ADVANCED SYNTHESIS OF GOLD AND IRON OXIDE HYBRID NANOCOMPOSITE MATERIALS AS MAGNETICALLY RECYCLABLE SUPERIOR CATALYST

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 ($Au–Fe_xO_y$) 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 $Au–Fe_xO_y$ hybrid nanocomposite materials. The application of $Au–Fe_xO_y$ 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, $Au–Fe_xO_y$ hybrid nanocomposites were successfully employed as catalyst towards oxidation of carbon monoxide (CO), Epoxidation, Benzyl alcohol oxidation, Peroxidase-like activity, reduction hydrogen peroxide (H_2O_2) *etc*. The $Au–Fe_xO_y$ hybrid nanocomposites catalysts enable an excellent magnetic separation method for its recyclization. Moreover, the

Author

Diganta Bhuyan
Department of Chemistry
Barnagar College
Sorbhog, Assam, India.
digantabhuyan@barnagarcollege.ac.in

hybrid matrix remarkably stabilizes the Au^0 NPs from being agglomerated and leached which ultimately enhances their reclabilty. It was obatined that $Au–Fe_xO_y$ exhibited high catalytic effectiveness rather than the Au^0 NPs alone because of synergetic effect which originates at interface of the gold and Iron oxide.

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

I. 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 (Fe_3O_4 or γ-Fe_2O_3) 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 Fe_xO_y is smaller than a critical value (~10–20 nm) and the temperature is above the blocking temperature, the Fe_xO_y nanocomposites show superparamagnetic behavior. At this point, no magnetic coercivity and remanence would be estalished in these nanocomposites and the agglomeration of Fe_xO_y NPs is very small at room temperature [14]. The above features of magnetic Fe_xO_y nanomaterials makes these a suitable candidate for selective capturing of targeting substrates, magnetic photonic and recyclable nanocatalysis application [15-17]. In addition, Fe_xO_y NPs act as T_2 contrasting agent in MRI. The Fe_xO_y 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 Fe_xO_y are has tremendous possibility to obtain a hybrid nanocomposite with superior and serendipitous catalytic activity than both Au and Fe_xO_y NPs individually.

This book chapter covers the recent developments in the synthesis of Au–Fe_xO_y hybrid nanocomposite and study of its catalytic activity. The outstanding and unique properties of Au NPs in combination with the Fe_xO_y 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 Fe_xO_y support. A brief elaborated result of various research groups along with the correlation between the catalyst morphology with the catalytic properties is discussed here.

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

In general, the morphology of Au-Fe_xO_y 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 Fe_xO_y 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–Fe_xO_y hybrid nanocomposites are limited to those which have applied as magnetically recoverable catalyst (MRC).

1. **Nanocomposites Structures**

- **Bifunctional Nanocomposite:** The Au–Fe_xO_y nanocomposites are generally bi-composite materials where Fe_xO_y 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 Fe_xO_y is generally modified with different surface modifying agent. For example, Y. -C. Chang *et al.* reported that surface of Fe_3O_4 NPs are modified with chitosan which is a good adsorber of metal ions. Then Au (III) ions are tethered on Fe_3O_4 NPs that are coated with chitosan and reduced to Au NPs with a $NaBH_4$ [31]. Y. Qiu *et al.* presented an alternative easy way to synthesize Au^0 NPs by using chitosan as reducer as well as stabilizer without employing any other stronger reducing agents or stabilizer e.g. $NaBH_4$ or trisodium citrate. Fe_3O_4/chitosan composite synthesized first and then chitosan reduces $AuCl_4^-$ to gold NPs [32]. F. Yan *et al.* published a simplistic method for preparation of bifunctional Fe_3O_4/Au nanocomposites by reducing with $NaBH_4$. In this method, the $AuCl_4^-$ that was adsorbed on the carboxylate functionalized Fe_3O_4 NPs [33]. C. Huang *et al.* published a successful method for the synthesis of porous Fe_3O_4 NPs and immobilization Au NPs with size less than 2 nm in porous Fe_3O_4 NPs modified by L-cysteine [34]. H. Woo *et al.* published the synthesis of hybrid Au NPs on Fe_3O_4 microspheres and the as-prepared Fe_3O_4 hybrid microspheres were further coated with polymer matrix so as to prevent the aggregation of Au NPs and oxidation of Fe_3O_4 hybrid microspheres [35].

- **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 Fe_xO_y 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 Fe_3O_4 @SiO_2@Au nanocomposite by employing a co-precipitation method that led to the generation of Fe_3O_4 and Au NPs immobilised on a silica matrix [36]. F. Chen *et al.* reported a ternary functionalised Fe_3O_4-graphene-Au nanocomposite where both Fe_3O_4 and Au NPs are supported on the reduced graphene oxide (GO). This research work also states that Fe_3O_4 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-Fe_3O_4. After functionalization with –NH_2 groups, the GO-Fe_3O_4 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@Fe_3O_4–Graphene ternary hybrid nanomaterial by "*in situ*" formation of Fe_3O_4 on graphene by using tetraethylene glycol (TEG) as both reductant and solvent for this synthesis method. Moreover, the Fe_3O_4–Graphene has acted as a support for loading Au NPs so as to prepare Au@Fe_3O_4– 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 Fe_3O_4 NPs, mentioned as γ-Fe_2O_3/Au/mSiO_2 [40].

- **Multifunctional/Multilayer Nanocomposite:** The aforementioned Au–Fe_xO_y nanostructures are all 'bi' or 'ternary' nanocomposite materials. Many researchers are very much interested in expanding the scope of utilization of Au–Fe_xO_y 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 Fe_xO_y core as it can stabilize the core and to inhibit its agglomeration. The coating of silica on Fe_xO_y NPs is gererally performed by using a sol−gel approach.The silica

layer is introduced during the synthesis of Au–Fe_xO_y nanocomposites to increase the stability of Fe_xO_y. Yeo *et al.*, recently published a work on the synthesis of Fe_3O_4@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 Fe_3O_4@SiO_2-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 Fe_3O_4@SiO_2@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].
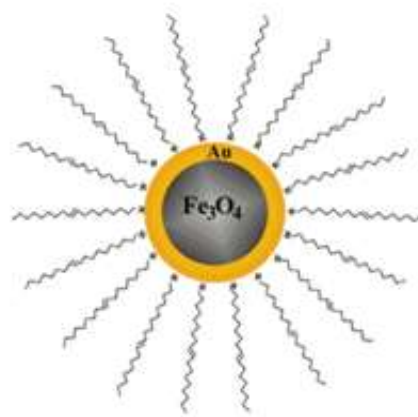
2. **Core/Shell Structures:** The nanoparticle having a single core which is fully coated by a shell is termed as core/shell structure. These core/shell nanocomposite materials combined with the advantageous nature of the core and shell, have attracted tremendous research interest for their unique physico-chemical 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 Fe_3O_4 are very exciting research topics since the Fe_3O_4 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 Fe_3O_4@P(4-VP–DVB)@Au microspheres where Au NPs are easily supported on the P(4-VP) shell by reducing $HAuCl_4$ in the dispersion of Fe_3O_4@P(4-VP–DVB) microspheres. A solvothermal method has been employed to synthesize peroxyacetic acid (PAA)-modified Fe_3O_4 NPs [52-53] where monomers of 4-VP has been embedded on the Fe_3O_4 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 Fe_3O_4@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 $HAuCl_4$ and the presence of $NaBH_4$ 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 Fe_3O_4@P(4-VP–DVB) microspheres.

F. Ke *et al.* [54] synthesized a metal organic framework (MOF) based porous core/shell Au catalyst, viz., Au-Fe_3O_4@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 Fe_3O_4@Au/PEGDMA microspheres by using hydrothermal methodology for the synthesis of Fe_3O_4 core with subsequent functionalization with (3-aminopropyl) trimethoxysilane for functionalization of the

surface $-NH_2$ 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 $HAuCl_4$ by using $NaBH_4$.

L. Wang, et al. [56] describes the preparation of core (Fe_3O_4)-shell (Au) NPs having high monodispersity. The Fe_3O_4 NPs of selected sizes are used as seed for reduction of Au precursors to synthesize Au-coated Fe_3O_4 NPs viz., $Fe_3O_4@Au$. A typical core-shell structure is also schematically represented in scheme 1 [56].

Scheme 1: Illustration of a Core-Shell $Fe_3O_4@Au$ nanoparticle having an outmost organic shell encapsulation (R) $-CO_2H$ or $-NH_2$ [Reprinted (adapted) with the permission from ref. 56. Copyright © 2005, American Chemical Society).

3. **Hetero-Structures:** The Au–Fe_3O_4 hetero-structures where the Au seeds are interfacially linked to Fe_3O_4 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-Fe_3O_4 hetero-structures by thermally decomposing iron oleate complex [Fe(OL)$_3$] with gold seeds of different sizes at 310 ^{o}C. The Au-Fe_3O_4 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-Fe_3O_4 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/Fe_3O_4 viz., Au/HNTs/Fe_3O_4 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 Fe_3O_4 NPs are embedded on the external wall of HNTs.

III. 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 Fe_xO_y 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.

IV. 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 $Au–Fe_xO_y$ nanocomposites and their catalytic activity study has emerged recently as a potential area of research [71, 72]. These $Au–Fe_xO_y$ 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 Fe_xO_y 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 Fe_xO_y support. It is speculated that the electronic structures of both the Au and Fe_xO_y support are modified by electron transfer across the interface,it resulted in the increase of surface oxygen vacancies on the Fe_xO_y support that become the active sites for oxygen absorption as well as activation in some reactions particularly CO oxidation. These $Au–Fe_xO_y$ nanocomposites materials have so far successfully demonstrated their catalytic activity towards CO oxidation, alcohol oxidation, epoxidation, reduction of H_2O_2 and peroxide like activity etc and it also exhibited a superior catalytic activity than Fe_xO_y and Au alone. These reactions are discussed in detail as following.

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 (CO_2) 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 H_2 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 CO_2 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 Au^{3+}) [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 ($Au/Fe_2O_3.MgO$) discover the enhanced rates of CO oxidation for a group of "active" metal oxides e.g. TiO_2, Fe_2O_3, CoO_x , NiO_x. Au–Fe_xO_y nanocomposites and their derivatives were demonstrated the catalytic effect towards CO oxidation [106-108]. It is found that the Au nanocatalysts supported on Fe_2O_3 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–Fe_xO_y nanocomposites explained that oxygen adsorption is supposed to be originating on the Fe_xO_y support or in the Au–Fe_xO_y 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 Fe_xO_y support dissociates immediately and produces lattice oxygen, that subsequently react at the Au–Fe_xO_y interface or after a oxygen spillover to the Au NPs.

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 H_2O_2 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 Fe_3O_4 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 Fe_3O_4 NPs towards epoxidation of styrene reported by C. Huang et al. states that immobilization of Au NPs on Fe_3O_4 NPs by using of L-cysteine led to the formation of the Au@L-cysteine-Fe_3O_4 nanocomposite having monodispersed Au NPs. The porous Fe_3O_4 NPs reportedly catalysed styrene epoxidation and the Au NPs immobilized on Fe_3O_4 support enhanced the nanocomposite catalyst's performance significantly [121].

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 Fe_3O_4-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 Fe_3O_4-SiO_2-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. **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 Fe_3O_4 NPs possess intrinsic peroxidase-like activity. From a chemistry point of view, the findings of L. Gao *et. al* is not unexpected, since Fe^{2+}/Fe^{3+} ions in solution, known as Fenton's reagent are reportedly catalyze the degradation of H_2O_2. In general, peroxidase enzyme catalyzes the oxidation of some organic compounds so as to develop a colour change with H_2O_2 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 H_2O_2 very slowly in absence of catalyst [137, 138]. The outcomes of the study by L. Gao *et. al.* concluded that spherically shaped Fe_3O_4 NPs of different sizes could catalyze the oxidation of the peroxidase substrate TMB with H_2O_2 hence produce a blue colour (λ_{max}= 652 nm). The peroxidase-like catalytic activity of Fe_3O_4 NPs is comparable with commonly used enzyme HRP. The Fe_3O_4 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 Fe_3O_4 NPs possess peroxidase-like catalytic activity towards different peroxidase substrates [137]. Apart from Fe_3O_4, various other nanomaterials is known which exhibit peroxidase-like activity e.g. graphene oxide [139], Au or Au@Pt nanocomposites [140, 141], single-walled carbon nanotubes [142], Co_3O_4 [143], FeS [144], CeO_2 [145] etc. But in case of Fe_3O_4 NPs, its magnetic recoverability provided a better option along with excellent the peroxidase-like activity.

The magnetically recoverable Fe_3O_4-Au nanohybrid exhibited enhanced peroxidase-like activity than Fe_3O_4 NPs [146]. The nature of the peroxidase-like catalytic activity of Fe_3O_4-Au may originate from its ability to catalyze the decomposition of H_2O_2

into $\cdot$OH free radicals [137]. The generated $\cdot$OH radicals might be stabilized by Fe_3O_4-Au nanohybrid by partial electron exchange interactions [147]. In case of Fe_3O_4-Au nanohybrid, the decoration of Au NPs changed the electronic structure at the interface of Au and Fe_3O_4 which could cause accelerated electron transfer. The partial electron transfer from the Fe_3O_4 to Au NPs facilitates H_2O_2 adsorption and the activation. Thus, the interaction occurs between Au and Fe_3O_4 NPs endows high catalytic efficiency of the nanohybrid.

5. **Reduction of H_2O_2:** Y. Lee *et al.* reported a unique synthesis process for generation of Au NPs, Fe_3O_4 NPs, and Au-Fe_3O_4 nanocomposite. Here, single-component gold and magnetite NPs are found directly from the Au-Fe_3O_4 nanocomposite by either magnetite etching or by gold etching [148].The comparative activity study of gold, magnetite and Au-Fe_3O_4 nanocomposite as catalyst for H_2O_2 reduction shows that the Au-Fe_3O_4 nanocomposite offers the highest catalytic efficiency. The H_2O_2 reduction reaction catalyzed by gold and magnetite NPs individually confirmed that the enhanced catalytic ability of Au-Fe_3O_4 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 Fe_3O_4 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-Fe_3O_4 nanocomposite are less active for reduction of O_2 reaction in alkaline medium [150]. These research works confirmed the interaction between gold and magnetite, but gold NPs in the Au-Fe_3O_4 nanohybrid should not exhibit enhanced catalytic activity for the reduction of H_2O_2. The enhanced catalytic activity found in case of Au-Fe_3O_4 nanohybrid must originates from the magnetite. So, the reductive power does not originates from the free iron ions that could catalyze the decomposition of H_2O_2, 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-Fe_3O_4 nanohybrid can be tuned, hence Au-Fe_3O_4 nanohybrid offers an ideal catalytic system for exploring one of the most facinating topic i.e. synergetic effects.. This tuning capability of Au-Fe_3O_4 nanohybrid material could allow the fabrication of active Au-Fe_3O_4 nanohybrid for highly sensitive detection of H_2O_2 [148].

V. CONCLUSION

The synthesis Au-Fe_xO_y 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–Fe_xO_y hybrid nanocomposite structures but different peripheries rendered them very attractive for specific applications. The inherent modularity of the synthesis process for Au–Fe_xO_y 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–Fe_xO_y 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–Fe$_x$O$_y$ hybrid nanocomposite in the forseeable future to advance materilas chemistry, engineering and biology in multi-disciplinary research.

VI. ACKNOWLEDGEMENTS

REFERENCES

[1]   Caruso, F., Nanoengineering of particle surfaces, Adv. Mater., 13, 11, 2001.
[2]   Li, X., Wan, M., Wei, Y., Shen, J., Chen, Z., Electromagnetic functionalized and core-shell micro/nanostructured polypyrrole composites, J. Phys. Chem. B, 110, 14623, 2006.
[3]   Roca, M., Haes, A. J., Silica-void-gold nanoparticles: temporally stable surface-enhanced raman scattering substrates, J. Am. Chem. Soc., 130, 14273, 2008.
[4]   Yi, D. K., Lee, S. S., Ying, J. Y., Synthesis and applications of magnetic nanocomposite catalysts, Chem. Mater., 18, 2459, 2006.
[5]   Feng, X., Mao, C., Yang, G., Hou, W., Zhu, J. J., Polyaniline/Au composite hollow spheres: synthesis, characterization, and application to the detection of dopamine, Langmuir, 22, 4384, 2006.
[6]   Salgueirio-Maceira, V., Correa-Duarte, M. A., Spasova, M., Liz-Marzan, L. M., Farle, M., Composite silica spheres with magnetic and luminescent functionalities, Adv. Funct. Mater., 16, 509, 2006.
[7]   Mangeney, C., Bousalem, S., Connan, C., Vaulay, M., Bernard, S., Chehimi, M. M., Latex hollow particles of reactive polypyrrole: preparation, properties, and decoration by gold nanospheres, Langmuir, 22, 10163, 2006.
[8]   Li, P., Wei, Z., Wu, T., Peng, Q., Li, Y., Au-ZnO hybrid nanopyramids and their photocatalytic properties, J. Am. Chem. Soc., 133, 5660, 2011.
[9]   Halaby, S. A., Kenny N. S., Murphy, J. A., Method of making a magnetic recording and storage device, US 3892888 A 19750701, 1975.
[10]   Legodi, M. A., Waal, D. D., The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste, Dyes Pigm., 74, 161, 2007.
[11]   Aliyan, H., Fazaeli, R., Jalilian, R., Fe$_3$O$_4$@mesoporous SBA15: A magnetically recoverable catalyst for photodegradation of malachite green, Appl. Surf. Sci., 276, 147, 2013.
[12]   Chin, S. F., Makha, M., Raston, C. L., Saunders, M., Magnetite ferrofluids stabilized by sulfonato-calixarenes, Chem. Commun., 1948, 2007.
[13]   Tifenauer, L. X., Tschirky, A., Kuhne, G., Andres, R. Y., In vivo evaluation of magnetite nanoparticles for use as a tumor contrast agent in MRI, Magn. Reson. Imaging, 14, 391, 1996.
[14]   Jeong, U., Teng, X., Wang, Y., Yang, H., Xia, Y., Superparamagnetic colloids: controlled synthesis and niche applications, Adv. Mater., 19, 33, 2007.
[15]   Chen, Z., Hong, G., Wang, H., Welsher, K., Tabakman, S. M., Sherlock, S. P., Robinson, J. T., Liang, Y., Dai, H., Graphite-coated magnetic nanoparticle microarray for few-cells enrichment and detection, ACS Nano, 6, 1094, 2012.
[16]   Ge, J., Lee, H., He, L., Kim, J., Lu, Z., Kim, H., Goebl, J., Kwon, S., Yin, Y., Magnetochromatic microspheres: rotating photonic crystals, J. Am. Chem. Soc., 131, 15687, 2009.
[17]   Ge, J., He, L., Hu, Y., Yin, Y., Magnetically induced colloidal assembly into field-responsive photonic structures, Nanoscale, 3, 177, 2011.
[18]   Hu, F., MacRenaris, K. W., Waters, E. A., Schultz-Sikma, E. A., Eckermann, A. L., Meade, T. J., Highly dispersible, superparamagnetic magnetite nanoflowers for magnetic resonance imaging, Chem. Commun., 46, 73, 2010.
[19]   Xuan, S., Wang, F., Lai, J. M. Y., Sham, K. W. Y., Wang, Y-X. J., Lee, S-F, Yu, J. C., Cheng, C. H. K., Leung, K. C-F., Synthesis of biocompatible, mesoporous Fe$_3$O$_4$ nano/microspheres with large surface

area for magnetic resonance imaging and therapeutic applications, ACS Appl. Mater. Interfaces, 3, 237, 2011.

[20] Xuan, S., Wang, Y. X. J., Yu, J. C., Leung, K. C-F., Tuning the grain size and particle size of superparamagnetic Fe_3O_4 microparticles, Chem. Mater., 21, 5079, 2009.

[21] Zeng, S., Yong. K-T., Roy, I., Dinh, X-Q., Yu, X., Luan, F., A review on functionalized gold nanoparticles for biosensing applications, Plasmonics, 6, 491, 2011.

[22] Daniel, M-C., Astruc, D., Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology, Chem. Rev., 104, 293, 2004.

[23] Adler, D. C., Huang, S-W., Huber, R., Fujimoto, J. G., Photothermal detection of gold nanoparticles using phase-sensitive optical coherence tomography, Opt. Express, 16, 4376, 2008.

[24] Hirsch, L. R., Stafford, R. J., Bankson, J. A., Sershen, S. R., Rivera, B., Price, R. E., Hazle, J. D., Halas, N. J., West, J. L., Nanoshell-mediated near-infrared thermal therapy of tumors under magnetic resonance guidance, PNAS, 100, 13549, 2003.

[25] Skrabalak, S. E., Chen, J., Au, L., Lu, X., Li, X., Xia, Y. N., Gold nanocages for biomedical applications, Adv. Mater., 19, 3177, 2007.

[26] Yavuz, M. S., Cheng, Y., Chen, J., Cobley, C. M., Zhang, Q., Rycenga, M., Xie, J., Kim, C., Song, K. H., Schwartz, A. G., Wang, L. V., Xia, Y., Gold nanocages covered by smart polymers for controlled release with near-infrared light, Nat. Mater., 8, 935, 2009.

[27] Corma. A., Garcia, H., Supported gold nanoparticles as catalysts for organic reactions, Chem. Soc. Rev., 37, 2096, 2008.

[28] Corma, A., Attempts to fill the gap between enzymatic, homogeneous, and heterogeneous catalysis, Catal. Rev.-Sci. Eng., 46, 369, 2004.

[29] Nkosi, B., Adams, M. D., Coville, N. J., Hutchings, G. J., Hydrochlorination of acetylene using carbon supported gold catalysts: A study of catalyst Reactivation, J. Catal., 128, 378, 1991.

[30] Bond, G. C., Thompson, D. T., Catalysis by gold, Catal. Rev. Sci. Eng., 41, 319, 1999.

[31] Chang, Y-C., Chen, D-H., Catalytic reduction of 4-nitrophenol by magnetically recoverable Au nanocatalyst, J. Hazard. Mater., 165, 664, 2009.

[32] Qiu, Y., Ma, Z., Hu, P., Environmentally benign magnetic chitosan/ Fe_3O_4 composites as reductant and stabilizer for anchoring Au NPs and their catalytic reduction of 4-nitrophenol, J. Mater. Chem. A, 2, 13471, 2014.

[33] Yan, F., Sun, R., Facile synthesis of bifunctional Fe_3O_4/Au nanocomposite and their application in catalytic reduction of 4-nitrophenol, Mater. Res. Bull., 57, 293, 2014.

[34] Huang, C., Zhang, H., Sun, Z., Zhao, Y., Chen, S., Tao, R., Liu, Z., Porous Fe_3O_4 nanoparticles: synthesis and application in catalyzing epoxidation of styrene, J. Colloid Interface Sci., 364, 298, 2011.

[35] Woo, H., Park, K. H., Hybrid Au nanoparticles on Fe_3O_4 @polymer as efficient catalyst for reduction of 4-nitrophenol, Catal. Commun., 46, 133, 2014.

[36] Kokate, M., Dapurkar, S., Garadkar, K., Gole, A., Magnetite-silica-gold nanocomposite: one-pot single-step synthesis and its application for solvent-free oxidation of benzylalcohol, J. Phys. Chem. C, 119, 14214, 2015.

[37] Chen, F., Wang, Y., Chen, Q., Han, L., Chen, Z., Fang, S., Multifunctional nanocomposites of Fe_3O_4 -graphene- Au for repeated use in simultaneous adsorption, in situ SERS detection and catalytic reduction of 4-nitrophenol in water, Mater. Res. Express, 1, 045049, 2014.

[38] Hu, J., Dong, Y-L., Chen, X-J., Zhang, H-J., Zheng, J-M., Wang, Q., Chen, X-G., A highly efficient catalyst: In situ growth of Au nanoparticles on graphene oxide- Fe_3O_4 nanocomposite support, Chem. Eng. J., 236, 1, 2014.

[39] Lu, B., Zhang, Z., Hao, J., Tang, J., Facile synthesis of Au@ Fe_3O_4-graphene and Pt@ Fe_3O_4-graphene ternary hybrid nanomaterials and their catalytic properties, RSC Adv., 4, 21909, 2014.

[40] Ren, L., Teng, C., Zhu, L., He, J., Wang, Y., Zuo, X., Hong, M., Wang, Y., Jiang, B., Zhao, J., Preparation of uniform magnetic recoverable catalyst microspheres with hierarchically mesoporous structure by using porous polymer microsphere template, Nanoscale Research Letters, 9, 163, 2014.

[41] Yeo, K. M., Shin, S., Lee, I. S., Reductive dissolution of Fe_3O_4 facilitated by the Au domain of an Fe_3O_4/Au hybrid nanocrystal: formation of a nanorattle structure composed of a hollow porous silica nanoshell and entrapped Au nanocrystal, Chem. Commun., 46, 64, 2010.

[42] Zhu, Y., Shen, J., Zhou, K., Chen, C., Yang, X., Li. C., Multifunctional magnetic composite microspheres with in situ growth Au nanoparticles: a highly efficient catalyst system, J. Phys. Chem. C, 115, 1614, 2011.

[43] Liu, B., Zhang, D., Wang, J., Chen, C., Yang, X., Li, C., Multilayer magnetic composite particles with functional polymer brushes as stabilizers for gold nanocolloids and their recyclable catalysis, J. Phys. Chem. C, 117, 6363, 2013.

[44] Xuan, S., Wang, Y-X. J., Yu, J. C., Leung, K. C-F., Preparation, characterization, and catalytic activity of core/shell Fe_3O_4@Polyaniline@Au nanocomposites, Langmuir, 25, 11835, 2009.

[45] Cornell, R. M., Sehwertmann, U., The iron oxides, structure properties reactions occurences and uses, 1, Willy VCH: Gmbh & Co. KgaA, Weinheim, 1996.

[46] Keane, M. A., The hydrogenation of o-, m-, and p-xylene over Ni/SiO_2, J. Catal., 166, 347, 1997.

[47] Geus., J. W., Preparation and properties of iron oxide and metallic iron catalysts, Appl. Catal., 25, 313, 1986.

[48] Martin, B. R., Dermody, D. J., Reiss, B. D., Fang, M., Lyon, L. A., Natan, M. J., Mallouk, T. E., Orthogonal self-assembly on colloidal gold-platinum nanorod, Adv. Mater., 11, 1021, 1999.

[49] Huo, L., Li, W., Lu, L., Cui, H., Xi, S., Wang, J., Zhao, B., Shen, Y., Lu, Z, Preparation, structure, and properties of three-dimensional ordered α-Fe_2O_3 nanoparticulate film, Chem. Mater., 12, 790, 2000.

[50] Matijevic, P. E., Hench, L. L., Ulrich, D. B., Colloid science of composites system science of ceramic chemical processing, 463, Wiley: New York, 1986.

[51] Guo, W., Wang, Q., Wang, G., Yang, M., Dong, W., Yu, J., Facile hydrogen-bond assisted polymerization and immobilization method to synthesize hierarchical Fe_3O_4@poly(4 vinylpyridine-codivinylbenzene)@Au nanostructures and their catalytic applications, Chem. Asian J., 8, 1160, 2013.

[52] Deng, H., Li, X., Peng, Q., Wang, X., Chen, J., Li, Y., Monodisperse magnetic single-crystal ferrite microsphere, Angew. Chem. Int. Ed., 44, 2782, 2005.

[53] Huang, X., Zhuang, J., Chen, D., Liu, H., Tang, F., Yan, X., Meng, X., Zhang, L., Ren, J., General strategy for designing functionalized magnetic microspheres for different bioapplications, Langmuir, 25, 11657, 2009.

[54] Ke, F., Wang, L., Zhu, J., Multifunctional Au- Fe_3O_4@MOF core-shell nanocomposite catalysts with controllable reactivity and magnetic recyclability, Nanoscale., 7, 1201, 2015.

[55] Zhang, W., Liu, B., Zhang, B., Bian, G., Qi, Y., Yang, X., Li, C., Synthesis of monodisperse magnetic sandwiched gold nanoparticle as an easily recyclable catalyst with a protective polymer shell, Colloids Surfaces A, 466, 210, 2015.

[56] Wang, L., Luo, J., Fan, Q., Suzuki, M., Suzuki, I. S., Engelhard, M. H., Lin, Y., Kim, N., Wang, J. Q., Zhong, C. –J., Monodispersed core-shell Fe_3O_4@Au nanoparticles, J. Phys. Chem. B, 109, 21593, 2005.

[57] Lin, F. H., Chen, W., Liao, Y. H., Doong, R. A., Li, Y., Effective approach for the synthesis of monodisperse magnetic nanocrystals and M- Fe_3O_4 (M = Ag, Au, Pt, Pd) heterostructures, Nano Res., 4, 1223, 2011.

[58] Lin, F. H., Doong, R. A., Bifunctional Au− Fe_3O_4 heterostructures for magnetically recyclable catalysis of nitrophenol reduction, J. Phys. Chem. C, 115, 6591, 2011.

[59] Wang, C., Yin, H., Dai, S., Sun, S., A general approach to noble metal-metal oxide dumbbell nanoparticles and their catalytic application for CO oxidation, Chem. Mater., 22, 3277, 2010.

[60] Lee, Y., Garcia, M. A., Huls, N. A. F., Sun, S., Synthetic tuning of the catalytic properties of Au- Fe_3O_4 nanoparticles, Angew. Chem. Int. Ed., 49, 1271, 2010.

[61] Hu, J., Zhou, S., Sun, Y., Fang, X., Wu, L., Fabrication, properties and applications of janus particles, Chem. Soc. Rev., 41, 4356, 2012.

[62] Choi, S. H., Na, H. B., Park, Y. I., An, K., Kwon, S. G., Jang, Y., Park, M., Moon, J., Son, J. S., Song, I. C., Moon, W. K., Hyeon, T., Simple and generalized synthesis of oxide-metal heterostructured nanoparticles and their applications in multimodal biomedical probes, J. Am. Chem. Soc., 130, 15573, 2008.

[63] Peng, S., Lee, Y. Wang, C., Yin, H., Dai, S., Sun, S., A facile synthesis of monodisperse au nanoparticles and their catalysis of CO oxidation, Nano Res., 1, 229, 2008.

[64] Yu, H., Chen, M., Rice, P. M., Wang, S. X., White, R. L., Sun, S. H., Dumbbell-like bifunctional Au-Fe3O4 nanoparticles, Nano Lett., 5, 379, 2005.

[65] Mu, B., Zhang, W., Wang, A., Facile fabrication of superparamagnetic coaxial gold /halloysite nanotubes/ Fe_3O_4 nanocomposites with excellent catalytic property for 4-nitrophenol reduction, J. Mater. Sci., 49, 7181, 2014.

[66] Serpell, C. J., Cookson, J., Ozkaya, D., Beer, P. D., Core@shell bimetallic nanoparticle synthesis via anion coordination, Nat. Chem., 3, 478, 2011.

[67] Hashmi, A. S. K., Hutchings, G. J., Gold catalysis, Angew. Chem., Int. Ed., 45, 7896, 2006.

[68] Arcadi, A., Alternative synthetic methods through new developments in catalysis by gold, Chem. Rev., 108, 3266, 2008.

[69] Mitsudome, T., Kaneda, K., Gold nanoparticle catalysts for selective hydrogenations, Green Chem., 15, 2636, 2013.

[70] Pina, C. D., Falletta, E., Prati, L., Rossi, M., Selective oxidation using gold, Chem. Soc. Rev., 37, 2077, 2008.

[71] V., polshettiwar, Luque, R., Fihri, A., Zhu, H., Bouhrara, M., Basset, J. –M.., Magnetically recoverable nanocatalysts, Chem. Rev., 111, 3036, 2011.

[72] Leung, K. C-F., Xuan, S., Zhu, X., Wang, D., Chak, C-P., Lee, S-F., Hob, W. K-W., Chung, B. C-T., Gold and iron oxide hybrid nanocomposite materials, Chem. Soc. Rev., 41, 1911, 2012.

[73] James, A. R., Nolf, M. M., Hampson, N. B., Stephen, R. T., Carbon-monoxide poisoning- a public health perspective, Toxicology, 145, 1, 2000.

[74] Kevin R. H, Stephen R. T., Pathophysiology and treatment of carbon monoxide poisoning, J. Toxicol., Clin. Toxicol, 32, 613, 2008.

[75] Fawell, T. A., Moon, R. E., Fracian, P. J., Mebane, G. Y., Theil, D. R., Piantadosi, C. A., Warehouse workers headache. carbon monoxide poisoning from propane fueled forklifts, J. Occup. Med , 34, 5, 1992.

[76] Shakun, J. D., Clark, P. U., He, F., Marcott, S. A., Mix, A. C., Liu, Z., Bliesner, B. O., Schamittner, A., Bard, E., Global warming preceded by increasing carbon dioxide concentration during the last deglaciation, Nature, 484, 49, 2012.

[77] Song, C., Fuel processing for low-temperature and high-temperature fuel cells challenges, and opportunities for sustainable development in the 21st century, Catal. Today, 77, 17, 2002.

[78] Wu, P., Du, P., Zhang, H., Cai, C., Graphdiyne as a metal-free catalyst for low-temperature CO oxidation, PCCP, 16, 5640, 2014.

[79] Huang, S., Hara, K., Fukoka, A., Green catalysis for selective CO oxidation in hydrogen for fuel cell, Energy Environ. Sci., 2, 1060, 2009.

[80] [Allian, A. D., Takanabe, K., Fujada, K. L., Hao, X., Truex, T. J., Cai, J., Buda, C., Neurock, M., Iglesia, E., Chemisorption of CO and mechanism of CO oxidation on supported platinum nanoclusters, J. Am. Chem. Soc, 133, 4498, 2011.

[81] Liu, K., Wang, A., Zhang, T., Recent advances in Preferential Oxidation of CO Reaction over Platinum Group Metal Catalysts, ACS Catal, 2, 1165, 2012.

[82] Teschner, D., Wootsch, A., Tellinger, O. P., Kröhnert, J., Vass, E. M., Havecker, M., Zafeiratos, S., Schnörch, P., Jentoft, P. C., Gericke, A. K., Schlögl, R., Partial pressure dependent in situ spectroscopic study on the preferential CO oxidation in hydrogen (PROX) over Pt/ceria catalysts, J. Catal. 249, 318, 2007.

[83] Pozdnyakova, O., Teschner, D., Wootsch, A., Kröhnert, J., Steinhauer, B., Sauer, H., Toth, L., Jentoft, F. C., Gericke, A. K., Paál, Z., Schlögl, R., Preferential CO oxidation in hydrogen (PROX) on ceria-supported catalysts, part II: oxidation states and surface species on Pd/CeO2 under reaction conditions, suggested reaction mechanism, J. Catal, 237, 17, 2006.

[84] Pozdnyakova, O., Teschner, D., Wootsch, A., Kröhnert, J., Steinhauer, B., Sauer, H., Toth, L., Jentoft, F. C., Gericke, A. K., Paál, Z., Schlögl, R., Preferential CO oxidation in hydrogen (PROX) on ceria-supported catalysts, part I: oxidation states and surface species on Pd/CeO$_2$ under reaction conditions, suggested reaction mechanism, J. Catal, 237, 1, 2006.

[85] Wootsch, A., Descorme, C., Duprez, D., Preferential oxidation of carbon monoxide in the presence of hydrogen (PROX) over ceria–zirconia and alumina-supported Pt catalysts, J, Catal, 225, 259, 2004.

[86] Bourane, A., Bianchi, D., Oxidation of CO on a Pt/Al$_2$O$_3$ Catalyst: from the surface elementary steps to light-off tests: I. kinetic study of the oxidation of the linear CO Species, J. Catal, 202, 34, 2001.

[87] Wojciechowski, B. W., Aspey, S. P., Kinetic studies using temperature-scanning: the oxidation of carbon monoxide, Appl. Catal. A: Gen., 190, 1, 2000.

[88] Liu, Y., Fu, Q., Stephanopoulos, M. F., Preferential oxidation of CO in H$_2$ over CuO-CeO$_2$ catalysts, Catal. Today, 93-95, 241, 2004.

[89] Wang, H., Liu, C. J., Preparation and characterization of SBA-15 supported Pd catalyst for CO oxidation, Appl. Catal., B: Environ., 106, 672, 2011.

[90] Venderbosch, R. H., Prins, W., Swaaij, W. P. M., Platinum catalyzed oxidation of carbon monoxide as a model reaction in mass transfer measurements, Chem. Eng. Sci, 53, 3355, 1998.

[91] Ertl, G., Self organization in reactions at surfaces, Surf. Sci, 287-288, 1, 1993.

[92] Haruta, M., Kobayashi, T., Sano, H., Yamada, N., Novel gold catalysts for the oxidation of carbon monoxide at a temperature far below 0°c, Chem. Lett., 16. 405, 1987.

[93] Haruta, M., Yamada, N., Kobayashi, T., Iijima, S., Gold catalysts prepared by coprecipitation for low temperature oxidation of hydrogen and of carbon monoxide, J. Catal, 115, 301, 1989.

[94] Hustchings, G. J., New directions in gold catalysis, Gold Bull, 37, 3, 2004.

[95] Hashmi, A. S. K., Hutchings G. J., Gold-atalyse, Angew. Chem. 118, 8064, 2006.

[96] [96]   Min, B. K., Friend C. M., Heterogeneous gold-based catalysis for green chemistry: low-temperature co oxidation and propene oxidation, Chem. Rev., 107, 2709, 2007.

[97] Tsubota, S., Haruta, M., Kobayashi, T., Ueda, A., Nakahara, Y., Preparation of highly dispersed gold on titanium and magnesium oxide, Stud. Surf. Sci. Catal, 63, 695, 1991.

[98] Li, W. C., Comotti, M., Schuth, F., Highly reproducible syntheses of active Au/TiO_2 catalysts for CO oxidation by deposition-precipitation or impregnation, J. Catal. 237, 190, 2006.

[99] Xu, C., Su, J., Xu, X., Liu, P., Zhao, H., Tian, F., Ding, Y., Low temperature CO oxidation over unsupported nanoporous gold, J. Am. Chem. Soc, 129, 42, 2007.

[100] Chen, M. S., Goodman D. W., The structure of catalytically active gold on titania, Science, 306, 252, 2004.

[101] Lopez, N., Janssens, T. V. W., Clausen, B. S., Xu, Y., Mavrikakis, M., Bligaard T., Norskov, J. K., On the origin of the catalytic activity of gold nanoparticles for low-temperature CO oxidation, J. Catal., 223, 232, 2004.

[102] Kotobuki, M., Leppelt, R., Hansgen, D. A., Widmann, D., Behm, R. J., Reactive oxygen on a Au/TiO_2 supported catalyst, J. Catal., 264, 67, 2009.

[103] Yoon, B., Hakkinen, H., Landman, U., Worz, A. S., Antonietti, J-M., Abbet, S., Judai, K., Heiz, U., Charging effects on bonding and catalyzed oxidation of CO on Au8 clusters on MgO, Science, 307, 403, 2005.

[104] Carrettin, S., Hao, Y., Guerrero, V. A., Gates, B. C., Trasobares, S., Calvino, J. J., Corma, A., Increasing the number of oxygen vacancies on TiO_2 by doping with iron increases the activity of supported gold for CO oxidation , Chem. Eur. J. 13, 7771, 2007.

[105] Guzman, J., Gates B. C., Catalysis by supported gold: correlation between catalytic activity for CO oxidation and oxidation states of gold, J. Am. Chem. Soc., 126, 2672, 2004.

[106] Hutchings, G. J., Hall, M. S., Carley, A. F., Landon, P., Solsona, B. E., Kiely, C. J., Herzing, A., Makkee, M., Moulijn, J. A., Overweg, A., Fierro-Gonzalez, J. C., Guzman, J., Gates, B. C., Role of gold cations in the oxidation of carbon monoxide catalyzed by iron oxide-supported gold, J. Catal., 242, 71, 2006.

[107] Weiher, N., Bus, E., Delannoy, L., Louis, C., Ramaker, D. E., Miller, J. T., Bokhoven, J. A. van., Structure and oxidation state of gold on different supports under various CO oxidation conditions, J. Catal, 240, 100, 2006.

[108] Liu, Y., Jia, C-J., Yamasaki, J., Terasaki, O., Schuth, F., Highly active iron oxide supported gold catalysts for CO oxidation: how small must the gold nanoparticles be, Angew. Chem. Int. Ed., 49, 5771, 2010.

[109] Schubert, M. M., Hackenberg, S., Veen, A. C. V., Muhler, M., Plzak, V., Behm, R. J, CO oxidation over supported gold catalysts- "inert" and "active" support materials and their role for the oxygen supply during reaction, J. Catal., 197, 113, 2001.

[110] Yin, H., Wang, C., Zhu, H., Overbury, S. H., Sun, S., Dai, S., Colloidal deposition synthesis of supported gold nanocatalysts based on Au- Fe_3O_4 dumbbell nanoparticles, Chem. Commun., 4357, 2008.

[111] Scire, S., Crisafulli, C., Minico, S., Condorelli, G. G., Mauro A. D., Selective oxidation of CO in H_2 rich stream over gold/iron oxide: An insight on the effect of catalyst pretreatment, J. Mol. Catal., 284, 24, 2008.

[112] Laha, S. C., Kumar, R., Selective epoxidation of styrene to styrene oxide over TS-1 using urea–hydrogen peroxide as oxidizing agent, J. Catal., 204, 64, 2001.

[113] Faveri, G. D., Ilyashenko, G. Watkinson, M., Recent advances in catalytic asymmetric epoxidation using the environmentally benign oxidant hydrogen peroxide and its derivatives, Chem. Soc. Rev., 40, 1722, 2011.

[114] Guidotti, M., Pirovano, C., Ravasio, N., Lazaro, B., Fraile, J. M., Mayoral, J. A., Coq. B., Galarneau, A., The use of H_2O_2 over titanium-grafted mesoporous silica catalysts: a step further towards sustainable epoxidation, Green Chem., 11, 1421, 2009.

[115] Ruddy, D. A., Tilley, T. D., Highly selective olefin epoxidation with aqueous H_2O_2 over surface modified TaSBA15 prepared via the TMP method, Chem. Commun., 3350, 2007.

[116] Ding, Y., Gaoa, Q., Li, G., Zhang, H., Wang, J., Yan, L., Suo, J., Selective epoxidation of cyclohexene to cyclohexene oxide catalyzed by keggin-type heteropoly compounds using anhydrous urea-hydrogen peroxide as oxidizing reagent and acetonitrile as the solvent, J. Mol. Catal. A: Chem., 218, 161, 2004.

[117] Devos, D. E., Sels, B. F., Jacobs, P.A., Practical Heterogeneous catalysts for epoxide production, Adv. Synth. Catal., 345, 457, 2003.

[118] Kotani, M., Koike, T., Yamaguchi, K., Mizuno, N., Ruthenium hydroxide on magnetite as a magnetically separable heterogeneous catalyst for liquid-phase oxidation and reduction, Green Chem., 8, 735, 2006.

[119] Amali, A. J., Rana, R. K., Stabilisation of Pd (0) on surface functionalized Fe_3O_4 nanoparticles: magnetically recoverable and stable recyclable catalyst for hydrogenation and Suzuki–Miyaura reactions, Green Chem., 11, 1781, 2009.

[120] Zhang, D., H., Li, G. D. Lia, J. X., Chen, J. S., One-pot synthesis of Ag– Fe_3O_4 nanocomposite: a magnetically recyclable and efficient catalyst for epoxidation of styrene, Chem. Commun., 29, 3414, 2008.

[121] Huang, C., Zhang, H., Sun, Z., Zhao, Y., Chen, S., Tao, R., Liu, Z., Porous Fe_3O_4 nanoparticles: synthesis and application in catalyzing epoxidation of styrene, J. Colloid Interface Sci., 364, 298, 2011.

[122] Pinnaduwage, D. S. Zhou, L., Gao, W., Friend, C. M., Chlorine Promotion of Styrene Epoxidation on Au(111), J. Am. Chem. Soc., 129, 1872, 2007.

[123] Choudhary, V. R., Jha, R., Jana, P., Epoxidation of styrene by TBHP to styrene oxide using barium oxide as a highly active/selective and reusable solid catalyst, Green Chem., 8, 689, 2006.

[124] Ullmann, F., Ullmann's encyclopedia of industrial chemistry, Wiley-VCH Verlag: Weinheim, Germany, 4, 701, 2003.

[125] Zondervan, C., Hage, R., Feringa, B. L., Selective catalytic oxidation of benzyl alcohols to benzaldehydes with a dinuclear manganese (IV) complex, Chem. Commun., 419, 1997.

[126] Lu, A-H., Li, W-C., Hou, Z., Schuth, F., Molecular level dispersed Pd clusters in the carbon walls of ordered mesoporous carbon as a highly selective alcohol oxidation catalyst, Chem. Commun., 1038, 2007.

[127] Liotta, L. F., Venezia, A. M., Deganello, G., Longoa, S., Martorana, A., Schay, Z., Guczi, L., Liquid phase selective oxidation of benzyl alcohol over Pd-Ag catalysts supported on pumice, Catal. Today, 66, 271, 2001.

[128] Yadav, G. D., Mistry, C. K., Oxidation of benzyl alcohol under a synergism of phase transfer catalysis and heteropolyacids, J. Mol. Catal. A: Chem., 172, 135, 2001.

[129] Chaudhary, V. R., Dumbre, D. K., Uphade, B. S., Narkhede, V. S., Solvent free oxidation of benzyl alcohol to benzaldehyde by tetra-butylhydroperoxide using transition metal containing layered double hydroxides and/or mixed hydroxides, J. Mol. Catal. A: Chem., 215, 129, 2004.

[130] Enache, D. I., Edwards, J. K., Landon, P., Solsona-Espriu, B., Carley, A. F., Herzing, A. A., Watanabe, M., Kiely, C. J., Knight, D. W., Hutchings, G. J., Solvent-free oxidation of primary alcohols to aldehydes using Au-Pd/ TiO2 catalysts, Science, 311, 362, 2006.

[131] Zheng, N., Stucky, G. D., A general synthetic strategy for oxide-supported metal nanoparticle catalysts, J. Am. Chem. Soc., 128, 14278, 2006.

[132] Srinivas, N., Radharani, V., Radhakrishnan, M., Kulkarni, S. S., Raghavan, K. V., Liquid phase selective oxidation of alcohols over modified molecular sieves, J. Mol. Catal. A: Chem., 172, 187, 2001.

[133] Mitsodume, T., Mikami, Y., Funai, H., Mizugaki, T., Jitsukawa, K., Kaneda, K., Oxidant-free alcohol dehydrogenation using a reusable hydrotalcite-supported silver nanoparticle catalyst, Angew. Chem., Int. Ed., 47, 138. 2008.

[134] Gonzalez-Arellano, C., Campelo, J. M., Macquarrie, D. J., Marinas, J. M., Romero A. A., Luque, R., Efficient microwave oxidation of alcohols using low-loaded supported metallic iron nanoparticles , ChemSusChem, 1, 746, 2008.

[135] Mori, K., Hara, T., Mizugaki, T., Ebitani, T., Kaneda, K., Hydroxyapatite-supported palladium nanoclusters: a highly active heterogeneous catalyst for selective oxidation of alcohols by use of molecular oxygen, J. Am. Chem. Soc., 126, 10657, 2004.

[136] Kokate, M., Dapurkar, S., Garadkar, K., Gole, A., Magnetite-silica-gold nanocomposite: one-pot single-step synthesis and its application for solvent-free oxidation of benzylalcohol, J. Phys. Chem. C, 119, 14214, 2015.

[137] Chen, J., Zhang, Q., Wang, Y., Wan, H., Size-dependent catalytic activity of supported palladium nanoparticles for aerobic oxidation of alcohols, Adv. Synth. Catal., 350, 453, 2008.

[138] Polshettiwar, V., Varma, R. S., Nanoparticle-supported and magnetically recoverable palladium (Pd) catalyst: a selective and sustainable oxidation protocol with high turnover number, Org. Biomol. Chem., 7, 37, 2009.

[139] Gao, L., Zhuang, J., Nie, L., Zhang, J., Zhang, Y., Gu, N., Wang, T., Feng, T., Yang, D., Perrett, S., Yan, X., Intrinsic peroxidase-like activity of ferromagnetic nanoparticle, Nat. Nanotechnol., 2, 577, 2007.

[140] Liu. S., Lu, F., Xing, R., Zhu, J., Structural effects of Fe_3O_4 nanocrystals on peroxidase-like activity, Chem. Eur. J., 17, 620, 2011.

[141] Song, Y., Qu, K., Zhao, C., Ren, J., Qu, X., Graphene oxide: intrinsic peroxidase catalytic activity and its application to glucose detection, Adv. Mater., 22, 2206, 2010.

[142] Wang, X., Wu, Q., Shan, Z., Huang, Q., BSA-stabilized Au clusters as peroxidase mimetics for use in xanthine detection, Biosens. Bioelectron., 26, 3614, 2011.

[143] He, W., Liu, Y., Yuan, J., Yin, J., Wang, X., Hu, X., Zhang, K., Liu, J., Chen, C., Ji, Y., Gao, Y., Au@Pt nanostructures as oxidase and peroxidase mimetics for use in immunoassays, Biomaterials., 32, 1139, 2011.

[144] Song, Y., Wang, X., Zhao, C., Qu, K., Ren, J., Qu, X., Label-free colorimetric detection of single nucleotide polymorphism by using single-walled carbon nanotube intrinsic peroxidase-like activity, Chem. Eur. J., 16, 3617, 2010.

[145] Yin, J., Cao, H., Lu, Y., Self-assembly into magnetic Co_3O_4 complex nanostructures as peroxidase, J. Mater. Chem., 22, 527, 2012.

[146] Dai, Z., Liu, S., Bao, J., Ju, H., Nanostructured FeS as a mimic peroxidase for biocatalysis and biosensing, Chem. Eur. J., 15, 4321, 2009.

[147] Asati, A., Santra, S., Kaittanis, C., Nath, S., Perez, J. M., Oxidase-like activity of polymer-coated cerium oxide nanoparticles, Angew. Chem. Int. Ed., 48, 2308, 2009.

[148] Sun, H., Jiao, X., Han, Y., Jiang Z., Chen, D., Synthesis of Fe_3O_4-Au Nanocomposites with enhanced peroxidase-like activity, Eur. J. Inorg. Chem., 109, 2013.

[149] Zhang, Z., Berg, A., Levanon, H., Fessenden, R. W., Meisel, D., On the interactions of free radicals with gold nanoparticles, J. Am. Chem. Soc., 125, 7959, 2003.

[150] Lee, Y., Garcia, M. A., Huls, N. A. F, Sun, S., Synthetic tuning of the catalytic properties of Au- Fe_3O_4 nanoparticles, Angew. Chem. Int. Ed., 49, 1271, 2010.

[151] Valden, M., Lai, X., Goodman, D. W., Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties, Science, 281, 1647, 1998.

[152] Lee, Y., Loew, A., Sun, S., Surface and structure-dependent catalytic activity of Au nanoparticles for oxygen reduction reaction, Chem. Mater, 22, 755, 2010.

[153] Hsueh, C. L., Huang, Y. H., Wang, C. C., Chen C. Y., Degradation of azo dyes using low iron concentration of fenton and fenton-like system, Chemosphere, 58, 1409, 2005.

[154] Gao, L., Zhuang, Z., Nie, L., Zhang, J., Zhang, Y., Gu, N., Wang, T., Feng, J., Yang, D., Perrett, S., Yan, X., Intrinsic peroxidase-like activity of ferromagnetic nanoparticles, Nat. Nanotechnol., 2, 577, 2007.