentally [59]. Besides, the α -Fe₂O₃ nanorods have greater surface areas compared to pure nanoparticles and that could produce more activity sites for gas sensing, which has been demonstrated in detecting the HCHO in the ambient atmosphere [57]. Thereby the α -Fe₂O₃ nanorod array is an active nanostructure with multiple functions. For the photoelectric activity of the material, the behaviors of the photogenerated charges (the photogenerated electron transfer at the surface and interface of the material) directly determine the performance of the system. Therefore, it could study the transfer behaviors of the photogenerated electrons in the α -Fe₂O₃ nanorod array on spectrum for better photoelectric applications. The SPV (surface photovoltage) technique is a well-suitable and more direct method to characterize the behavior of the photoinduced charges. In [71], the authors are explain the mechanisms of charge transfer at the surface of the nanorod array and at the interface between

the nanorods and the substrate via the analysis of the photovoltage spectra. They also discuss the quantum size effect in the α -Fe₂O₃ nanorod array by the comparison of the SPV spectra under different illuminating directions on the system.

4.3 Nanocrystalline semiconductor thin films

Nanocrystalline semiconductor thin films prepared from colloidal suspensions are of great interest. Such thin film electrodes are named 'nanostructured electrodes'. In the literature, α -Fe₂O₃ electrode has been reported to be thermodynamically stable towards photoanodic decomposition over the entire pH range. Though high-photoconversion efficiencies were already shown for polycrystalline Fe₂O₃ pellets [73] and single crystalline Fe₂O₃ samples [74], thin films are generally preferred in order to avoid the high resistivities encountered in, for example, single crystals, and to reduce the cost for fabrication [72]. Photocurrent quantum efficiency is only 0.8% at the maximum of the photocurrent spectrum [74]. Trapping of electrons by oxygen-deficient iron site, low mobility of holes, recombination of electrons and holes, are responsible for the poor photocurrent efficiency. Moreover, in the nanocrystalline α -Fe₂O₃ semiconductor thin film/electrolyte system, the mechanism of photo-induced charge separation and transportation are still unknown and the topics are open to further studies. Compared to the bulk semiconductor electrode, the mechanism of photocurrent generation in nanostructured thin film is quite different. In a conventional photoelectrochemical cell employing single-crystal or polycrystalline materials, the charge separation was facilitated by the space charge layer at the electrode/electrolyte interface [75]. The potential gradient of the space charge layer region promotes the flow of electrons and holes in the opposite direction. In this nanostructured system, the electrolyte can penetrate the whole colloidal porous film up to the surface of the back contact. The semiconductor/electrolyte junction occurs at each nanoparticles, much like a normal colloidal system. Under illumination, the light absorption in any individual colloidal particles will generate an electron-hole pair [76]. If the kinetics of whole transfer to the electrolyte is much faster than the recombination process, electrons can create a gradient in the electrochemical potential between the particle and the back-contact. Very recently, an exceptionally high photocurrent of 2.7 (mA/cm²) at a bias of 1.23(V) relative to the reversible hydrogen electrode (RHE) under simulated sunlight was reported for porous films synthesized using atmospheric pressure chemical vapor deposition (APCVD) [75]. While this breakthrough represents a major step forward, practical applications still require an additional ~4 times improvement in photocurrent. In order to achieve this, more detailed insights into the origin of the high photoresponse are required. The key ingredients for the high performance of the APCVD films seem to be (i) Si doping, which is thought to induce a favorable morphology during film growth [76], (ii) the presence of a thin SiO₂ interfacial layer between the Fe₂O₃ and the transparent conducting

substrate [75], and (iii) the addition of a cobalt catalyst [75]. In [72], Roel van de Krol, Cristina S. Enache and Yongqi Liang revealed the effects of Si doping and the addition of a thin interfacial layer (in this case SnO_2) between the transparent conducting substrate (TCO) and the Fe_2O_3 . Toward this end, thin dense undoped and Sidoped Fe_2O_3 films are deposited onto conductive glass substrates by spray pyrolysis. Although spray pyrolysis will not generally yield the high degree of texturing that is required for optimal performance, the ease of doping and smooth film morphology greatly simplifies the photoelectrochemical characterization of the material. The photoresponse and the electrical characteristics of the deposited films are studied for various Si concentrations and the effect of a thin SnO_2 interfacial film is investigated.

5. Conclusions

This paper outlines the main properties of iron oxide nanoparticles and their various photoelectrochemical applications. A short general presentation is provided. Many novel approaches are described in the use of photoelectrochemistry such as solar energy conversion, water splitting, photocatalysts for the removal of organic and inorganic species from aqueous or gas phase. Sometimes, surface modification of magnetic carriers is necessary for photocatalysts delivery in the work zone or in order to protect them from chemical degradation or agglomeration according to the environments in which they will be used. The coating can also be performed in order to add new functionalities to the magnetic core, such as biological stealth, optical properties, catalytic or adsorbing capacity. The core-shell and core-shell-shell structures and nanocomposites structures are particularly interesting architectures in photocatalysts. The applications of nano materials to photoelectrochemistry are gradually increasing, and are a challenging area for future research. The solutions of these future problems from this area are in connection with new technological advances in surface chemistry, physics, geochemistry, and not the last, mathematics and informatics for modeling new experiments. Moreover, it is possible that further research will lead to solve the energy and the Earth cleaning problem.

The use of magnetic materials in these research fields is restricted only by the imagination of researchers who create and exploit them.

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