**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 functionality have been intensively investigated by the materials scientist due to their serendipitous physicochemical properties and potential applicability. Gold and iron oxide (Au–FexOy) hybrid 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 and so on. These nanocomposites generally exhibited a core/shell or a binary nanostructure which can be modified with different functional moieties on the surface to enhance their stability and compatibility. The advance in controlling functional peripheries can provide an avenue for synthesizing next-generation, complex Au–FexOy hybrid nanocomposite materials. The successful application of such nanocomposites is highly dependent on their morphology, composition, stability of the materials under different conditions. Therefore, the thriving combination of Au and FexOy are promising to obtain a hybrid nanocomposite with advantageous and serendipitous properties from both individual Au and FexOy nanoparticles (NPs). Recently, Au–FexOy hybrid nanocomposites and their derivatives were successfully demonstrating catalytic activity towards carbon monoxide (CO) oxidation, reduction of hydrogen peroxide (H2O2) etc. The Au–FexOy nanocomposites enable a better separation method for recycling the nanocatalysts from the reaction mixture by using external magnet. Furthermore, the hybrid material matrix significantly stabilizes the Au NPs from agglomeration and leaching which enhances their catalytic lifetime. It was found that Au–FexOy exhibited a higher catalytic efficiency than the Au NPs alone due to the synergetic effect that occurs at the interface of the metal and 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 components have attracted increasing interest to materials scientists owing to their extraordinary physicochemical properties and potential applications in the field of catalysis, photonics, electronics, biotechnology and nanotechnology 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 different functional moieties and reactive groups on the surface to enhanced stability and compatibility [7, 8]. The advantage of controlling the functional moieties and reactive groups can provide an avenue for synthesizing advanced nanocomposite materials. The successful applications of such nanocomposites are highly dependent on their morphology, composition and stability of the particles under different conditions. Therefore, many researchers have devoted their effort for the fabrication of different nanocomposite materials in order to develop novel multi-functional 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, which are highly interesting both from the fundamental point of view and 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 typical cubic inverse spinel structure and they are favourable for fabricating magnetic hybrid nanocomposites because of their intrinsic magnetic features along with the nanosize and surface effects. When the grain size of FexOy is below a critical value (~10–20 nm) and the temperature is above the blocking temperature, the hybrid nanocomposites show superparamagnetic behavior. At this point no magnetic remanence and coercivity would be found in these materials and the aggregation phenomenon of these hybrid particles is negligible at room temperature [14]. The above features of magnetic FexOy nanomaterials makes these a suitable candidate for selective capturing of targeting substrates, recyclable nanocatalysis, and magnetic photonic application [15-17]. In addition, FexOy NPs act as T2 contrasting agent in magnetic resonance imaging. They can accelerate the transverse relaxation of water protons and thus shortening the spin–spin proton relaxation time [18–20].

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

Among the different multidisciplinary application of Au NPs, catalysis is a topic of much current interest. There are several general reasons that explain this interest. One of them is the fact that the catalytic activity of Au is directly related to the particle size in the nanometer length scale and the catalytic property can disappear completely as the particle size grows into the micrometric scale [27]. The second factor that explains the interest in catalysis by Au NPs is the fact that it was believed for a long time that Au was devoid of any catalytic activity. Thus, understanding the reasons of this catalytic activity, expanding the scope to other reactions, optimizing and finding the reaction mechanisms for gold catalyzed reactions is a new field in heterogeneous catalysis [27]. Finally, there is a third factor that justifies the importance of the research in Au NPs comes from the fact that since very small colloidal or supported Au NPs have to be prepared, one can imagine that catalysis by Au NPs represent a bridge between homogeneous and heterogeneous catalysis [28] These two disciplines have developed fairly independently up to now, but nanoparticles can provide a point of convergence for both fields. Thus, gold catalysis is a paradigmatic example of those properties that are only observed in nanoparticles. The catalysis in gold has derived benefits for tailoring solid nanostructured surfaces showing unexpected catalytic properties. In fact, the application of gold in catalysis only became an important research area several years after the first report on its catalytic potential for ethyne hydrochlorination [29] and it is now considered an active promoter of many fundamental reactions for organic synthesis such as oxidation and hydrogenation [30].

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

This book chapter covers the recent development of the synthesis and catalytic properties of the Au–FexOy hybrid nanocomposite, highlighting the exciting contribution to the art of catalysis. The unique, outstanding properties of nanometre-scale Au, a biocompatible non-toxic metal in combination with the FexOy have allowed the development of a new generation of stable and selective hybrid nanocomposite catalyst for the many important organic reactions. There is also some synergetic effect that occurs at the interface of the Au and FexOy support. A critical discussion of the results of different research groups is presented along with attempts to correlate the catalytic properties with catalyst morphology.

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

In general, the morphology of Au–FexOy hybrid nanocomposite materials can be divided into three main categories-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 more attention from material scientists and chemists due to their advantageous and serendipitous catalytic properties superior from both individual Au and FexOy NPs. Various advanced synthetic methods have been recently reported for the 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 basically 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 facile way to prepare gold NPs using chitosan as the reducing and stabilizing agent without any other stronger protecting or reducing agents, such as citrate or NaBH4. Fe3O4/chitosan composite synthesized first and then chitosan reduces AuCl4− to gold NPs [32]. F. Yan *et al.* reported a simple, facile and efficient method to synthesize bifunctional Fe3O4/Au nanocomposites by direct NaBH4 reduction of AuCl4− 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 gold NPs on Fe3O4 microspheres and these Fe3O4 microspheres were then coated with polymer to make the Au NPs easier to load and to prevent the aggregation and oxidation of Fe3O4 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 iron oxide 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−one-step process for the synthesis of a novel magnetite−silica−gold nanocomposite. Coprecipitation of iron salts by gold chloride−sodium silicate complex leads to the formation of magnetite and Au NPs impregnated into a silica matrix [36]. F. Chen *et al.* reported another ternary nanocomposite of Fe3O4-graphene-Au i.e. Fe3O4 NPs and Au NPs loaded on the carbon basal planes of reduced grapheme Oxide. Author’s states that Fe3O4 NPs are chosen to further functionalize graphene to endow the hybrid materials with a magnetically recycling catalyst support [37]. Jing Hu *et al.* reported an alternative simple and green route for in situ growth of gold shell or grown gold NPs attached on the graphene oxide–iron oxide nanocomposite (GO-Fe3O4) was established. After functionalized with amino groups, the GO-Fe3O4 nanocomposites can absorb negatively charged Au NPs which acted as gold seeds. Then the HAuCl4 solution provides gold precursor with glucose serving as reducing reagent, whereby the crystal growth leads to the in situ growth of gold shell or grown gold NPs attached on the surface of GO-Fe3O4 [38]. B. Lu *et al.* presented a general and effective approach for preparation of Au@Fe3O4–G ternary hybrid nanomaterial by in situ nucleation and growth of Fe3O4 on the surface of graphene in tetraethylene glycol (TEG) solution where TEG, a nontoxic and environmentally friendly agent, acts as both solvent and reductant. Furthermore, the Fe3O4–G was employed as a two dimensional support for loading Au NPs to synthesize Au@Fe3O4–G ternary hybrid materials [39]. L. Ren *et al.* reported an efficient method for the synthesis of uniform mesoporous silica microspheres embedded with Fe3O4 and Au NPs, designated as γ-Fe2O3/Au/mSiO2, using porous polymer microspheres as template and the ternary as γ-Fe2O3/Au/mSiO2 composite are obtained after calcinations to remove the polymer template and organic agents [40].

**2.1.3. Multifunctional/multilayer nanocomposite**

The above-mentioned Au–FexOy structures are basically bi/ternary composite materials. Many scientists are interested in extending the scope of Au–FexOy nanocomposites by introducing more layers/multiple functionality of material on them in a view to synthesize ‘‘all in one’’ nanocomposites. Silica layer coating is common after the synthesis of the FexOy core due to its ability to stabilize the FexOy core and prevent its aggregation. To coat a silica layer onto FexOy NPs, tetraethylorthosilicate (TEOS) is typically used for a sol–gel reaction. During the synthesis of Au–FexOy nanocomposites, the silica layer is introduced in order to increase size and stability of FexOy. As reported by Yeo *et al.*, the Fe3O4@Au core/satellite composite is coated with a silica layer. By selective etching of the Fe3O4 core with NaBH4, hollow silica NPs embedded with Au NPs were synthesized [41]. Y. Zhu *et al.* reported construction of multifunctional magnetic composite microspheres with in situ growth Au NPs in multilayer polyelectrolyte films (MPFs); designated as Fe3O4@SiO2-LBL-Au (0) microspheres. The MPFs are especially attractive for encapsulating metal NPs because their layer-by-layer (LBL) deposition is both convenient and versatile [42]. B. Liu *et al.* reported synthesis of multilayer Fe3O4@SiO2@PHEMA-g-PDMAEMA Microspheres and the Au NPs were facilely loaded into the functional PDMAEMA brushes through the in situ reduction due to their strong coordinate interaction [43].

**2.2. Core/shell structures**

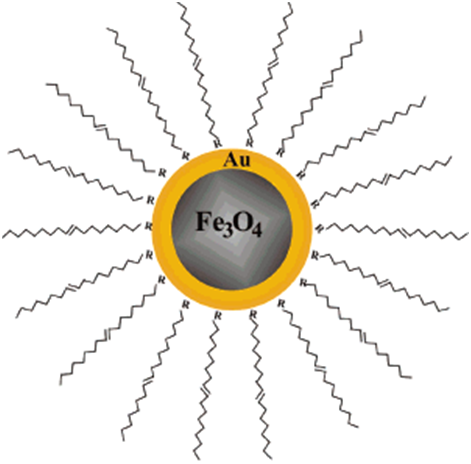
A nanoparticle with a single core and fully covered with a shell coating is known as Core/shell nanocomposite. This core/shell-structured composite materials which combine with the advantageous properties of both materials of the core and the shell, have attracted increasing interest to materials scientists due to their unique physicochemical properties that has been employed in various potential applications in the areas of photonics, biotechnology, catalysis and nanotechnology [3-6, 44]. The surface of the uniform core/shell nanocomposite could be further functionalised with new ligands to give well-defined structures. Furthermore, these specific core/shell structures which possess the ability to be modified with different charges, functions, or reactive moieties on the surface with enhanced stability and compatibility provide an avenue for the synthesis of complex composite materials.

The design and synthesis of various core/shell architectures based on Fe3O4 are important research subjects as this magnetite, with a cubic inverse spinel structure, has been widely studied because of their potential applications as ferrofluids, catalysts, biological assays, chemical sensors, and electrophotographic developers [45-50]. Scientist and researchers have developed different strategies to synthesize different magnetic core/shell composite materials.

W. Guo *et al.* [51] propose a simple hydrogen-bond-assisted polymerization method to synthesize well-defined core-shell Fe3O4@P(4-VP–DVB)@Au microspheres where Au NPs are easily embedded into the P(4-VP) shell through reduction of HAuCl4 in Fe3O4@P(4-VP–DVB) microsphere dispersion. A solvothermal method has been applied 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-bond 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 owing to the strong affinity of pyridine group toward H+ and thus provide the route of 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 in presence of NaBH4 causes shrinkage of P(4-VP) chains, thus causing the reduced and growing Au NPs to be embedded into the outer P(4-VP) shell of the synthesized Fe3O4@P(4-VP–DVB) microspheres.

F. Ke *et al.* [54] synthesized a MOF based porous magnetic core-shell Au catalyst, Au-Fe3O4@MIL-100(Fe) by a versatile layer-by-layer assembly method. It has been observed that by adjusting the assembly cycle number, the shell thickness in core-shell structures can be controlled. W. Zhang *et al.* [58] have designed and prepared monodisperse magnetic sandwiched Fe3O4@Au/PEGDMA core–shell microspheres by adopting hydrothermal method for preparation of magnetite core with subsequent modification of (3-aminopropyl) trimethoxysilane (APS) for introduction of the surface amino 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 in presence of NaBH4 as reductant. By altering the weight ratios of EGDMA monomers to magnetite core during polymerization process the thicknesses of the outer polymeric shells could be controlled.

L. Wang, et al. [56] describes of the synthesis and assembly of core (Fe3O4)-shell (Au) NPs with high monodispersity. Fe3O4 NPs of selected sizes were used as seeding materials for the reduction of gold precursors to produce gold-coated Fe3O4 NPs (Fe3O4@Au). A typical core-shell structure is also schematically represented in scheme 1 [56].



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

**2.3. Heterostructures**

Different from the core-shell nanoparticles, the Au–Fe3O4 heterostructures in which the Au seeds are interfacially linked to Fe3O4 NPs, are versatile nanomaterials that exhibit the unique physicochemical and catalytic properties [57–62].

F.-H. Lin *et al.*[58] demonstated the synthesis of dumbbell- and flower-like Au-Fe3O4 heterostructures by thermal decomposition of ironoleate complex (Fe(OL)3) in the presence of Au seeds of different sizes at 310 oC. The Au-Fe3O4 heterostructures possess bifunctional properties with high magnetization and excellent catalytic activity. It has been found that the change in magnetic and catalytic properties of the heterostructured nanocatalysts is due to the different epitaxial linkages in dumbbell- and flower-like heterostructures. Y. Lee *et al.* [64] synthesized 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]. Iron then nucleated and grew on the Au NPs. the Fe NPs are oxidized to Fe3O4 NPs upon exposure to air, giving Au-Fe3O4 NPs [64]. B. Mu *et al.* [65] reported a novel superparamagnetic gold/halloysite nanotubes/Fe3O4 (Au/HNTs/Fe3O4) nanocomposite by selective modification of the inner lumen and external wall of HNTs. The lumen of HNTs serves as nanoconfined reactor for the synthesis of Au nanorods where Fe3O4 NPs are deposited on the external wall of HNTs via the electrostatic assembly under the mild condition in order to prevent the structure of HNTs from destroying.

**3. CHARACTERIZATION**

The presence of structural functions and the ligand integrity in the nanocomposites can be characterized through Nuclear magnetic resonance (NMR), Fourier-transform infrared (FTIR), and ultraviolet/visible (UV/vis) absorption spectroscopies. The ligand’s atoms adjacent to the Au or FexOy core would give broad NMR signals with alternation in the signal integration. The identities of the functional group of the ligands can be identified through FTIR spectroscopy. UV/visible spectroscopy can be used to monitor the plasmonic absorption of Au nanoparticles. Small-angle X-ray scattering (SAXS) and X-ray diffraction could be used to determine the composition of the nanomaterials. Other techniques such as X-Ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDX) could provide elemental information and ratio on the nanocomposite surface. thermogravimetric analysis (TGA) could provide the percentage composition information of organic and inorganic composites at different decomposition temperatures. Inductively coupled plasma optical emission spectroscopy (ICP-OES) could be used to estimate the Au and Fe metal contents [66]. Scanning electron microscopy (SEM) could be used to reveal the general morphologies for nanocomposites possessing an average size over 200 nm. Au–FexOy nanocomposites at sizes between 10 to 1000 nm with different contrasts for Au and Fe could be visualized through High-resolution transmission electron microscopy (HR-TEM). Atomic force microscopy (AFM), scanning tunneling microscopy (STM), aberration-corrected scanning transmission electron microscopy (AC-STEM) and atomic-number-sensitive high-angle annular dark field (HAADF) imaging [66] could be employed to reveal high resolution images at a sub-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 potent heterogeneous catalyst for various important reactions such as low-temperature carbon monoxide oxidation, hydrogenation, alcohol oxidation, alkene oxidation, reductive catalysis of nitrohydrocarbons and organic synthesis etc [27, 67-70]. However, the high cost of the gold precursor 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 material matrix significantly stabilizes the Au NPs from agglomeration and leaching, leading to its catalytic lifetime enhancement. There is also some synergetic effect that occurs at the interface of the metal and oxide support. It is believed that the electronic structures of both the metal and the oxide support are modified by electron transfer across the interface, giving rise to oxygen vacancies on the interfacial oxide support that become active sites for oxygen absorption and activation in some reactions particularly carbon monoxide oxidation. These Au–FexOy nanocomposites materials have so far successfully demonstrated their catalytic activity towards CO oxidation, epoxidation, alcohol oxidation, 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 of research with implications for fuel cell design. The main utility lies in the removal of carbon monoxide (CO) from the fuel cell’s feed gas as 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 (e.g., 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 alkali metals and reducible metal oxide have attracted wide attention for their significantly improved catalytic activities in the low-temperature range. In spite of stoichiometric simplicity of this CO oxidation reaction, many mechanistic details remain unresolved and reported turnover rates, activation energies, and kinetic rate equations throughout previous reports, at least in part because of undetected transport corruptions of measured rates [88, 89].CO oxidation also remains one of the enduring and classic examples of structure insensitivity; its turnover rate is essentially independent of metal dispersion, even though the structure and coordinative unsaturation of exposed metal atoms are known to differ among clusters of different size [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 systems in heterogeneous catalysis [92-94].Most of the studies have been focused on the origin of the unique catalytic activity of Au NPs. Specifically, preparation of active gold catalysts [95-97] influences 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 the oxidation state of the active gold species (metallic, Au+ or Au3+) [103-105],and the oxygen supply pathways [103-105].Unfortunately, however, many reports are highly controversial and the debate is likely to continue for some time owing to the sensitivity and complexity of gold catalysis. Taking the influence of gold particle size as an example, it has been believed that Au NPs of 2–5 nm are the active species for CO oxidation [106].

For Au NPs supported on transition metal oxides, the oxidation of CO is an exothermic reaction with extremely low catalytic activation barriers [106].A thorough 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 (Fe2O3, TiO2, NiO*x*, CoO*x*). Au–FexOy nanocomposites and their derivatives were successfully demonstrated the catalytic effect towards carbon monoxide oxidation [106-108]. Au catalysts supported on reducible transition metal oxides such as Fe2O3 exhibit a significantly enhanced 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 the Au NPs as a consequence of the Schottky junction at the metal semiconductor interface. It also assumed that oxygen adsorbing on the FexOy support dissociates immediately, producing lattice oxygen, which can subsequently react at the interface or after a spillover of oxygen to the metallic Au NPs.

**4.2. Epoxidation**

Epoxides are very important chemicals in synthetic organic chemistry as well as in industry. These are largely used for the synthesis of key intermediates and in many important organic transformation reactions. Most importantly, these chemicals are widely used in the synthesis of several perfume materials, anthelmintic preparations, epoxy resins, plasticizers, drugs, sweeteners, etc. Therefore the synthesis of an epoxide by an easier method and a low cost route is of great interest to researchers working in this field [110-114].Despite successes in homogeneous catalysis, there is a clear demand for solid materials that catalyze epoxidation reactions with easily available oxidants such as H2O2 and organic peroxides. In response to this, heterogeneous epoxidation remains a very active field of research, with totally new and improved materials being proposed over the last few years [115].

Nano-sized magnetically recyclable catalysts (MRCs) developed in recent years facilitates the catalysts to be recycled conveniently using an external magnet and hence high activity and easy separation are integrated in nano-sized MRCs. Fe3O4 can be completely recovered by means of an external magnetic field owing to its magnetic property. So it is often used as a magnetically separable catalyst and catalyst support [116-118].Styrene oxide, an important and versatile intermediate for fine chemicals and pharmaceuticals, is the expected product when styrene is epoxidized [119,120].The catalytic activity of Fe3O4 NPs 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-Fe3O4 nanocomposite with the uniform distribution of Au NPs. The porous Fe3O4 NPs reportedly catalysed epoxidation of styrene and the immobilizationof Au NPs significantly improved the performanceof the catalyst [121].

**4.3. Benzyl alcohol oxidation**

Benzaldehyde is a very important organic intermediate used in flavors such as almond and cherry and in various fragrances for soaps and toiletries. It is also used in the manufacture of pharmaceuticals such as ampicillin, pesticides such as dibenzoquat, dyes such as triphenylmethane green, and perfumes and flavorimg agents such as cinnamaldehyde, amyl cinnamaldehyde, hexyl cinnamaldehyde, etc. It is also used in the manufacture of fireproof structural foam ferrocene polymers, for example, phenol benzaldehyde resins, etc. It is generally prepared either by hydrolysis of benzal chloride or by oxidation of toluene [122]. Oxidation of toluene is the preferred process used in industry. Because the prices of toluene have increased a lot in the past decade as a result of an increase in the petroleum prices, the benzal chloride route is becoming economically competitive with that of oxidation of toluene. However, benzaldehyde from benzal chloride contains chloride impurities. Such a benzaldehyde is not suitable for use in the pharmaceutical industry. So, many new processes for benzaldehyde synthesis are being developed. There are many reports in the literature elucidating the synthesis of benzaldehyde from benzyl alcohol [123-134].However, in most of these reports, stress had been laid upon the preparation of different catalysts to increase the rates and selectivity of benzaldehyde formation.

However magnetically recyclable catalyst offer an added advantage of being magnetically separable, thereby eliminating the requirement of catalyst filtration after completion of the reaction. Magnetically recyclable catalyst Fe3O4-Pd nanocomposite was successfully tested as catalyst for synthesis of chlorine-free benzaldehyde using a sustainable oxidation protocol and high turnover number was achieved [135].Recently, M. Kokate *et al.* synthesized a novel Fe3O4-SiO2-Au nanocomposite and demonstrated its catalytic activity for the solvent-free oxidation of benzyl alcohol to 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 widely found in an organism. It main function is to catalyze the decomposition of peroxides and the oxidation of some substrates inside organism. Apart from this, the activity of Peroxidase has wide range of practical applications. For example, its ability to catalyse oxidation of various organic substrates so as to reduce their toxicity and to produce a colour change is frequently used in wastewater treatment or as a detection tool. Horseradish peroxidase (HRP) is a natural peroxidase and is generally extracted from plants but it is very expensive, difficult to store and can easily become inactive [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, this finding is not unexpected, as Fe2+/Fe3+ ions in solution (Fenton’s reagent) are known to catalyze the breakdown of hydrogen peroxide. In practical measurements, peroxidase catalyzes the oxidation of the substrates to develop a colour change in the presence of H2O2. 3, 3, 5, 5-tetramethylbenzidine (TMB) is commonly used as a peroxidase substrate because it is colourless and 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 containing materials 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 gold nanoparticles changed the electron structure at the interface which may accelerate the electron transfer. Moreover, the partial electron transfer from Fe3O4 to gold facilitates H2O2 adsorption and activation. Thus, the interaction between gold and Fe3O4 NPs endows high catalytic activity 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 obtained directly from the Au-Fe3O4 nanocomposite by either Au etching or Fe3O4 etching [148].The direct comparison of all three as-synthesized NPs as catalyst for H2O2 reduction and shows that the Au-Fe3O4 nanocomposite offers the enhanced catalysis. By studying the H2O2 reduction catalyzed by the individual Au and Fe3O4 NPs, experimental demonstration proved that the enhanced catalysis of Au-Fe3O4 arises from the polarization effect at the Au-Fe3O4 interface, where Fe3O4 becomes more active. Previous research has shown that Au NPs deposited on various oxide supports, including iron oxide supports, are catalytically more active for oxidation reaction due to the Au NP polarization towards the support at the interface [149].However, recent study by Y. Lee *et al.* observed that Au NPs in Au-Fe3O4 NPs are less active for oxygen 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. Therefore, 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. As the sizes of both Au and Fe3O4 in the Au-Fe3O4 structure can be tuned synthetically, the Au-Fe3O4 NPs offer an ideal catalyst 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 versatility of synthesizing Au-FexOy hybrid nanocomposite materials has been exploited in the effective synthesis of nanocomposites of bifunctional, ternary functional and multifunctional/multilayer structure. Other morphological architectures that attract particular interest are core-shell and heterostructures. Efforts are generally focused on synthesizing novel core-shell and multifunctional/multilayer composite structures to overcome their synthetic challenges. Indeed, the physicochemical properties of the core materials would be reduced in the core/shell and multifunctional/multilayer Au–FexOy hybrid nanocomposite structures but different functional peripheral surfaces, rendering them particularly attractive as multi-functional probes for specific applications. The inherent modularity of the overall 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 application of these materials. There are indications that Au–FexOy hybrid nanocomposite with core/shell and multifunctional/multilayer architectures might possess unprecedented activity for various industrially important catalytic process. It also offered an alternative magnetic separation of the catalyst rather than tedious filtration and centrifugation method. It would be interesting to explore such Au–FexOy hybrid nanocomposite in the near future to advance chemistry, biology and engineering in multi-disciplinary research.

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