**Advanced synthesis of gold and iron oxide hybrid nanocomposite materials as magnetically recyclable superior catalyst**

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**ABSTRACT**

Advanced magnetic nanocomposites with different morphology and multiple functionalities have been intensively investigated by the materials scientist due to their serendipitous physico-chemical properties and potential applicabilities. Gold and iron oxide (Au–FexOy) nanocomposites inherited excellent stability, solvent compatibility, magnetic separability, post-modification ability etc. All of these properties greatly enhanced their extensive applications in different fields such as diagnostic, drug delivery, biosensor, catalysis etc. These nanocomposites generally exhibited a binary or a core/shell or nanostructure that can be modified with various functional groups on the surface to enhance their compatibility and stability.The advance in research for controlling functional peripheries, can provide various route for synthesizing next-generation Au–FexOy hybrid nanocomposite materials. The successful application of Au–FexOy nanocomposites is highly dependent on their composition, morphology, stability of the as-synthesized materials under different conditions. Therefore, the booming combinations of gold and Iron oxide are promising to obtain a hybrid nanocomposite with serendipitous and advantageous properties from both Au and FexOy nanoparticles (NPs). Recently, Au–FexOy hybrid nanocomposites were successfully employed as catalyst towards oxidation of carbon monoxide (CO), Epoxidation, Benzyl alcohol oxidation, Peroxidase-like activity, reduction hydrogen peroxide (H2O2) *etc*. The Au–FexOy nanocomposites enable a relatively better separation method for recycling the nanocatalysts by using external magnet. Furthermore, the hybrid material matrix remarkably stabilizes the Au0 NPs from being agglomerated and leached which ultimately enhances their reclabilty. It was found that Au–FexOy exhibited significantly catalytic effectiveness than the Au0 NPs alone because of the synergetic effect which occurs at interface of the gold and Iron oxide support.

*Keywords:*Hybrid nanocomposite, Au–FexOy, Bifunctional, Ternary-functional, Core/shell, Multifunctional, Heterostructures, MRC, CO oxidation, synergetic effect, Epoxidation, Peroxidase-like activity *etc*.

1. **INTRODUCTION**

Synthesis of nanocomposite material having different functional moieties have generated increasing interest to materials scientists owing to their extraordinary physico-chemical properties and potential applications in catalysis, photonics, electronics, nanotechnology and biotechnology etc [1–6]. These nanocomposites can be synthesized in different morphology such as core/shell or binary nanostructure type and these are generally modified with various functional moieties and reactive groups on the surface to enhanced compatibility as well as stabilty [7, 8]. The advantage of controlling the functional moieties and reactive groups can provide an approach for synthesizing advanced nanocomposite materials. The successful applications of such nanocomposites are dependent on their morphology, composition and stability of the particles under various conditions. So, many researchers have devoted their effort for the synthesis of different nanocomposites in order to generate novel materials that possess serendipitous properties.

Magnetic nanocomposites are belongs to the family of advanced nanomaterials. The growing interest in the magnetic nanocomposites is caused by their non-trivial magnetic properties that are highly interesting for existing and future potential applications of such nanocomposites as magnetic storage media, pigment, photocatalysis, ferrofluid technology and magnetic resonance imaging etc [9-13]. Magnetic iron oxide (Fe3O4 or γ-Fe2O3) nanomaterials posses a cubic inverse spinel structure and they are favourable for fabricating magnetic hybrid nanocomposites because of their intrinsic magnetic property along with the nanodimension and surface effects. When the grain size of FexOy is smaller than a critical value (~10–20 nm) and the temperature is above the blocking temperature, the FexOy nanocomposites show superparamagnetic behavior. At this point, no magnetic coercivity and remanence would be estalished in these nanocomposite materials and the aggregation of FexOy NPs is negligible at room temperature [14]. The above features of magnetic FexOy nanomaterials makes these a suitable candidate for selective capturing of targeting substrates, magnetic photonic and recyclable nanocatalysis application [15-17]. In addition, FexOy NPs act as T2 contrasting agent in magnetic resonance imaging (MRI). The FexOy NPs can accelerate the transverse relaxation protons of water and thereby shortening the spin–spin relaxation time of proton [18–20].

On the other hand, Au NPs are widely used in many fields for their unique optical properties that can have various applications such as detecting, sensing and imaging [21, 22]. Recently, much advancement of the synthesis of Au NPs was made with better biocompatibility, in biomedical applications for disease diagnosis and therapeutics. Au NPs could be easily synthesized and conjugated with many functionalizing moeities such as surfactants, dendrimers, ligands, proteins and oligonucleotides etc [21, 22]. The surface functionalization strategy improved the capability of Au NPs in targeting drugs for photothermal therapy having reduced cytotoxic effects in different cancers, gene therapy and other diseases [23-26].

Among the different multidisciplinary applications of Au NPs, catalysis is a topic of current interest to the researcher. There are several reasons which explain this interest. One among the several reasons for choice of Au NPs as catalyst is that the catalytic activity of gold is directly related to the particle size when the particle size grows into the micrometric scale, the catalytic property can disappear completely [27]. The second factor that explains the research interest in Au NPs is the fact that it was believed for a long time that gold was devoid of any catalytic activity. Thus, the effort to understand the reasons of catalytic activity of Au NPs, expand the scope to other reactions. Moreover, the optimization of size of Au NPs and finding the reaction mechanisms for Au NPs catalyzed reactions opens a new era in heterogeneous catalysis [27]. Finally, the third factor actually justifies the importance of the research in Au NPs which is that since supported Au NPs have to be synthesized, researchers can imagine that catalysis by Au NPs represent a bridge between heterogeneous and homogeneous catalysis [28]. These two disciplines have developed independently up to now, but NPs can provide a point of concurrence for both fields. Thus, the catalysis by Au NPs is a quintessential example of those properties that are only observed in NPs. The gold catalysis has derived benefits for tailoring solid porous nanostructured materials having high surface area for showing unexpected catalytic properties. So, the application of nanostructured gold in catalysis became an important research area many years after the first report on its catalytic activity for ethyne hydrochlorination [29] and gold is now considered an active promoter of various fundamental organic reactions such as oxidation, hydrogenation etc [30].

Therefore, the thriving combination of Au NPs and FexOy are has tremendous possibility to obtain a hybrid nanocomposite with superior and serendipitous catalytic activity than both Au and FexOy NPs individually.

This book chapter covers the recent development in the synthesis and catalytic properties of the Au–FexOy hybrid nanocomposite, highlighting the thrilling contribution to the art of catalysis. The outstanding and unique properties of nanometre scale gold in combination with the FexOy have fueled the development of a new generation of selective and stable hybrid nanocomposite catalyst for the various important organic reactions. There is also some synergetic effect which occurs at the interface of the Au NPs and FexOy support. A thorough discussion of the results of many research groups is presented along with attempts to correlate the catalyst morphology with the catalytic properties.

1. **SYNTHESIS, CHARACTERIZATION AND MORPHOLOGY STUDY OF GOLD AND IRON OXIDE HYBRID NANOCOMPOSITES**

In general, the morphology of Au-FexOy hybrid nanocomposite materials can be categorised into nanocomposites, core-shell and heterostructures. The nanocomposites are further sub-categorized into bi-functional, ternary functional and multifunctional/multilayer. It is noteworthy that core-shell and multifunctional/multilayer nanoparticles have drawn much attention from material scientists and chemists due to their advantageous and serendipitous catalytic properties superior from both individual Au and FexOy NPs. In recent years, various advanced synthesis methodology have been reported for synthesis of core-shell and multifunctional/multilayer with tunable sizes. Here discussions on the synthesis methodologies for Au–FexOy hybrid nanocomposites are limited to those which have applied as magnetically recoverable catalyst (MRC).

**2.1. Nanocomposites structures**

**2.1.1. Bifunctional nanocomposite**

The Au–FexOy nanocomposites are generally bi-composite materials where FexOy are first synthesized and then gold precursor salts are immobilized and reduced with a suitable reducing agent. For successful immobilization of gold precursor salts the surface of FexOy are generally modified with different surface modifying agent. For example, Y. -C. Chang *et al.* reported that surface of Fe3O4 NPs are modified with chitosan which is a good adsorber of metal ions. Then Au (III) ions are immobilized on chitosan coated Fe3O4 NPs and reduced to Au NPs with a NaBH4 [31]. Y. Qiu *et al.* presented an alternative easy way to prepare Au0 NPs using chitosan as the reducing as well as stabilizing agent without any other reducing agents or stronger protecting, such as NaBH4 or trisodium citrate. Fe3O4/chitosan composite synthesized first and then chitosan reduces AuCl4− to gold NPs [32]. F. Yan *et al.* reported a simplistic method for preparation bifunctional Fe3O4/Au nanocomposites by reduction of using NaBH4 as reducing agent. In this method, the AuCl4− that was adsorbed on the carboxylate functionalized Fe3O4 particles [33]. C. Huang *et al.* reported successful synthesis of porous Fe3O4 NPs and immobilization Au NPs with size less than 2 nm in porous Fe3O4 NPs modified by L-cysteine [34]. H. Woo *et al.* synthesized hybrid Au NPs on Fe3O4 microspheres and these Fe3O4 hybrid microspheres were coated with polymer matrix so as to prevent the aggregation of Au NPs and oxidation of Fe3O4 hybrid microspheres [35].

**2.1.2. Ternary-functional nanocomposite**

On the other hand, both gold and iron oxide are anchored in third support where catalytic activity of gold and magnetically recoverability of the composite due to the presence of FexOy is mainly focused. The effect of the support also influences the catalytic activity in some cases. As for example M. Kokate *et al.* reported a simple one-pot process for the synthesis of a novel Fe3O4 @SiO2@Au nanocomposite by employing a co-precipitation method that leads to the formation of Fe3O4 and Au NPs impregnated into a silica matrix [36]. F. Chen *et al.* reported another ternary functionalised nanocomposite of Fe3O4-graphene-Au *i.e.* both Fe3O4 and Au NPs are supported on the basal planes of reduced graphene oxide (GO). This research work also states that Fe3O4 NPs are selected to further functionalize graphene to endow the hybrid material it’s magnetically recyclabilty [37]. Jing Hu *et al.* reported an alternative facile and green route for “*in situ*” growth of Au NPs attached on the GO-Fe3O4 was established. After functionalization with –NH2 groups, the GO-Fe3O4 nanocomposites can adsorb Au NPs which acted as gold seeds, then the chloroauric acid solution provides gold precursor while glucose serving as reducing reagent [38]. B. Lu *et al.* presented an effective approach for the generation of Au@Fe3O4–Graphene ternary hybrid nanomaterial by “*in situ*” growth of Fe3O4 on the surface of graphene in tetraethylene glycol (TEG) solution where TEG, acts as both solvent and reductant. Furthermore, the Fe3O4–Graphene was employed as a two dimensional (2D) support for loading Au NPs to prepare Au@Fe3O4– Graphene hybrid materials [39]. L. Ren *et al.* reported a very good method for the synthesis of uniform sized mesoporous silica microspheres embedded with Au and Fe3O4 NPs, designated as γ-Fe2O3/Au/mSiO2 [40].

**2.1.3. Multifunctional/multilayer nanocomposite**

The aforementioned Au–FexOy structures are basically bi or ternary composite materials. Many researchers are very much interested in extending the scope of Au–FexOy nanocomposites material by introducing multiple functionality in a view to generate “*all in one*” nanocomposites. The coating of silica layer is common after the preparation of the FexOy core due to their ability to stabilize the FexOy core and to prevent its aggregation. The coating of silica layer onto FexOy NPs is typically performed using a sol–gel reaction.The silica layer is introduced during the synthesis of Au–FexOy nanocomposites in order to increase the stability of FexOy. As per research paper reported by Yeo *et al.*, the Fe3O4@Au core/satellite nanocomposite is coated with a silica layer by selective etching of the Fe3O4 core with NaBH4 [41]. Y. Zhu *et al.* reported the synthesis of multifunctional magnetic nanocomposite microspheres with “*in situ*” growth of Au NPs in multilayer polyelectrolyte films (MPFs) which is designated as Fe3O4@SiO2-LBL-Au(0) microspheres. The MPFs are very attractive for encapsulation of metal NPs as their layer-by-layer (LBL) deposition is both versatile and convenient [42]. B. Liu *et al.* synthesized a multilayer Fe3O4@SiO2@PHEMA-g-PDMAEMA microspheres nanocomposites. In the as-syntesized material, the Au NPs were effectively loaded into the functional PDMAEMA brushes through the “*in situ*” reduction [43].

**2.2. Core/shell structures**

A nanoparticle with a single core, fully covered by a shell coating is termed as Core/shell structure. These core/shell nanocomposite materials that combine with the advantageous properties of the core and the shell, have attracted increasing research interest due to their unique physico-chemical properties. The uniqueness of the core/shell nanocomposite has been employed in various applications, e.g. photonics, biotechnology, catalysis and nanotechnology [3-6, 44]. The surface of the core/shell nanocomposite could be functionalised further with new organic/inorganic ligands to give well defined structures. Moreover, these specific core/shell nanostructures which could be modified with different reactive moieties on the surface with enhanced compatibility and stability provide an avenue for the fabrication of complex nanocomposite materials.

The design and synthesis of different core/shell architectures based on Fe3O4 are very exciting research topics since the Fe3O4 has been widely studied because of their potential applications as catalysts, ferrofluids, biological assays, electrophotographic developers, chemical sensors etc [45-50]. In recent years, researchers have developed various strategies to synthesize different magnetic core/shell nanocomposite materials.W. Guo *et al.* [51] reported a facile method to synthesize well-defined core-shell Fe3O4@P(4-VP–DVB)@Au microspheres where Au NPs are easily supported into the P(4-VP) shell through reduction of HAuCl4 in Fe3O4@P(4-VP–DVB) microsphere dispersion. A solvothermal method has been employed to synthesize peroxyacetic acid (PAA)-modified Fe3O4 NPs [52-53] where monomers of 4-VP has been adsorbed on the surface of Fe3O4 NPs *via* strong hydrogen bonding interaction between their pyridine moieties as a Lewis base electron donor and PAA as a polyacid electron acceptor. Under acidic pH, the surface of Fe3O4@P(4-VP–DVB) microspheres tend to be protonated and stretch due to the strong affinity of pyridine group toward H+. It provides the route for growth of Au NPs embedded into the outer P(4-VP) shell. In fact, P(4-VP) chains stretch by the addition of HAuCl4 and the presence of NaBH4 causes shrinkage of P(4-VP) chains, hence this led to the reduction and growth of Au NPs to be supported into the outer P(4-VP) shell of the as-synthesized Fe3O4@P(4-VP–DVB) microspheres.

F. Ke *et al.* [54] synthesized a metal organic framework (MOF) based porous magnetic core-shell Au catalyst, Au-Fe3O4@MIL-100(Fe) by a very versatile layer-by-layer (LBL) assembly method. It has been observed that, by adjusting the assembly cycle number, the thickness of the shell in core-shell structures can be tuned. W. Zhang *et al.* [58] have synthesized a monodisperse magnetic sandwiched Fe3O4@Au/PEGDMA core–shell microspheres by using hydrothermal method for the synthesis of Fe3O4 core with subsequent modification with (3-aminopropyl) trimethoxysilane (APS) for functionalization of the surface –NH2 groups, P(EGDMA) shell has been prepared by a distillation precipitation polymerization process and the sandwiched Au NPs are formed through a “*in situ”* reduction of HAuCl4 by using NaBH4 as reducing agent.

L. Wang, et al. [56] describes the preparation of core (Fe3O4)-shell (Au) NPs having high monodispersity. The Fe3O4 NPs of selected sizes are used as seed for the reduction of gold precursors to synthesize gold-coated Fe3O4 NPs (Fe3O4@Au). A typical core-shell structure is also schematically represented in scheme 1 [56].



**Scheme 1**. Illustration of a Core-Shell Fe3O4@Au nanoparticle having an outmost organic shell encapsulation (R) -CO2H or -NH2 [Reprinted (adapted) with permission from ref. 56. Copyright © 2005, American Chemical Society).

**2.3. Heterostructures**

The Au–Fe3O4 heterostructures where the Au seeds are interfacially linked to Fe3O4 NPs, are versatile nanomaterials that exhibit the unique physico-chemical and catalytic properties [57–63].

F.-H. Lin *et al.*[58] demonstated the synthesis of flower and dumbbell-like Au-Fe3O4 heterostructures by thermal decomposition of iron oleate complex [Fe(OL)3] in the presence of Au seeds of different sizes at 310 oC. The Au-Fe3O4 heterostructures possess high magnetization and superb catalytic activity. It has been observed that the change in magnetic and catalytic behaviour of the heterostructured nanocatalysts is due to the different epitaxial linkages in flower and dumbbell-like heterostructures. Y. Lee *et al.* [64] prepared a dumbbell-like Au-Fe3O4 NPs by injecting [Fe(CO)5] into a 1-octadecene solution containing the Au seeds that are made by the reduction of HAuCl4·3H2O by tert-butylamine–borane (TBAB) in 1,2,3,4-tetrahydronaphthalene (tetralin) and oleylamine [63]. B. Mu *et al.* [65] reported a novel superparamagnetic gold/halloysite nanotubes/Fe3O4 (Au/HNTs/Fe3O4) nanocomposite by selective changing of the inner lumen and external wall of HNTs. The lumen of HNTs serves as nanoconfined reactor for the generation of Au nanorods where Fe3O4 NPs are deposited on the external wall of HNTs via the electrostatic assembly under the mild synthesis condition so as to prevent the structure of HNTs from destroying.

**3. CHARACTERIZATION**

The presence of the ligand integrity and structural functions in the nanocomposites can be characterized through Fourier transform infra-red (FTIR), Nuclear magnetic resonance (NMR) and ultraviolet/visible (UV/vis) spectroscopies. The ligand’s atoms adjacent to the FexOy core or Au would give broad NMR signals with alternation in the signal integration. The identities of the functional group of the ligands be identified through FTIR spectroscopy. UV/vis spectroscopy can be used to monitor the surface plasmon property of Au NPs. X-ray diffraction (XRD) and Small-angle X-ray scattering (SAXS) be used to evaluate the composition of the nanomaterials. Other techniques such as energy-dispersive X-ray spectroscopy (EDX) and X-Ray photoelectron spectroscopy (XPS) provide elemental information as well as ratio on the nanocomposite surface. Thermogravimetric analysis (TGA) is used to find the percentage composition of organic and inorganic composites at different decomposition temperatures. Inductively coupled plasma optical emission spectroscopy (ICP-OES) are used to estimate the loading amount Au and Fe metal [66]. Field emission scanning electron microscopy (FESEM) is used to observe the morphologies for nanocomposites. Au–FexOy nanocomposites at sizes between 10 to 100 nm with different ratio for Au and Fe are visualized through High-resolution transmission electron microscopy (HR-TEM). Scanning tunneling microscopy (STM), Atomic force microscopy (AFM), and atomic-number-sensitive high-angle annular dark field (HAADF) imaging [66] are employed to find high resolution images at a less than 10 nm scale.

**4. MAGNETICALLY RECYCLABLE CATALYTIC ACTIVITY OF GOLD-IRON OXIDE NANOCOMPOSITES**

In the last few decades, supported Au nanocatalyst have been emerged as a potent heterogeneous catalyst for various important reactions such as low-temperature carbon monoxide (CO) oxidation, hydrogenation, alcohol oxidation, alkene oxidation and organic synthesis etc [27, 67-70]. However, the high cost of the gold salt and tedious separation processes like centrifugation is the major challenges faced for the supported Au nanocatalyst. The synthesis of Au–FexOy nanocomposites and their catalytic activity study has been emerged recently as a potential area of research [71, 72]. These Au–FexOy nanocomposites materials are magnetically recoverable and magnetic separation is an effective separation method which proved to be advantageous over the filtration and centrifugation as it is simple, time saving and prevents the loss of the nanocatalyst [71]. Furthermore, the hybrid FexOy nanocomposites matrix significantly stabilizes the Au NPs from leaching and agglomeration, which led to enhance its catalytic lifetime. There is also some synergetic effect which occurs at the interface of the metal and oxide support. It is speculated that the electronic structures of both the metal and oxide support are modified by electron transfer across the interface.This phenomemnon results in the rise to oxygen vacancies on the interfacial oxide support that become the potential active sites for oxygen absorption and activation in some reactions particularly CO oxidation. These Au–FexOy nanocomposites materials have so far successfully demonstrated their catalytic activity towards CO oxidation, alcohol oxidation, epoxidation, reduction of H2O2 and peroxide like activity etc and it also exhibited a superior catalytic activity than FexOy and Au alone. These reactions are discussed in detail as following.

**4.1. CO oxidation**

Carbon monoxide (CO) is a gaseous molecule very poisonous for humans, as it bonded to the iron of the blood hemoglobin molecules which reduces the oxygen uptake and leading to immediate death of the affected person [73-75].To avoid release of CO into the atmosphere, one choice is to convert CO into carbon dioxide (CO2) by an oxidation reaction. Although carbon dioxide is a greenhouse gas and responsible for global warming, but it is not hazardous for human health [76].Another motivation made this CO oxidation reaction, a considerable subject area, because of research with implications for fuel cell design. The main issue with practical use CO fuel cell lies in the removal of carbon monoxide from the fuel cell’s feed gas since CO molecules can poison the catalyst used in most low temperature fuel cells [77-81].The Preferential Oxidation (PROX) process generally used for CO Oxidation to remove small amounts of CO to ppm level from the H2 rich stream that is used as a fuel in the polymer−electrolyte membrane fuel cells [77-86].The development of highly active, selective catalyst that operates within a wide temperature range 80−180 °C and has good resistance against CO2 and steam is the key to the application of PROX [87].In the past few decades, various catalyst systems have been developed for this PROX process of CO oxidation, which include metals such as Pt, Pt/Fe, Pt/Ru, Au NPs etc. placed upon a ceramic support [81-86]. The catalyst that modified with promoters such as reducible metal oxide and alkali metals have attracted widespread attention for their significantly improved catalytic activities in low-temperature. In spite of stoichiometric simplicity of this CO oxidation reaction, many mechanistic details remain undiscovered. The reported activation energies, turnover rates, and kinetic rate equations in previous research reports, at least in part because of undetected transport corruptions of measured rates [88, 89].The CO oxidation reaction also remains one of the classic and enduring examples of structure insensitivity; the turnover rate of this reaction is essentially independent of metal dispersion even though the coordinative and structural unsaturation of exposed metal atoms are dffer among clusters of different sizes [80].

Since the pioneering works of Haruta *et al.* [90, 91],CO oxidation over supported Au NPs has become one of the most extensively studied reactions in heterogeneous catalysis [92-94].The researchers are mostly focused on finding the origin of the unprecedented catalytic activity of Au NPs. The main factors for unique catalytic acivity of Au NPs are the synthesis methodology of active gold catalysts [95-97] which affect the size and shape of the Au NPs [98, 99],the role of the support [100-102], the oxidation state of the active gold species (metallic, Au+ or Au3+) [103-105],and the oxygen supply pathways [103-105].However, many research reports are highly controversial and the debate is likely to continue for some time due to the complexity and sensitivity of gold catalysis. The influence of Au NPs size on its catalytic efficiency is an example; it has been believed that Au NPs of 2–5 nm size are the active species for CO oxidation [106].

For Au NPs that are supported on transition metal oxides, the CO oxidation is an exothermic reaction with extremely low catalytic activation barriers [106].A detail comparison of gold catalysts on different support materials as well as activity measurements for Au on mixed oxides (Au/Fe2O3.MgO) reveal enhanced CO oxidation rates for a group of “active” support materials (TiO2, Fe2O3, NiO*x*, CoO*x*). Au–FexOy nanocomposites and their derivatives were demonstrated the catalytic effect towards CO oxidation [106-108]. The Au nanocatalysts supported on reducible transition metal oxides such as Fe2O3 exhibit a significantly higher activity for CO oxidation, which is attributed to their ability to provide reactive oxygen.

The origin of catalytic activity of Au NPs is highly controversial. For example, M. M. Schubert *et al.* [109] proposed several models to resolve this controversy. But the best model fit to Au–FexOy nanocomposites explained that oxygen adsorption is believed to occur on the FexOy support or at the Au–FexOy interface especially in the proximity of Au NPs as a consequence of Schottky junction at the metal semiconductor interface. It is also assumed that oxygen adsorbing on the FexOy support dissociates immediately, producing lattice oxygen, which subsequently react at the interface or after a spillover of oxygen to the metallic Au NPs.

**4.2. Epoxidation**

Epoxides are an important class of chemicals in synthetic organic chemistry. These are used largely for the synthesis of key intermediates in various important organic transformations. Most importantly, epoxides have widespread applications in the synthesis of anthelmintic preparations, perfume materials, drugs, epoxy resins, plasticizers, sweeteners, etc. Therefore, the synthesis of epoxides by a low cost route and facile method is of great interest to researchers [110-114].Despite successes in homogeneous catalyst for epoxidation reaction, there is a clear need for hetergeneous solid catalyst that could catalyse epoxidation reactions with readily available oxidants such as H2O2 and organic peroxides. In response to this, heterogeneous epoxidation become a very attractive field of research with totally novel and improved materials [115].

The magnetically recyclable catalysts (MRCs) synthesized in recent years facilitates the catalysts to be recycled using an external magnet. Hence, easy separation and high activity are integreted on MRCs. The Fe3O4 is a material that can be completely recovered with an external magnet; therefore it is often used as a MRC and the support for other catalyst [116-118]. Styrene oxide, an important and versatile intermediate for the pharmaceuticals and fine chemicals industry, is the product when styrene is epoxidized [119,120].The catalytic activity of Fe3O4 NPs towards epoxidation of styrene reported by C. Huang et al. which states that immobilization of Au NPs on Fe3O4 NPs with the assistance of L-cysteine, leading to formation of theAu@L- cysteine-Fe3O4 nanocomposite with the uniform size distribution of Au NPs. The porous Fe3O4 NPs reportedly catalysed epoxidation of styrene and the Au NPs immobilized on Fe3O4 support significantly improved the catalyst’s performance [121].

**4.3. Benzyl alcohol oxidation**

Benzaldehyde is a very important organic compound and it is widely used in various fragrances for soaps and toiletries. It has also found its use in the manufacture of drugs e.g., ampicillin, dyes e.g., triphenylmethane green, pesticides e.g., dibenzoquat, perfumes and flavorimg agents e.g., cinnamaldehyde, amyl cinnamaldehyde, hexyl cinnamaldehyde, etc. It is also used in the manufacture of fireproof structural foam ferrocene polymers. It is generally synthesized either by oxidation of toluene or by hydrolysis of benzal chloride [122]. The oxidation of toluene is the preferred process in industrial preparation of benzaldehyde. In recent years, the prices of toluene have increased a lot as petroleum prices are increasing day by day, so the benzal chloride route is becoming economically competitive with that of oxidation of toluene. However, benzaldehyde synthesized from benzal chloride contains chloride impurities. Therefore, such a benzaldehyde is not suitable for use in the pharmaceutical industry. Hence, due to high demand, many new processes for synthesis of benzaldehyde are being developed. There are many research reports found in the literature which elucidates the synthesis of benzaldehyde from benzyl alcohol [123-134].However, in most of these reports, efforts have been made in the synthesis of different catalysts so as to increase the selectivity of benzaldehyde formation.

However, MRCs offer an added advantage of being magnetically separable, thereby eliminating the requirement of catalyst filtration after completion of the reaction. Magnetically recyclable Fe3O4-Pd nanocomposite catalyst was successfully tested for the synthesis of chlorine-free benzaldehyde by employing a sustainable oxidation protocol and high turnover number was achieved in the process [135].Recently, M. Kokate *et al.* prepared a novel Fe3O4-SiO2-Au nanocomposite and demonstrated its catalytic activity for the solventless oxidation of benzyl alcohol to benzaldehyde using O2 as oxidant. The catalyst is magnetically recyclable and exhibited high conversion of benzyl alcohol as well as excellent selectivity for the desired product benzaldehyde [136].

**4.4. Peroxidase-like activity**

Peroxidase is a redox enzyme found in almost all organisms. It main function is to catalyze the degradation of peroxides and the oxidation of some substrates inside organism. Apart from this, the activity of Peroxidase has wide range of practical applications. It has ability to catalyse oxidation of various organic substrates so as to reduce their toxicity and to produce a colour change. Peroxidase is frequently used as a detection tool or in wastewater treatment. Horseradish peroxidase (HRP) is a natural peroxidase. It is generally extracted from plants but it has many demerits such as its expensiveness, difficulty for storage and can easily become inactive under room temperature [137].

In a study, a surprising discovery was made by L. Gao *et. al.* revealed that Fe3O4 NPs possess intrinsic peroxidase-like activity. From a chemistry point of view, the findings of L. Gao *et. al* is not unexpected, as Fe2+/Fe3+ ions in solution (Fenton’s reagent) are known to catalyze the breakdown of H2O2. In practical measurements, peroxidase catalyzes the oxidation of the organic substrates to develop a colour change in the presence of H2O2. The compound, viz. 3, 3, 5, 5-tetramethylbenzidine (TMB) is commonly used as a peroxidase substrate because it is colourless and get oxidized by H2O2 very slowly [137, 138].The outcomes of the study by L. Gao *et. al.* concluded that spherical shaped Fe3O4 NPs of different sizes (30, 150 and 300 nm) could catalyzed the oxidation of the peroxidase substrate TMB in the presence of H2O2 to produce a blue colour reaction (maximum absorbance at 652 nm). The enzymatic peroxidase activities of Fe3O4 NPs are comparable with commonly used enzyme HRP. The Fe3O4 NPs also catalysed oxidation of di-azo-aminobenzene (DAB) to give a brown color and o-phenylenediamine (OPD) to give an orange color. These results indicate that the Fe3O4 NPs have peroxidase-like activity towards typical peroxidase substrates [137].Apart from Fe3O4, various otherperoxidase-like nanomaterials has been reported such as graphene oxide [139],Au or Au@Pt nanocomposites [140, 141],single-walled carbon nanotubes [142],Co3O4 [143],FeS [144],CeO2 [145] etc. But in case of Fe3O4 NPs, its magnetic recoverability provided a better option along with excellent the peroxidase-like activity.

The magnetically recoverable Fe3O4-Au nanocomposites exhibited enhanced peroxidase-like activity than Fe3O4 NPs [146].The nature of the peroxidase-like activity of Fe3O4-Au may originate from its ability to catalyze the decomposition of H2O2 into **·**OH radicals [137].The generated **·**OH radicals might be stabilized by Fe3O4-Au nanocomposites by means of partial electron exchange interactions [147].In case of Fe3O4-Au nanocomposites, the decoration of Au NPs changed the electron structure at the interface which may accelerate the electron transfer. Moreover, the partial electron transfer from Fe3O4 to Au NPs facilitates H2O2 adsorption and the activation. Thus, the interaction between Au and Fe3O4 NPs endows high catalytic efficiency upon the composites.

**4.5. Reduction of H2O2**

Y. Lee *et al.* reported a unique synthesis method for generation of Au NPs, Fe3O4 NPs, and Au-Fe3O4 nanocomposite. Here, single-component Au and Fe3O4 NPs are found directly from the Au-Fe3O4 nanocomposite by either Fe3O4 etching or byAu etching [148].The direct comparison of all three as-synthesized NPs as catalyst for H2O2 reduction shows that the Au-Fe3O4 nanocomposite offers the highest catalytic activity. The reduction of H2O2 catalyzed by the individual Au and Fe3O4 NPs proved that the enhanced catalytic ability of Au-Fe3O4 arises from the polarization effect at the Au-Fe3O4 interface, where Fe3O4 becomes more active. In the previous research, it has shown that Au NPs deposited on various oxide supports, including Fe3O4 supports, are catalytically more active for oxidation reaction due to the polarization of Au NP towards the support at the interface [149].However, in a recent study by Y. Lee *et al.* observed that Au NPs in Au-Fe3O4 nanocomposite are less active for O2 reduction reaction in alkaline solution [150]. These studies indicate that there is an interaction between Au and Fe3O4, but Au NPs in the Au-Fe3O4 structure should not show the enhanced catalysis for the H2O2 reduction reaction. The enhanced catalysis observed in Au-Fe3O4 NPs must come from the Fe3O4, for which the polarization at the interface makes the Fe3O4 NP more active for H2O2 reduction. So, the reduction activity does not arise from the free Fe ions that can catalyze the H2O2 decomposition, as in Fenton’s reaction [151, 152],but rather comes from the surface of the Fe3O4 NPs [152-154],this activity is further enhanced by their epitaxial link with Au NPs. Since the sizes of both Au and Fe3O4 in the Au-Fe3O4 structure can be controlled synthetically, the Au-Fe3O4 NPs offer an ideal catalytic system for studying synergetic effects that are controlled not only by Au but also by Fe3O4. This nanostructure tuning capability should also allow the development of active Au-Fe3O4 NPs for highly sensitive H2O2 detection [148].

**5. CONCLUSION**

The synthesis Au-FexOy hybrid nanocomposite materials have been exploited in the effective synthesis of bifunctional, ternary functional and multifunctional/multilayer structure. Other morphological architectures that attract particular interest are core-shell and heterostructures. The researchers are generally put their efforts on synthesizing novel core-shell and multifunctional/multilayer composite structures to overcome their challenges in the synthesis of these materials. Indeed, the physico-chemical properties of the core materials would be decreased in the core/shell and multifunctional/multilayer Au–FexOy hybrid nanocomposite structures but different functional peripheral surfaces rendered them in particularly attractive multi-functional probes for specific applications. The inherent modularity of the synthesis process for Au–FexOy hybrid nanocomposite may allow for synthesis of many other analogous hybrid nanocomposites with different metals/metal oxides in which either the core or periphery can be modified to suit the needs of any given applications. There are indications that Au–FexOy hybrid nanocomposite with core/shell and multifunctional/multilayer architectures might possess unprecedented catalytic activity for various industrially important processes. It also offered an alternative magnetic separation method of the catalyst rather than tedious filtration and centrifugation method. It would be interesting to explore such Au–FexOy hybrid nanocomposite in the forseeable future to advance chemistry, engineering and biology in multi-disciplinary research.

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