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ABSTRACT

In this review article, electron spin resonance (ESR) spectroscopy is widely reported in the research of various broad research areas of nanotechnology, nanodevices, and transition metals. In this review report, author suggest methodological considerations for ESR as pertains to magnetism, and proper incubation time with spin trapping agents. Based on author literature analysis, each spin trapping agent should be given the proper incubation time. For nanomaterials having magnetic properties, it is useful to remove these nanomaterials via centrifugation after reacting with spin trapping agents. This review article summarizes some of the more relevant transition metals or magnetic nanomaterials achievements of ESR and Spin Trapping applications in with varying magnetic spin orientations studies.

Keywords: nanotechnology, spin trapping agents, nanomaterials, magnetic materialsetc.

INTRODUCTION

Electron Spin Resonance (ESR) spectroscopy, also known as Electron Paramagnetic Resonance (EPR) spectroscopy, which is a technique applied to identify the transitions persuade by electromagnetic radiation (EMR) between the dissimilar energy-levels of spins of \bar{e} in the existence of a static magnetic field. ESR spectroscopy is an influential and powerful method which is used to study the characteristics of unpaired electrons in paramagnetic species. So, this method has been fully engaged to characterize the properties of the materials which are having no paired electrons or paramagnetic [1-4].

The magnetic properties which begin from the magnetic moment accompanying with spin of \bar{e} . In ferromagnetic materials, sets of atoms together bind into an areas called domains, where, all the electrons are having the same magnetic orientation. Important and basic alterations are reported in the ferromagnetic materials, when the size is decreased [5].

ESR spectroscopy has developed as a direct and powerful technique to identify free radicals, arises from the chemical or in biological systems. Longstanding interest is developed in employing ESR methods to categorize and calculate the amount of free radicals in biological systems, and also study the mechanism of interaction between the biologically related systems & metal ions organic molecules & nanomaterials [6-9]. ESR, is generally performs to characterize the physical properties of several nanomaterials including the functionalized magnetic nanoparticles [10-12].

In this review article, the author reported a new approach for the behavior of ESR spectroscopy and transition metals or magnetic nanomaterials. ESR spectroscopic measurement techniques were used to study the crystalline size-dependent magnetic properties of transition nanomaterials.

Basic Principles of the ESR Technique

ESR spectroscopy is constructed on the absorption of microwave radiation by paramagnetic substances which contains unpaired electrons when exposed to a resilient magnetic field. It is also known as EMR or Electron Paramagnetic Resonance (EPR) which is a subdivision of absorption spectroscopy, where radiations of microwave frequency region (0.04 – 25cm) is absorbed by the paramagnetic materials to induce the transitions between magnetic energy levels of electrons with their unpaired spins.

When any compound or a molecule with an unpaired electron is located in a strong magnetic field [13], the spin of an unpaired \bar{e} can line-up in two ways, creating two spin states $m_s = \pm 1/2$. The alignment can either be parallel (along the direction) to the magnetic field or Zeeman levels which corresponds to the lower energy state $m_s = - 1/2$ antiparallel (Opposite) (to the direction of the applied magnetic field $m_s = + 1/2$

The energy difference is given by the equation

$$\Delta E = E_{+1/2} - E_{-1/2} = h\nu = g\beta B$$

where ν is the frequency of radiation, h is Planck's constant, g is known as the g-factor, β is the Bohr magneton, and B is the strength of the magnetic field.

The g-factor is a unit less measurement of the intrinsic magnetic moment of the \bar{e} , and its value for a free \bar{e} is 2.0023. The value of g

$$g = \frac{h\nu}{\beta B}$$

using the magnetic field and the frequency of the spectrometer, the concept of g can be roughly equated to that of chemical shift in nuclear magnetic resonance (NMR) [14].

Working Theory of ESR

A microwaves and static magnetic field are used to perceive the behavior of the unpaired \bar{e} in the material which is being studied. All the data about the condition of the sample can be assessed by the behaviours of electrons. The working principle of ESR spectroscopy encompasses the collaboration of paramagnetic species with a static magnetic field and microwave radiation. Its working principles can be explained stepwise in following way:

a) **Preparation of sample:** The sample is prepared under strict check, which contains paramagnetic species like free radicals or complexes of transition metal. The sample is usually either in the form of a solution or powder.

b) **Application of Magnetic Field:** A static magnetic field is generated by using very powerful magnets. The sample is then, positioned in this magnetic field, that splits the levels of energy connected with the \bar{e} spins of the paramagnetic species.

c) **Microwave Irradiation:** Microwaves with a definite frequency range, between 9000–10000 MHz (9–10 GHz) region are applied to the prepared sample, and a collection of paramagnetic centers, such as free radicals, is exposed to microwaves at a fixed frequency.

d) **Signal Detection Process:** The reduction in power of microwave, results from the absorption of energy by the paramagnetic species, is identified and documented by the ESR instrument. The important thing which is relevant to the signal is that, by increasing an external magnetic field, the gap between the states of energy is broadened till it matches the microwave energy.

e) **Data Analysis:** The documented ESR spectrum, which signifies the absorption of microwave energy at different magnetic field strengths, is then analyzed.

Multiple Resonance Technique

Double-resonance or multiple resonance technique, in which the levels of energy of the ^1H and ^{13}C spins are matched, to the rotating frame of the Hartman–Hahn condition [15]. Under this situation, the energy may be exchanged between the two coupled spin systems. The result is a growth of the ^{13}C magnetization at the expense of the ^1H magnetization. The process involves following four phases [16]:

- (a) Polarization of the ^1H spin system,
- (b) Spin-locking of the protons in the rotating frame,
- (c) Establishment of contact between the carbons and the protons,
- (d) Measurement of the magnetization of the carbon nucleus.

Advanced Materials of Electron Spin Resonance:

The ESR method is a very powerful tool for reviewing the dynamics and structure of paramagnetic species, including the free radicals. It can be applied in the several fields of researches, like biology, medicine, applications of nanomaterials and polymers, dating of geological and archaeological findings, and environmental studies [17]. The spectrum of the advanced materials covered includes the polymer materials, semiconducting materials, glasses and ceramics, and superionic materials and optoelectronics, ESR imaging and microscopy as well as certain developing techniques [18]. The advanced ESR facilities at Argonne for the analysis of the structure and function of artificial and natural photosynthetic assemblies, bio hybrid complexes, catalytically active transition metal complexes, metallo-organic frameworks, and organic photovoltaic materials [19]. All the varieties of advanced materials including the optical materials, electro-ceramics, glasses, catalysts, and polymers are comprising of randomly oriented small crystallites. The spectra of ESR of such materials is the cover of the spectra from all possible orientations of the paramagnetic center or radical species with respect to the external magnetic field.

Electron Spin Resonance Spin-Trapping Technique

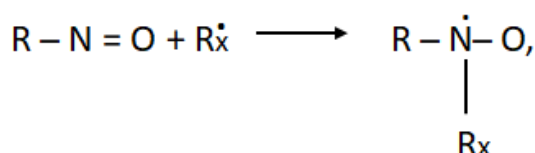
Spin trapping is an analytical technique working in the biology and chemistry for the recognition and

detection of short-lived free radicals by using of ESR or \bar{e} produce more stable nitroxide radicals. Spin trapping permits to determine, if short-lived free radicals are involved as reaction intermediates by searching the reactive radical to construct more stable radicals, detectable by ESR. This technique involves reaction of the firstly generated radical with an additional organic compound, which is known as spin trap, that produces the stable radical adducts from whose ESR spectra information about the original radical may be achieved [21]. This method is very useful in identifying radical intermediates in aqueous solution at room temperature and using small reaction volumes. This technology is also very helpful in the area of radical polymers. For example, the application of spin traps helps to solve various problems in complex-radical polymerization and copolymerization [22].

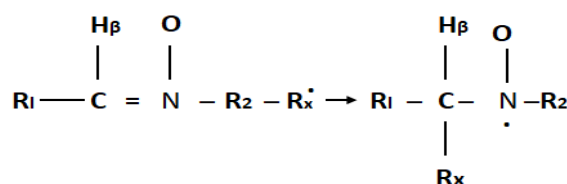
Spin Trap Concentration in Radicals

Spin trapping is an analytical method which is used to discover and recognize the transient free radicals, although this is not limited to radical species as, nitrones are susceptible to nucleophilic addition reactions. Nitron is a functionality which is chemically same in reactivity to carbonyl compounds as aldehydes and ketones [23]. Spin trapping involves the addition reaction of the free radical of interest to a diamagnetic compound, to produce a relatively long-lived free radical product, spin adduct (usually a nitroxide), which is expectantly collected to a high concentration. In positive cases, the resulting ESR spectrum permits the identification of the original radical [24].

Two types of spin traps have been developed, nitron and nitroso compounds. A Nitroso compound, such as MNP (2-methyl-2-nitrosopropane), provides considerably more data as comparing to nitrones. Nitrones as the radical to be trapped adds directly to the nitroso nitrogen.



With nitrones some information is vanished because the trapped radical adds to a carbon adjacent to the nitrogen.



Nevertheless, the most popular spin traps, DMPO (5,5-Dimethylpyrr-line-I-oxide), PBN (α -phenyl-N-tert-butyl nitron), α -(4-pyridyl-1-oxide) N-tart-butyl nitron have a β -hydrogen that provides the considerable information about the radical trapped [24-25].

Magnetic Nanomaterials

According to the today's situation of nanomaterials, they have many magnetic physicochemical, and electrical properties; amongst them, magnetism can influence the ESR signal of the material. A magnetic nanomaterial in a positive control system. Magnetic nanoparticles (MNPs) have a higher surface area to volume ratio, outstanding mechanical strength, and biocompatibility, while the conducting polymers are more beneficial for their effortlessness of synthesis, environmental stability, cheapness, and biocompatibility. Magnetic nanoparticles have entirely discrete magnetic properties. A large number of magnetic domains make up the majority of ferromagnetic materials, and each domain has parallel magnetic moments that are isolated by domain walls [25].

When the magnetic moments are kept in a single domain of ferromagnetic NPs, the magnetic anisotropy energy [26] (ΔE) is calculated as follows:

$$\Delta E = K_{\text{eff}} V$$

Where K_{eff} is the anisotropy constant, and V is the volume of the nanoparticles. When it comes to stop the magnetization from rotating, thermal energy ($K_B T$) is the limiting factor. Both ferromagnetism and superparamagnetism may be seen in the large and small NPs, respectively shown in given figure.

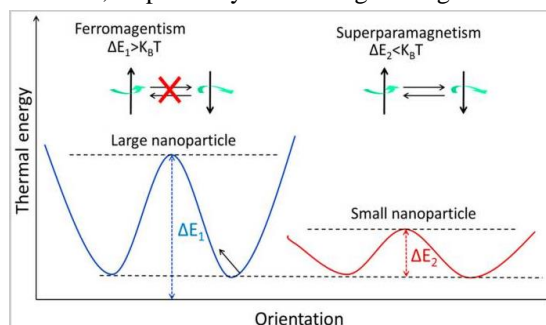


Figure: The energy levels of magnetic NPs with varying magnetic spin orientations [25].

ESR measurements of magnetic nanomaterials

Many magnetic platforms have very tiny sized and high magnetic susceptibility and loss of magnetism after eliminating the magnetic field. Nonetheless, tiny nanoparticles result in a low saturation magnetization that decreases their utility. The magnetic structures of the ferromagnetic material consist of several magnetic domains, and so retain a significant magnetic moment in zero fields [27]. Nanoparticles superparamagnetics are chosen in biomedical applications as they have zero magnetization at room temperature and do not agglomerate [28-30]. The "critical size" depends upon the nature of material and temperature. When the size of the magnetic nanoparticle is smaller, the thermal variations may modify the structure of particle enough for the magnetic moment to change its direction. This condition of the magnetic nanoparticles ensemble is called superparamagnetism, since the magnetization of these particles turns to zero in zero external magnetic field, much like it would in the case of paramagnetism, but the individual magnetic moment of the particle is much higher than of any known paramagnetic ion. While the term superparamagnetism is widely used, there are usually not enough direct evidences provided for given magnetically separable catalyst to consist of superparamagnetic nanoparticles [31]. A single-domain particle presents all the spins aligned in the same direction. The critical size value depends on the material. A single-domain particle presents all the spins aligned in the same direction. The total magnetic

moment of the nanoparticles can be regarded as one giant magnetic moment, composed of all the individual magnetic moments of the atoms [32-33]. ESR spectroscopic measurement techniques were used to study the crystalline size-dependent magnetic properties of transition nanomaterials. ESR spectra is formed by two absorptions, one to the higher fields known as the electronic magnetic resonance (EMR) and an absorption around zero magnetic field appointed low-field microwave absorption and second is a nonresonant absorption considered as a sensitive detector of magnetic ordering [34-37].

CONCLUSIONS

In this paper, I have reviewed the historical and theoretical backgrounds of ESR behavior using transition metalsnanoparticles and its current studies in the physical and chemical sciences. ESR is significant method which is used to study the free radical mechanisms of nanoparticles or nanomaterial. Techniques of ESR spin trapping are very beneficial tools for identifying reactive oxygen species formation. Magnetic nanomaterials have been widely developed and applied in many fields, such as heterogeneous catalysis, and industrial applications. We hope that this review article can help to Electron Spin Resonance Behavior using Transition Metal Nanoparticles, by helping behavior to identify the best technologies or applications, and partners to measure magnetic materials properties.

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