

A Brief Review on UV-Visible Spectroscopy of Nanostructured Ferrite Materials

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Abstract: With the growing technology of semiconducting materials, it is essential to understand the photonic properties of materials. Optical absorption measurements of materials are widely used to evaluate the parameters such as the absorption coefficient, band gap energy, and lifetime of excited state, etc. UV-Visible spectroscopy is the tool to analyse the optical behaviour of materials. Ferrites are both thermally and chemically stable ferrimagnetic materials which consist of the properties of semiconducting materials that have been used for numerous electronic applications. Optical behaviour of ferrites refers to the study of their interaction with light and extracting information about band gap, refractive index, absorption coefficient, etc. From the absorption spectra of ferrites it was confirmed that they can absorb considerable amount of UV and visible light due to which it received enormous interest from researchers to apply as a photocatalyst in organic/inorganic dye degradation, pollutant removal from wastewater, etc. This review provides an overview of UV-Visible spectra of ferrites along with the qualitative and quantitative analysis of commonly used ferrites in photocatalytic activity.

Keywords: Spectroscopy; Semiconductor; Photocatalyst; Refractive Index; Band gap energy.

Introduction:

The optical properties of semiconducting materials received considerable attention owing to their tremendous applications in optical sensors and laser devices [1]. It was noticed that many physical and chemical characteristics of the materials show size dependency [2]. At nanoscale, measurement of the nanoparticle is comparable to the Bohr radius. The size dependent band gap in nanostructured semiconducting materials is the consequence of the phenomenon of "Quantum confinement" [3]. An extraordinary growth has been found in the research field of nano-structured

materials. Each materials have their own benefits as well as limitations [4]. In the thrust of suitable material for specific application the multidisciplinary research area opens a new direction of modern research. Amidst of various nanostructured materials “Ferrite nanoparticles” gained uttermost importance due to easy functionalization and distinguish feature which can be utilized in different biomedical applications like magnetic resonance imaging, drug delivery, diagnosis, and radiotherapy [5-7]. Besides medical application these ferrimagnetic nanoparticles are desirable in photocatalyst, electromagnetic shielding, magnetostrictive sensors, gas sensors, electronic devices, information storage, etc [7-10]. The chemical formula for spinel ferrites is MFe_2O_4 , where M represents a metallic alloy cations. The oxygen ions in spinal ferrites are closely attached within face centered cubic structure and forms two type of interstitial sites, namely tetrahedral (A) and octahedral (B) sites. The arrangement of metal subatomic particles in the structure of ferrites results either normal or inverse spinel structure. All divalent metal ions (M^{2+}) in normal spinel are occupy at A sites and all trivalent Fe^{3+} ions occupy at B sites. On other side if trivalent ions equally occupy at A and B sites and all divalent ions (M^{2+}) take up at ‘A’ sites it leads to inverse spinel structure. Ferrite nanoparticles consists of excellent magnetic properties along with novel electrical and optical properties which differ remarkably from bulk crystals.

Since their discovery, there has been an exponential increase of interest in ferrites, which is still growing. It still requires many engineering challenges to be addressed. The progressive use of more sophisticated and advanced instruments with high precision is utilized to characterize both the chemical and physical properties of materials at the nanoscale [10, 11]. The motive of the on going review is to explore all optical properties related absorption spectra and band gap of ferrite nanoparticles under UV-Visible spectroscopy.

Determination of Optical Parameters via UV-Visible Spectroscopy:

UV-Visible spectroscopy refers to soaking up, reflection, or conveyance spectra. The basic principle of UV-Visible spectroscopy is related to interaction of the specimen with photons of UV-Visible radiation. The transmitted radiation depends upon the amount of radiation absorbed by the molecules of the sample [12]. Absorption of photons takes place only at specific energy which is a measure of the materials optical band gap. The band gap of semiconducting material can be described in two types, a direct band gap or an indirect band gap [13]. A photocatalyst with a maximum band gap of about 3.1 eV is required to absorb visible light

energy. Materials exhibiting characteristic absorption bands in visible region are the potential materials for optical applications [14].

The optical parameters such as band gap (E_g), absorption index (k) and refractive index (n) has a important role in the research of optical materials. These can be evaluated from absorption spectra of the samples[15]. An American physicist Jan Tauc [16] introduced the concept of the Tauc model for the characterization of crystalline materials. Tauc gave a standard empirical formula for determining the band gap of semiconducting materials as a function of incident photon energy [17]. The Tauc relation to evaluate the optical bandgap (E_g) is shown below :

$$(F(R) h\nu)^m = A (h\nu - E_g) \quad (1)$$

$F(R)$ is Kubelka–Munk function and the value of ‘ m ’ denotes the nature of the transition. The value of $m = 2, 1/2$, represents the indirect and direct allowed transition with respect to each other . The values $3/2$, and 3 show a indirect and direct forbidden transition, respectively.

The formulas to calculate the refractive index (n) and absorption index(k)[18] are given as below:

$$k(\lambda) = \frac{-2\sin(\theta(\lambda))\sqrt{R(\lambda)}}{1+R(\lambda)-2\cos(\theta(\lambda))\sqrt{R(\lambda)}} \quad (2)$$

$$n(\lambda) = \frac{1-R(\lambda)}{1+R(\lambda)-2\cos(\theta(\lambda))\sqrt{R(\lambda)}} \quad (3)$$

where R , λ , and θ are reflectance, wavelength of incident photon, phase shift angle of the sample respectively.

Optical Properties of Nanostructured Ferrites:

The ultraviolet and visible region falls in the range of wavelength 190-380 nm and 380-800nm respectively of the electromagnetic radiation. Band gap of the energy of nanostructured materials is affected by several factors including crystal symmetry, crystal structure, induced lattice strain, quantum effects of the particles sizes, carrier attentiveness, existence of the dirty particles, surface roughness, etc[18]. The optical properties of the materials are fragile to their particle size. Therefore, it is necessary to understand the impact of crystallite size on optoelectronic applications of the material. When the particle size is decreases, band gap energy increases and hence, absorption is shifted to lower wavelength. This can be attributed to quantum confinement effect of nanoparticles and the induced defects in the energy levels [19, 20]. In the case of bulk sample, the formation of energy bands are owing to contribution of each energy levels due to huge presence of atoms . At the nanoscale, as the size of the particle is reduced, the

amount of overlapping orbitals or energy levels reduces, and the band width gets narrower. It increases the band gap between the valence band and the conduction band. Hence, the energy band gap of a nanoparticle is greater in comparison to the corresponding bulk particle [21]. The band gap region is forbidden for the movement of electrons. The larger the forbidden region, the bigger will be the barrier on the movement of electrons. Hence the nanoparticle electrical conductivity gets reduced.

A wide range of semiconducting band gap with ability of absorbing the visible light offers an advantage of enhanced photocatalytic activity of ferrites. Some of commonly used ferrites with important highlights and corresponding band gap are summarized in Table 1.

Table 1. Important Highlights of Optical Properties of Recently Reported Nanostructured Ferrites:

S. No.	Ferrites	Important Highlights	Ref.
1.	CuFe ₂ O ₄ , Cu _{0.5} Co _{0.5} Fe ₂ O ₄ and CoFe ₂ O ₄ respectively	<ul style="list-style-type: none"> • Synthesis route: Sol-gel auto combustion method. • Optical energy bandgap (eV): 1.58, 1.18 and 1.01 eV respectively. • Crystallite size (nm): 25, 34 and 38 nm respectively. <p>The strong absorption was found in the range of 500–600 nm for all samples.</p>	[21]
2.	Co _{0.5} Zn _{0.5} Fe ₂ O ₄	<ul style="list-style-type: none"> • Synthesis route: Co-precipitation method • Surfactant used: Ethanol, Polyethylene glycol (PEG), Acetic acid and Cetyl trimethylammonium bromide (CTAB). • Optical energy bandgap (eV) : 1.99-2.06 • Crystallite size (nm): 11.7 - 53.3 • It was observed that in the visible region all synthesized samples showed two distinct absorption edges at wavelength 550 nm and 700 nm. 	[22]
3.	MFe ₂ O ₄ (M = Cu, Zn, Ni and Co)	<ul style="list-style-type: none"> • Synthesis route: Sol-gel process. • Optical energy bandgap (eV) : 1.26–2.08 • Crystallite size (nm): 15–30 • For all samples an absorption edge was observed around 730 nm which promised to illustrate them suitably 	[23]

		for visible light photocatalysis.	
4.	$\text{Co}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$ ($x= 0.0, 0.1, 0.3, 0.5, 0.7, 0.9$ and 1.0)	<ul style="list-style-type: none"> • Synthesis route: Sol-gel combustion method • Optical energy bandgap (eV) : 2.09 -1.42 eV • Crystallite size (nm): 34-48 nm • A strong dependence on cation content, morphology, and crystalline size was seen at the determined optical band gaps from UV/Vis DRS measurements. 	[24]
5.	$\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$	<ul style="list-style-type: none"> • Synthesis route: Co-precipitation method • Optical energy bandgap (eV) : 3.47 eV • Crystallite size (nm): 28 nm • UV-Vis spectroscopy measurement showed in the visible range around 346nm an absorption peak was seen. 	[25]
6.	$\text{NiFe}_{2-x}\text{Nd}_x\text{O}_4$ ($x= 0.0, 1.0, 1.5$ and 2.0)	<ul style="list-style-type: none"> • Synthesis route: Co-precipitation method • Optical energy bandgap (eV) : 3.31-1.76eV • Crystallite size: 19-24nm • The enhanced photo-activity were observed with the addition of Nd^{+3} in nickel ferrite can be shown upward to the decrease of band gap by substitution. 	[26]
7.	$\text{Zn}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ($x=0.0, 0.25, 0.4, 0.65,$ and 0.85)	<ul style="list-style-type: none"> • Synthesis route: Sol-gel combustion method • Optical energy bandgap (eV) : 1.85-1.95 eV • Crystallite size (nm): 18-30nm • As Ni content increases the band gap also varies linearly. 	[27]
8.	$\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.00, 0.20, 0.40, 0.60, 0.80,$ 1.00)	<ul style="list-style-type: none"> • Synthesis route: Chemical co-precipitation method • Optical energy bandgap (eV) : 2.26-2.63 eV • Crystallite size (nm): 10-20nm • For all samples the higher absorbance was seen in the ultraviolet (UV) area . 	[28]
9.	$\text{Co}_{0.5}\text{Zn}_{0.5}\text{R}_x\text{Fe}_{2-x}\text{O}_4$ ($\text{R}= \text{Ce, Dy},$ $x=0.00, 0.01, 0.03$ and 0.05)	<ul style="list-style-type: none"> • Synthesis route: Hydrothermal method • Optical energy bandgap (eV) : 0.25-0.77 eV • Crystallite size (nm): 7-12nm • The band gap value for $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Dy}_x\text{Fe}_{2-x}\text{O}_4$ NPs upon increasing concentration of x become quite narrow. 	[29]
10.		• Synthesis route: Sol-gel combustion method	[30]

	$MnCe_xFe_{2-x}O_4$ ($x=0.03, 0.05, 0.07$ and 0.09)	<ul style="list-style-type: none"> • Optical energy bandgap (eV) : 2.3-2.8eV • Crystallite size (nm): 15-18nm • The alternative of cerium (Ce) ion in $MnFe_2O_4$ results to shifting of the wavelength in direction to the visible light. 	
11.	$Cd_xZn_{1-x}Fe_2O_4$ ($x=0.0, 0.3, 0.7,$ and 1.0)	<ul style="list-style-type: none"> • Synthesis route: Chemical co-precipitation method • Optical energy bandgap (eV): 1.46-1.95eV • Crystallite size (nm): 30-55nm • With the increase in cadmium concentration the absorption band slightly shifted . It was observed that with the decrease in Cd concentration the energy band gap also decreases . 	[31]

From table 1 it can be concluded that band gap of ferrites lie in the range of 2-3 eV which shows them effective under visible light. Hence it may be concluded that ferrites are capable for photocatalytic conversion of visible light energy for use in reduction and oxidation processes. Besides, ferrites get control of separation and can be used again as they can be parted away magnetically [22]. Photocatalyst are used in many ways including the removal of contaminants from air and water, smell control, germs inactivation, the inactivation of cancer cells, and etc [32,33]. Using this technology for the whitewash of potentially poisonous and harmful compounds from the environment has generated a great interest in the last decade. With this background, the newly developments on photocatalytic presentation of spinel ferrites (MFe_2O_4) are extensively checked out in the field of photocatalytic degradation of toxic pollutants [34]. It is generally with respect to their biocompatibility, restrictness of precursors, easy synthesis and magnetic property. Some recently reported photocatalytic activity of ferrites are concluded in table 2 given below .

Table 2. Recently Reported Photo-catalytic Application of Ferrites for Dye Degradation:

S. No.	Ferrites (Photocatalyst)	Dye	Important Highlights	Ref
1.	$Co_xMg_{1-x}Fe_2O_4$ ($x=0.0, 0.1, 0.3, 0.5, 0.7, 0.9$ and 1)	MB	<ul style="list-style-type: none"> • Irradiation source : Sunlight and Visible light • Best photocatalyst under: 	[24]

	(sol-gel combustion method)		<ul style="list-style-type: none"> • Sunlight: $MgFe_2O_4$ Degradation efficiency: 82%, Exposure time : 4 h • Visible light: $Co_{0.1}Mg_{0.9}Fe_2O_4$ Degradation efficiency: 79%, Exposure time : 4 h 	
2.	$NiFe_{2-x}Nd_xO_4$ (x= 0.0, 1.0, 1.5 and 2.0)	RB MB Rh-B MR MO	<ul style="list-style-type: none"> • Irradiation source : Visible light • Sample x=1.5 shows maximum degradation of 98%, 93%, 91%, 96%, and 94% of MB, MO, BG, and MR respectively 	[26]
3.	MFe_2O_4 , M= Co, Ni, Cu, and Zn (Co-precipitation method)	<ul style="list-style-type: none"> • MB • MO • BG • MR) 	<ul style="list-style-type: none"> • Irradiation source : Sunlight • $NiFe_2O_4$ showed maximum degradation of 89%, 92%, 93%, and 78% of MB, MO, BG, and MR respectively 	[35]
4.	$ZnFe_2O_4$ (Co-precipitation method)	• MB	<ul style="list-style-type: none"> • Irradiation source : Sunlight • Degradation efficiency: 99% • Exposure time : 2 h 	[36]
5.	$CoFe_2O_4$ (Synthesized via bimetal-organic frameworks template)	(BP-A)	<ul style="list-style-type: none"> • Irradiation source : Sunlight • Degradation efficiency: 80.3% • Exposure time : 40min 	[37]
6.	$NiFe_2O_4$ (Co-precipitation method)	IV	<ul style="list-style-type: none"> • Irradiation source: Sunlight • Degradation efficiency: 99% • Exposure time : 2 h 	[38]
7.	$Co_{0.25}Zn_{0.75}Fe_2O_4$ (Co-precipitation method)	RA	<ul style="list-style-type: none"> • Irradiation source: UV irradiation • Degradation efficiency: 90% • Exposure time : 3 h 	[39]
8.	$Mg_{0.5}Zn_{0.5}FeMnO_4$ (sol-gel method)	RB21	<ul style="list-style-type: none"> • Irradiation source : Visible light • Degradation efficiency: 96% • Exposure time : 30 Min 	[40]

(MB- Methylene blue, RhB- Rhodamine-B, MO- Methyl orange, MR- Methyl red, BG-Bromo green, IV- Irgalite violet, Bisphenol-A (BP-A), Reactive Blue 21 (RB21), RA- Red Amaranth)

Conclusions:In the present review article a brief background information about UV-Vis spectroscopy with important highlights of optical properties of some commonly used ferrites and their recent advantages in photocatalytic application are discussed.It included the current progresses in the scientific and technological characteristics of ferrite, which are emerging due to their excellent optical properties.From published articles it was concluded that method of synthesis has a remarkable impact on the constructional parameters of ferrites such as particle size, surface area,and crystallinity that affect the optical properties and hence, the entire process of photocatalysis.Hence, an excellent photocatalytic activity of ferrites can be achieved by selecting an appropriate method of synthesis which are crucial for fundamental, and application viewpoint.

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