**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 nanostructure that can be modifiable with various functional groups/moieties on the surface to enhance their compatibility and stability.The advancement in the research for controlling functionality can provide various routes for synthesizing novel Au–FexOy hybrid nanocomposite materials. The application of Au–FexOy hybrid nanocomposites is mostly dependent on their morphology, composition, stability of the as-synthesized materials. Therefore, the booming combinations of gold and Iron oxide are promising to get a hybrid nanocomposite with serendipitous and advantageous properties from both gold and iron oxide 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 hybrid nanocomposites catalysts enable an excellent magnetic separation method for its recyclization. Moreover, the hybrid matrix remarkably stabilizes the Au0 NPs from being agglomerated and leached which ultimately enhances their reclabilty. It was obatined that Au–FexOy exhibited high catalytic effectiveness rather than the Au0 NPs alone because of synergetic effect which originates at interface of the gold and Iron oxide.

*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 the researchers owing to their extraordinary physico-chemical properties and possible applications in catalysis, photonics, electronics, nanotechnology and biotechnology etc [1–6]. These nanocomposites can be synthesized in different morphology such as binary, ternary or core/shell 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 these nanocomposites are dependent on its morphology, composition and stability under various conditions. So, many researchers have devoted their effort for the synthesis of different nanocomposites in order to generate novel nanocomposites which have 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 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 have a cubic inverse spinel crystal structure and they are favourable for fabricating magnetically separable hybrid nanocomposites because of its intrinsic magnetic property along with the nanodimension and surface effect. 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 nanocomposites and the agglomeration of FexOy NPs is very small 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 MRI. The FexOy NPs can accelerate the transverse relaxation protons of water and thereby shorten the spin–spin relaxation time of proton [18–20].

On the other hand, Au NPs are used extensively for its 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 diagnosis and therapeutics. The synthesis of Au NPs is very easy now-a-days and the same can be conjugated with various functionalizing moeities such as surfactants, dendrimers, ligands, proteins and oligonucleotides etc [21, 22]. The surface functionalization strategy increased the capability of Au NPs by many folds for its applicabilty in photothermal therapy and the same reduced the cytotoxic effects in gene therapy, different cancers and other diseases [23-26].

Among the different multidisciplinary applications of Au NPs, catalysis is a topic of current research interest to the scientists. There are several reasons which explain this interest. One among the several reasons for choice of Au NPs as catalyst is that the catalytic effciency of Au is directly related to the particle’s size. When the particle size increases into the micrometer 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 does not have any catalytic activity. Thus, the effort is to understand the reasons of catalytic activity of Au NPs to expand its scope of utilization. Moreover, the optimization of the size of Au NPs and finding the mechanistic pathway 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 catalysis of Au NPs has derived benefits for the tailoring of porous nanostructured materials having high surface area for showing unexpected catalytic properties. So, the application of Au NPs in catalysis became an emerging research area a few years from the first report of its catalytic activity for hydrochlorination of ethyne [29] and Au NPs is now considered an excellent catalyst option of various fundamental organic reactions e.g. oxidation, hydrogenation etc [30].

So, the combination effect 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 developments in the synthesis of Au–FexOy hybrid nanocomposite and study of its catalytic activity. The outstanding and unique properties of Au NPs in combination with the FexOy have fueled the fabrication of a new generation of selective and stable hybrid catalyst for the various important organic reactions. There is also some synergetic effect which occurs in the interface of the Au NPs and FexOy support. A brief elaborated result of various research groups along with the correlation between the catalyst morphology with the catalytic properties is discussed here.

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

In general, the morphology of Au-FexOy hybrid nanocomposites are 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 NPs have attracted much attention from material scientists due to their advantageous and serendipitous catalytic properties superior from both individual Au and FexOy NPs. Recently, various advanced synthesis methodologies were 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 reducer. For successful immobilization of gold precursor salts, the surface of FexOy is 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 tethered on Fe3O4 NPs that are coated with chitosan and reduced to Au NPs with a NaBH4 [31]. Y. Qiu *et al.* presented an alternative easy way to synthesize Au0 NPs by using chitosan as reducer as well as stabilizer without employing any other stronger reducing agents or stabilizer e.g. NaBH4 or trisodium citrate. Fe3O4/chitosan composite synthesized first and then chitosan reduces AuCl4− to gold NPs [32]. F. Yan *et al.* published a simplistic method for preparation of bifunctional Fe3O4/Au nanocomposites by reducing with NaBH4. In this method, the AuCl4− that was adsorbed on the carboxylate functionalized Fe3O4 NPs [33]. C. Huang *et al.* published a successful method for the 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.* published the synthesis of hybrid Au NPs on Fe3O4 microspheres and the as-prepared Fe3O4 hybrid microspheres were further 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 influences of the support also affect the catalytic potency in some cases. As for example M. Kokate *et al.* reported an easy one-pot synthesis of novel Fe3O4 @SiO2@Au nanocomposite by employing a co-precipitation method that led to the generation of Fe3O4 and Au NPs immobilised on a silica matrix [36]. F. Chen *et al.* reported a ternary functionalised Fe3O4-graphene-Au nanocomposite where both Fe3O4 and Au NPs are supported on the reduced graphene oxide (GO). This research work also states that Fe3O4 NPs are used to further modify graphene to provide the nanohybrid material their magnetic recyclabilty [37]. Jing Hu *et al.* reported a facile and green route for “*in situ*” generation of Au NPs on the surface of GO-Fe3O4. After functionalization with –NH2 groups, the GO-Fe3O4 nanohybrid material has adsorbed Au NPs which was generated by using chloroauric acid solution as gold precursor while glucose serves as reducer [38]. B. Lu *et al.* presented a very effective method for the generation of Au@Fe3O4–Graphene ternary hybrid nanomaterial by “*in situ*” formation of Fe3O4 on graphene by using tetraethylene glycol (TEG) as both reductant and solvent for this synthesis method. Moreover, the Fe3O4–Graphene has acted as a support for loading Au NPs so as to prepare Au@Fe3O4– Graphene hybrid materials [39]. L. Ren *et al.* proposed a very good methodology for the fabrication of uniform sized mesoporous silica micro-spheres which is incorporated with Au and Fe3O4 NPs, mentioned as γ-Fe2O3/Au/mSiO2 [40].

**2.1.3. Multifunctional/multilayer nanocomposite**

The aforementioned Au–FexOy nanostructures are all ‘bi’ or ‘ternary’ nanocomposite materials. Many researchers are very much interested in expanding the scope of utilization of Au–FexOy nanocomposites material by introducing multiple functionality so as to generate “*all in one*” nanohybrid. The coating of silica layer is common choice after the fabrication of FexOy core as it can stabilize the core and to inhibit its agglomeration. The coating of silica on FexOy NPs is gererally performed by using a sol–gel approach.The silica layer is introduced during the synthesis of Au–FexOy nanocomposites to increase the stability of FexOy. Yeo *et al.*, recently published a work on the synthesis of Fe3O4@Au core/satellite nanohybrid coated with a silica [41]. Y. Zhu *et al.* reported the synthesis of multi-functional nanocomposite microspheres with “*in situ*” formation 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 nanocomposite. In the as-syntesized material, the Au NPs were effectively embedded on functional PDMAEMA brushes through the “*in situ*” reduction [43].

**2.2. Core/shell structures**

The nanoparticle having a single core which is fully coated by a shell is termed as core/shell structure. These core/shell nanocomposite materials combined with the advantageous nature of the core and shell, have attracted tremendous research interest for 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]. Moreover, these specific core/shell nanostructures could be modified with various functional moieties which enhance their compatibility and stability. These modifications provide an avenue of the fabrication of complex nanocomposite materials.

The design and fabrication of different core/shell structures of Fe3O4 are very exciting research topics since the Fe3O4 is extensively studied due to their potential applications as catalysts, ferrofluids, biological assays, electrophotographic developers, chemical sensors etc [45-50]. In recent years, researchers have developed various strategies to fabricate different magnetic core/shell nanocomposite materials.W. Guo *et al.* [51] reported a very easy method to prepare core-shell Fe3O4@P(4-VP–DVB)@Au microspheres where Au NPs are easily supported on the P(4-VP) shell by reducing HAuCl4 in the dispersion of Fe3O4@P(4-VP–DVB) microspheres. A solvothermal method has been employed to synthesize peroxyacetic acid (PAA)-modified Fe3O4 NPs [52-53] where monomers of 4-VP has been embedded on the Fe3O4 NPs *via* strong hydrogen bonding interaction between their pyridine moieties as an electron donor and PAA as electron acceptor. Under acidic pH, the surface of Fe3O4@P(4-VP–DVB) microspheres show tendency for protonation and stretch because of 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 stretched by using 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 on 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 core/shell Au catalyst, viz., Au-Fe3O4@MIL-100(Fe) by a very versatile layer-by-layer assembly process. It has been observed that, by adjusting the cycle number, the thickness of shell in core-shell structures can be tuned. W. Zhang *et al.* [58] have synthesized a monodisperse magnetic sandwiched core/shell Fe3O4@Au/PEGDMA microspheres by using hydrothermal methodology for the synthesis of Fe3O4 core with subsequent functionalization with (3-aminopropyl) trimethoxysilane 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.

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 reduction of Au precursors to synthesize Au-coated Fe3O4 NPs viz., 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 the permission from ref. 56. Copyright © 2005, American Chemical Society).

**2.3. Hetero-structures**

The Au–Fe3O4 hetero-structures 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 hetero-structures by thermally decomposing iron oleate complex [Fe(OL)3] with gold 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 catalytic behaviour of the hetero-structured nanocatalysts is due to the different epitaxial linkages in flower and dumbbell-like hetero-structures. Y. Lee *et al.* [64] prepared a dumbbell-like Au-Fe3O4 NPs by injecting [Fe(CO)5] into the solution of 1-octadecene that contain Au seeds, the same are made by the reduction of chloroauric acid by tert-butylamine–borane (TBAB) in tetralin and oleylamine [63]. B. Mu *et al.* [65] reported a superparamagnetic gold/halloysite nanotubes/Fe3O4 viz., Au/HNTs/Fe3O4 nanocomposite, by selective change of external wall and the inner lumen of HNTs. The lumen of HNTs serves as nano-confined reactor for the fabrication of Au nanorods where Fe3O4 NPs are embedded on the external wall of HNTs.

**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 close to the FexOy core or Au would generate broad NMR signals with alternation in the signal integration. The identities of the functional moieties of the ligands could be identified through FTIR spectroscopy. UV/vis spectroscopy are generally used to monitor the surface plasmon property of Au NPs. X-ray diffraction (XRD) and Small-angle X-ray scattering (SAXS) could be used to evaluate the composition of as-prepared nanocomposite. 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 out the amount of organic and inorganic mater of the nanocomposites at different 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 check the morphology of the nanocomposites. The High-resolution transmission electron microscopy (HR-TEM) is used to visualize the nanodimension of the hybrid material. The Scanning tunneling microscopy (STM), atomic-number-sensitive high-angle annular dark field (HAADF) imaging and Atomic force microscopy (AFM)[66] techniques are employed to find high resolution (HR) images at a less than 10 nm scale.

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

In the past few decades, supported Au nanocatalyst have been emerged as a potential heterogeneous catalyst for various important organic reactions e.g. 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 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]. Moreover, the hybrid FexOy nanocomposites matrix efficiently stabilizes the Au NPs from leaching and agglomeration, which led to enhance its catalytic recyclabilty. There is also some synergetic effect which originates in interface of the Au and FexOy support. It is speculated that the electronic structures of both the Au and FexOy support are modified by electron transfer across the interface,it resulted in the increase of surface oxygen vacancies on the FexOy support that become the active sites for oxygen absorption as well as 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 but it is not hazardous for human health [76].Another motivation made this CO oxidation reaction, an important topic because of its potential research in the design of fuel cell. The main issue which hinder the practical use of CO fuel cell is the problem associated with the removal of CO from the feed gas of fuel cells since CO molecules can poison the catalyst used in most fuel cells that operated at low temperature [77-81].The Preferential Oxidation (PROX) process generally used for CO oxidation to remove negligible amounts of CO to ppm level from the H2 stream that is used as a fuel in the polymer−electrolyte membrane fuel cells [77-86].The development of highly active as well as selective catalyst that operates within a wide temperature range (80−180 °C) also having good resistance against CO2 and steam is the key to the application of PROX [87].In past few years, various catalyst systems was 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 high catalytic activity at low-temperature. In spite of stoichiometric simplicity of this CO oxidation reaction, many mechanistic details remain undiscovered. The activation energies, turnover rates, and rate equations in previous research reports, at least in part due to 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 independent on dispersion of metal even though the structural unsaturation of exposed metal atoms is differing among clusters of different sizes [80].

Since the pioneering works of Haruta *et al.* [90, 91],CO oxidation reaction over supported Au NPs has became one of the most widely studied organic reaction 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 its synthesis methodology [95-97] which affect the size and shape of the Au NPs [98, 99],the role of the selected support [100-102], the oxidation state of gold (metallic, Au+ or Au3+) [103-105],and the oxygen supply pathways [103-105].However, a few research reports are highly controversial and the debate will continue for a few years since the sensitivity and complexity of catalysis by active gold species. The influence of Au NPs size on its catalytic efficiency is an example; it was observed that Au NPs of 2–5 nm size are most active as catalyst for CO oxidation [106].

When Au NPs are supported on iron oxides are employed as catalyst in the CO oxidation, it became exothermic a reaction having very low catalytic activation barriers [106].A detail comparison of Au catalysts embedded on various support and its activity measurements for Au with mixed oxides (Au/Fe2O3.MgO) discover the enhanced rates of CO oxidation for a group of “active” metal oxides e.g. TiO2, Fe2O3, CoO*x* , NiO*x*. Au–FexOy nanocomposites and their derivatives were demonstrated the catalytic effect towards CO oxidation [106-108]. It is found that the Au nanocatalysts supported on Fe2O3 showed a significantly high activity for CO oxidation reaction.

The origin of catalytic efficiency 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 supposed to be originating on the FexOy support or in the Au–FexOy interface, especially in the close proximity of Au NPs as a result of Schottky junction the interface. It is also believed that oxygen adsorbed on the FexOy support dissociates immediately and produces lattice oxygen, that subsequently react at the Au–FexOy interface or after a oxygen spillover to the Au NPs.

**4.2. Epoxidation**

Epoxides are very important chemicals in the synthetic organic chemistry. These are widely used for the synthesis of important intermediates in various organic transformations. Most importantly, epoxides have widespread use in the synthesis of anthelmintic preparations, perfumes, drugs, epoxy resins, plasticizers, sweeteners, etc. Therefore, the synthesis of epoxides by a low cost route and facile method is very important task [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 by using an external magnet; therefore it is often used as a MRC and the support for other catalyst [116-118]. Styrene oxide is a very important intermediate for the pharmaceuticals and fine chemicals industry synthesized by the epoxidation of styrene [119,120].The catalytic activity of Fe3O4 NPs towards epoxidation of styrene reported by C. Huang et al. states that immobilization of Au NPs on Fe3O4 NPs by using of L-cysteine led to the formation of theAu@L- cysteine-Fe3O4 nanocomposite having monodispersed Au NPs. The porous Fe3O4 NPs reportedly catalysed styrene epoxidation and the Au NPs immobilized on Fe3O4 support enhanced the nanocomposite catalyst’s performance significantly [121].

**4.3. Benzyl alcohol oxidation**

Benzaldehyde is a compound having significant importance and it is widely used as fragrances for toiletries and soaps. It has also found its use in the synthesis of drugs e.g., ampicillin, dyes e.g., triphenylmethane green, pesticides e.g., dibenzoquat etc. It is also used in the synthesis of ferrocene foam polymers which is a fireproof material. It is generally synthesized either by oxidation of toluene or by benzal chloride hydrolysis [122]. The toluene oxidation is the preferred process in industrial preparation of benzaldehyde. In recent years, the market value of toluene has increased immensely due to increase of petroleum prices day-by-day. Hence the synthesis of benzaldehyde from benzal chloride has become economically competitive with toluene oxidation route. But, chloride impurities are found in benzaldehyde which was synthesized from benzal chloride. Therefore, such a benzaldehyde can not be use in the drug industry. Hence, due to high demand, new methods for synthesis of benzaldehyde are on developement. The syntheses of benzaldehyde from benzyl alcohol are also reported by many research groups [123-134].But, in these reports, efforts have been made in the synthesis of various catalysts so as to enhance the selectivity for benzaldehyde.

However, MRCs offer an extra advantage for being magnetically separable, hence cancelling the requirement of filtration of catalyst after the reaction.The magnetically recyclable Fe3O4-Pd nanocomposite catalyst was successfully tested for the synthesis of benzaldehyde frer from chlorine by employing a green protocol and the high turnover number (TON) 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 solvent-free oxidation of benzyl alcohol to synthesize benzaldehyde using molecular oxygen 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 significant potential applications. It can also catalyse oxidation of various organic substrates so as to reduce their toxic effect and to show a colour change. Peroxidase is generally used as a detection tool or in wastewater treatment. Horseradish peroxidase (HRP) is actually a natural peroxidase. It is extracted from plants source 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, since Fe2+/Fe3+ ions in solution, known as Fenton’s reagent are reportedly catalyze the degradation of H2O2. In general, peroxidase enzyme catalyzes the oxidation of some organic compounds so as to develop a colour change with H2O2 as oxidant. The compound, viz. 3, 3, 5, 5-tetramethylbenzidine (TMB) is generally the choice as a peroxidase substrate due to it is colourless appearence and it get oxidized by H2O2 very slowly in absence of catalyst [137, 138].The outcomes of the study by L. Gao *et. al.* concluded that spherically shaped Fe3O4 NPs of different sizes could catalyze the oxidation of the peroxidase substrate TMB with H2O2 hence produce a blue colour (λmax= 652 nm). The peroxidase-like catalytic activity of Fe3O4 NPs is comparable with commonly used enzyme HRP. The Fe3O4 NPs also catalysed oxidation of di-azo-aminobenzene (DAB) to produce a brown color and o-phenylenediamine (OPD) to produce an orange color. The aforementioned results confirmed that the Fe3O4 NPs possess peroxidase-like catalytic activity towards different peroxidase substrates [137].Apart from Fe3O4, various othernanomaterials is known which exhibit peroxidase-like activity e.g. 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 nanohybrid exhibited enhanced peroxidase-like activity than Fe3O4 NPs [146].The nature of the peroxidase-like catalytic activity of Fe3O4-Au may originate from its ability to catalyze the decomposition of H2O2 into **·**OH free radicals [137].The generated **·**OH radicals might be stabilized by Fe3O4-Au nanohybrid by partial electron exchange interactions [147].In case of Fe3O4-Au nanohybrid, the decoration of Au NPs changed the electronic structure at the interface of Au and Fe3O4 which could cause accelerated electron transfer. The partial electron transfer from the Fe3O4 to Au NPs facilitates H2O2 adsorption and the activation. Thus, the interaction occurs between Au and Fe3O4 NPs endows high catalytic efficiency of the nanohybrid.

**4.5. Reduction of H2O2**

Y. Lee *et al.* reported a unique synthesis process for generation of Au NPs, Fe3O4 NPs, and Au-Fe3O4 nanocomposite. Here, single-component gold and magnetite NPs are found directly from the Au-Fe3O4 nanocomposite by either magnetite etching or by gold etching [148].The comparative activity study of gold, magnetite and Au-Fe3O4 nanocomposite as catalyst for H2O2 reduction shows that the Au-Fe3O4 nanocomposite offers the highest catalytic efficiency. The H2O2 reduction reaction catalyzed by gold and magnetite NPs individually confirmed that the enhanced catalytic ability of Au-Fe3O4 is due to the polarization effect at the interface of gold and magnetite. In a recent research work, it is revealed that gold NPs deposited on various meatl oxide supports e.g Fe3O4 supports, are catalytically more effective for oxidation type reactions due to the polarization of gold NP to the metal oxide support [149].Moreover, in a recent research work performed by Y. Lee *et al.* noticed that gold NPs in Au-Fe3O4 nanocomposite are less active for reduction of O2 reaction in alkaline medium [150]. These research works confirmed the interaction between gold and magnetite, but gold NPs in the Au-Fe3O4 nanohybrid should not exhibit enhanced catalytic activity for the reduction of H2O2. The enhanced catalytic activity found in case of Au-Fe3O4 nanohybrid must originates from the magnetite. So, the reductive power does not originates from the free iron ions that could catalyze the decomposition of H2O2, as we observed in case of Fenton’s reaction [151, 152],but rather arise from the peripheries of the magnetite NPs [152-154]. The catalytic activity for the aforementioned reaction is further increased by their epitaxial link with gold NPs. Since the sizes of both gold and magnetite in the Au-Fe3O4 nanohybrid can be tuned, hence Au-Fe3O4 nanohybrid offers an ideal catalytic system for exploring one of the most facinating topic i.e. synergetic effects.. This tuning capability of Au-Fe3O4 nanohybrid material could allow the fabrication of active Au-Fe3O4 nanohybrid for highly sensitive detection of H2O2 [148].

**5. CONCLUSION**

The synthesis Au-FexOy nanocomposites have been exploited in the fabrication 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 architectures to explore challenges arise in the practical applicability of these materials. Indeed, the physico-chemical properties of the metal oxide core would be decreased in the multifunctional/multilayer and core/shell Au–FexOy hybrid nanocomposite structures but different peripheries rendered them very attractive for specific applications. The inherent modularity of the synthesis process for Au–FexOy hybrid nanocomposite may allow for synthesis of other analogous hybrid nanocomposites with selected metals/metal oxides where either the core or periphery can be functionalized to suit the needs of any required 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 materilas chemistry, engineering and biology in multi-disciplinary research.

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