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Photochemical preparation and application research of Au nanoparticles

DONG Shou-an(董守安), SUN Jia-lin(孙加林)

(Kunming Institute of Precious Metals, Kunming 650221, China)

Abstract: Gold nanoparticles protected by organic small molecular compounds or macromolecule have attracted considerable attention and their preparation is one of hotspots in the nano-chemical material field due to their ongoing and potential applications in optics, electronics, catalysts and biosensors. In recent years there are many liquid phase chemistry methods to prepare monodispersed gold particles. Among them, the photochemical method is quite attractive because of its some important advantages for size-controlled synthesis of gold nanoparticles. Therefore, in this paper the recent progress of the photochemical preparing Au nanoparticle materials was briefly introduced and mainly emphasized authors' own works of this area.

Key words: gold; nanoparticles; photochemical preparation; catalytic application; review

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1 Introduction

In recent years, many investigations show that the nanoscale materials of precious metals are a novel field with full vitality and developing prospect. As concerns gold, the potential of gold clusters or nanoparticles as building blocks for fabricating nanoscale circuitry and quantal device has emerged by atom manipulation or self-assembly[1-8]. The application for transparent conduction film materials of gold nanoparticles and low temperature gold nano-paste are considerably attractive. In catalytic action aspect, the bulk gold is chemical inert, historically, gold was regarded to be no catalytical activity. However, nanotechnology has transformed gold from a marginal into a very effective catalyst with unique properties. The gold catalyst, consisting of nano-particulate gold on oxide supports, can be used for a wide variety of reactions and many of these have potential for applications in pollution control, chemical processing and fuel cells[9-12]. In the biomedical field, gold and silver nanoparticles (or their composite) not only possess novel optical, electric, magnetic and structural properties, but also have favorable biocompatibility. Therefore, they have great important exploitability in the nanobiology and biomedicine[13-17].

At the present time, the study on the materials of gold nanoparticles is very active. A number of novel properties are being constantly found. If gold nanoparticles protected by monolayer are regarded as an example, their investigations and applications were shown in Fig. 1. In a word, gold, as indicated in some comment, is considered as a key element for green nanotechnology[18], and gold nanoparticles are regarded

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Biography: DONG Shou-an(born in 1942), Male, Professor.

as a renaissance in gold chemistry[19].

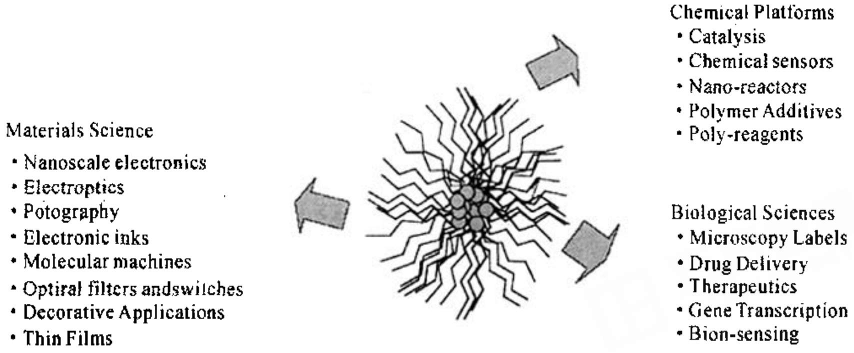

Fig. 1 Possible application areas for monolayer-protected clusters

In the present review, we will briefly introduce about the preparation method and technology of gold nanoparticles and emphasize the photochemical synthesis and characterization in recent progress, simultaneously including our own works of this area as well as possible application in the catalytic action of gold nanoparticles.

2 Survey on the preparation method and technology of gold nanoparticles

Currently, the preparation of gold nanoparticles can be divided into two classes, i. e. physical and chemical method. The essential of physical method consists in subdividing bulk precursors to nanoparticles by top down. It mainly includes: (1) the condensation method of vaporized atoms in an inert carrier gas by sputtering bulk gold and gas phase deposition method from an organic metal compound precursor and so on[6,7]; (2) in the presence of the protective agent, such as cyclodextrin, sodium dodecanesulphonate or Poly(amidoamine) dendrimers etc., by laser ablation onto nanoparticles from bulk gold in aqueous solution[20-24]. This method can obtain clean clusters, nanoparticles and nano-film materials, and also control the size of gold nanoparticles by changing radiation frequency of pulsed laser and the concentration of surfactants. However, there are high cost of instruments and low yield in the physical preparations.

The chemical procedures start from reduction of metal ions to metal atoms, and subsequently control aggregation of atoms. The strength of chemistry in materials science is its versatility in designing and synthesizing new materials, which can be processed and fabricated into final components by bottom up. Chemical synthesis permits the manipulation of matter at the molecular level. Because the mixing at the molecular level can achieve good chemical homogeneity and mass preparation of metal particles is easily realizable in the solution. Therefore, the chemical synthesis method for low dimension materials attracts widely interest.

In liquid phase chemistry method the synthesis of monodispersed gold nanoparticles with different sizes and shapes can be perform in the presence of various protective agents, such as end capping agents with different functional groups, soluble polymers and surfactants, and that nanoscale materials with various dimensions (1D, 2D or 3D) can be also constructed by self-assembly method[25-30]. Now, there are many liquid phase chemistry methods to prepare gold particles in both aqueous and nonaqueous solvents, including the use of chemical reductants[27-41], electrochemical method[42-48], sonochemical method[49,50] and photochemical method[51-64] and so on. The aim of investigations is all focused on obtaining size-controlled monodispersed gold nanoparticles, because of size dependency for their applications.

The preparations of gold nanoparticles by various chemical reductive agents are convenient and rapid, among them citrate reductant was widely used for various variety[27-35]. Nevertheless, there are also some potential difficulties in chemical preparing process, such as adsorbing pollution of excess reductant and its oxidation products for the product, requiring carefully controlling reaction conditions for synthesizing size-controlled particles etc.

Electrochemical method usually used for the preparation of rod-shaped gold particles and self-assembly structure. In this procedure a gold electrode is used as the sacrificial anode and a platinum electrode as the cathode, using rodlike micelle formed by cetyltrimethyl ammonium chloride (or bromide) as template. When a porous alumina or polycarbonate membrane materials was acted as template, gold nano-rods can be electrochemically deposited in the channel of the porous template. After removing the template by the dissolution method, rod-shaped particles were released from the support. The advantages of electrochemical preparation are to efficiently control the aspect ratio of gold nanoparticles and favorable for the study of optical[42,44-46], electrical properties[43] and self-assembly[48]. However, the preparation procedure is quite complex.

Among these preparations, liquid phase photochemical reduction methods with gold complex are considerably attractive because of its novelty and following some important advantages: (1) controlled reduction of metal ions can be carried out without using excess reducing agent, no adsorbing pollution occurs in the process; (2) the reduction reaction is uniformly performed in the solution, the radiation is absorbed regardless of the presence of light-absorbing solutes and products; (3) the rate of reaction is well known, since the number of reducing equivalents generated by radiation is well defined. In addition, from the point of view of practice application, the photochemical method is more competitive without the needs of specific instrument. Thereby, since 1990 the photochemical preparations of gold nanoparticles were adopted and studied by a number of scientists[51-64]. Although this method is not as widespread as the chemical reduction method, its application potential in the synthesis and self-assembly of metal nanoparticles is prospective.

3 Photochemical synthesis and characterization of gold nanoparticles

3.1 Synthesis by micelles as template

In the photochemical preparation of gold nanoparticles, the size-controlled synthesis, similar to the reduction method with chemical reductants, can be carried out in aqueous solution or organic solvents, using macromoleculer polymers[55-57], dendrimers[58] or various surfactants[52,63,64] to form the micelle or reverse micelle as soft templates. Substantively, the stability of gold particles is mainly due to the steric hindrance of the organic macromolecules, preventing nanoparticle coagulation. Fig.2 and Fig.3 illustrate the protective action of polymer and dendrimer compound for preparing gold nanoparticle or cluster in aqueous solution, respectively.

In general, the surface resonance plasmon absorption spectrum of gold nanoparticles in preparing process was characterized by UV-Vis spectrometer. The size and shape of particles were determined with transmission electron microscope (TEM) and selected area electron diffraction and X-ray diffraction were used for studying crystal structure of nanoparticles. Sometimes, with aids of X-ray photoelectron spectroscopy and scanning electron microscope, aggregation of small gold particles to form colloidal gold and gold metal film can be investigated[56,57].

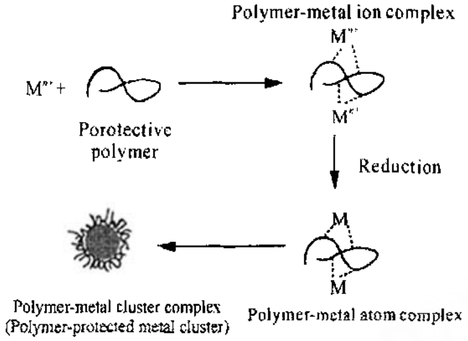

Fig.2 The reduction process of metal salts in the presence of a stabilizing polymer[65]

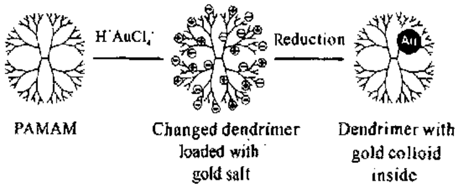

Fig.3 Dendrimer nanotemplating in aqueous solution[66]

In order to obtaining monodispersed gold nanoparticles, the photochemical preparation usually was carried out in aqueous-alcoholic solution or nonaqueous medium, using poly(vinyl alcohol) (PVP) or poly (vinylpyrrolidone) (PVA) as the protective agent. For size-controlled synthesis of nonaqeous colloidal gold particles, M.Y. Han *et al*.[52] reported an effective photochemical route. The experiment was performed in a higher polar and viscous formamide medium in the presence of PVP, size-controlled gold colloid can be achieved by changing the molar ratio of PVP to HAuCl4. Due to the higher degree of dissociation of $AuCl_4$ in the formamide and the direct reduction by the photogenerated free radical from the coordinated formamide molecules, well disperse and uniform gold particles were prepared much more easily in formamide than in water. A Coulomb staircase was clearly observed at room temperature on the resulting uniform gold particles of 12 nm prepared in the nonaqueous system.

In our photochemical investigation, the spherical colloidal gold particles were prepared by various wavelength UV irradiations, using PEG with different degree of polymerization as protective agents in aqueous solution containing $HAuCl_4$[67]. It is found that the particle size decreases with an increase of PEG polymerization degree and the shape also tends uniformity. When PEG polymerization degree is certain, gold particle size becomes bigger with increasing UV irradiation wavelength. The mechanism on PEG to stabilize gold nanoparticles was assumed to be protective action of forming pseudo-crown ether structure. In the photochemical synthesis of using anionic surfactant (sodium dodecyl sulfate) to form spherical micelle as the templating[68], we studied the affects of the organic reagents, such as methanol, n-propanol and acetone on the formation of gold nanoparticles. It is found that the surface plasmon absorption band of gold particles characterized by UV-Vis spectra was shifted to shorter wavelength direction in order mentioned reagents, and particle size characterized by TEM also decreased with above order. A monodispersed colloid gold with an average particle diameter of 7.5 nm was obtained in the water-acetone system containing 2.45×10^{-4} mol/l Au(III) $-$ 4.13×10^{-3} mol/l $C_{12}H_{25}SO_3Na$. Although no complex forms between $AuCl_4^-$ and $C_{12}H_{25}SO_3Na$, the spherical micelle formed by long chain hydrophobic group and larger hydrophilic group in $C_{12}H_{25}SO_3Na$ molecule in aqueous solution seems a microreactor of gold parcticles, efficiently preventing their irreversible aggregation. When sodium dodecylsulphonate surfactant was used for protective agent, gold particle size became small due to increasing hydrophobic chain length. The average diameter of the particles was 6.7 nm under optimum experimental conditions[69].

3.2 Size-controlled growth by seed-mediated technique

The use of preformed metallic seeds as nucleation centers in nanoparticle synthesis is an important technique for size control of particle growth. First small particles are prepared and then they are used as seeds to prepare bigger particles by through reducing metal precursor compound. This growth method could offer the advantage of separating the nucleation and growth steps in time. Thus, improved monodisperse nanoparticles with different sizes can be obtained. Of course, in some cases additional nucleation can also occurs in the presence of seeds, suggesting that seeds promote nucleation. This is the reason why seed-mediated method is not guaranteed to be satisfactory for all preparations. For the size-controlled synthesis by seed-mediated, chemical reduction method such as the use of citrate or borohydride-reduced which can generate 20—100 nm gold nanoparticles in diameters has been investigated in detail[70,71]. Recently, K. Mallick *et al*.[59] reported a photochemical synthesis of colloidal Au particles of different size by seeding approach. The seed particles were prepared by UV irradiation in the presence of a neutral micelle of Triton X-100 (chemically known as poly(oxyethylene) iso-octyl phenyl ether), and then they were grown to larger size by the addition of $AuCl_4^-$ ions and again UV irradiation under the same experimental condition. Monodispersed gold particles of different size (~20—80 nm) have been synthesized by this method. This process can be described by the following schematic (Fig. 4).

We proposed a novel photochemical approach to prepare gold nanoparticles of controlled size by seed-mediated growth under the UV solar radiation on plateau, using a PEG aqueous solution system containing acetone for rapid photoreaction synthesis[72]. Our aim is to utilize solar energy to new material synthesis, because solar energy is enormous and clear energy source. This is a goal sought by scientists at all times in the high-technology. In this work, we first prepared nearly monodispersed colloidal gold particles with UV 300 nm irradiation and then used them as seeds to grow into larger particles by the addition of Au (III) ions under the solar radiation. The growth of the seeds and influence of the UV solar energy on the growth were studied in detail. The results show that the colloidal gold particales with improved monodispersity and 10.2—66.4 nm in diameter can be generated by varying the molar ratio of seed to Au(III) ion and by step seeding. No additional nucleation occurred during the seed-mediated growth. It is suggested that PEG can coordinate to Au(III) ions before reduction, forming a polymer-metal ion complex (Fig. 2), and then such a complex was reduced under UV solar radiation, resulting in well dispersed colloidal gold particles protected by PEG pseudo-crown ether structure.

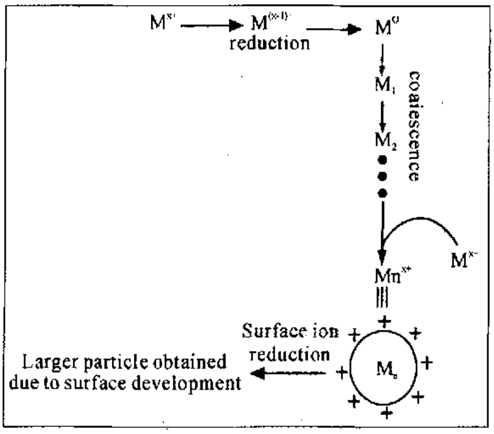

Fig. 4 Schematic representation of the development of metal cluster

The effect of the plateau UV solar radiation intensity (Author's laboratory locates the city of Kunming in Yunnan plateau of north latitude 25°02′, the elevation here is 1850 meters) on reduction reaction of Au

(III) ions showed that it is feasible to synthesize gold nanoparticles in larger scale under the UV solar radiation on the plateau with the higher elevation, because of rapid reduction reaction in the selective solution system (Fig. 5) and using a seed-mediated growth technique.

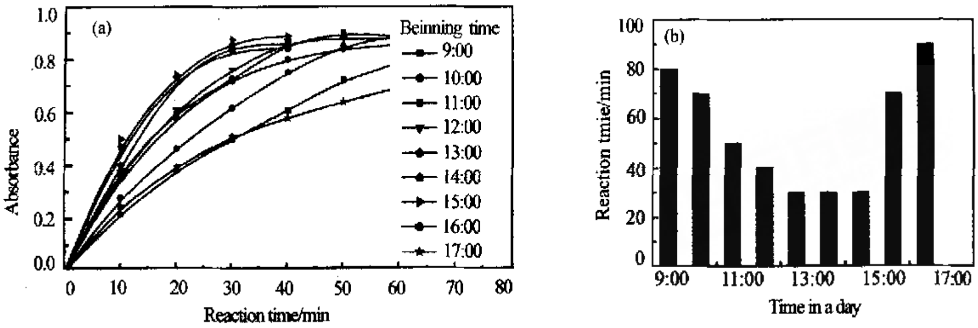

Fig. 5 Effect of the UV solar radiation intensity in a day on reduction reaction of Au(III) ions (a); Distribution of the UV solar radiation intensity in a day indicated by reaction time (b)

3.3 Synthesis of bimetal core/shell structure particles

Optical and catalytic properties of bimetallic nanoparticles are the subject of considerable interest. Consequently, a number of methods have been developed for fabricating the composite nanoparticle structure, especially Au-Ag nanoparticles with core-shell structure. Except the chemical preparation with sodium citrate[73], K. Mallik *et al.*[51] reported a synthesis route by a UV-photoactivation technique. In this work, gold particles with better monodispersity were prepared by UV irradiation in aqueous solution in the presence of TX-100 and were used as seed particles. Then, the required amount of gold seed particles, $AgNO_3$ and TX-100 solution were mixed and again kept under UV light for forming Au core/Ag shell type structure.

Based on the photo-reduction of $HAuCl_4$ (or $AgNO_3$) in PEG-acetone solution[72], we proposed a photochemical method for synthesizing colloidal Au core/Ag shell nanoparticles[74]. In this procedure, the preformed monodispersed gold nanoparticles with the average diameter 3.9 nm were used as seeds, in PEG-acetone-$AgNO_3$ solution the seed particles added act as nucleation centers and catalyzed the reduction of silver ion on their surface under UV irradiation, forming composite nanoparticle structure with a core of Au and a part or complete enveloped shell of Ag. The optical property and the sizes of the bimetallic colloidal particles were characterized in the range of the molar ratio of Au /Ag from 4/1 to 1/4. The results showed that the optical property of Au-Ag composite particles was completely different from their alloying particles. The composite nano-structure formed was assumed to be similar to strawberry shape at the molar ration of Au /Ag from 4/1 to 1/1; and at the 1/4 molar ratio, the Au core/Ag shell type structure with a striking feature of forming interconnected network appears.

Based on the reaction of silver nanoparticles with CN^- ions[75,76], the Au core/Ag shell nanoparticle structure was confirmed again by the CN^- dissolution experiments. In PEG-acetone aqueous system, the mechanism of photo-reducing $HAuCl_4$ and $AgNO_3$ and forming core-shell structure could be illustrated in Fig. 6.

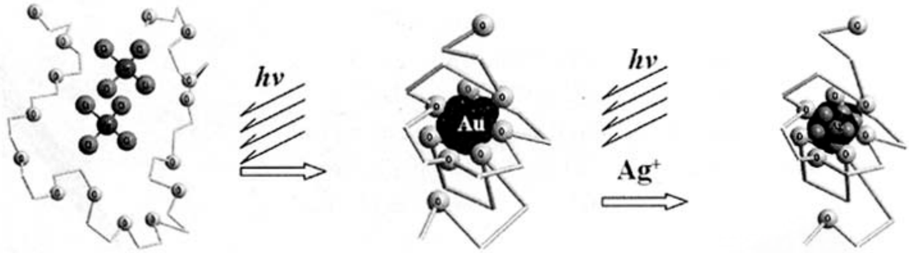

Fig.6 Scheme of forming mechanism for bimetallic Au core/Ag shell structure

The formation of Au core-Ag shell nanoparticles using photochemically reduced phosphotungstate Keggin ions was described by S. Mandal *et al*.[77] The characterized high-resolution TEM image was shown in Fig.7.

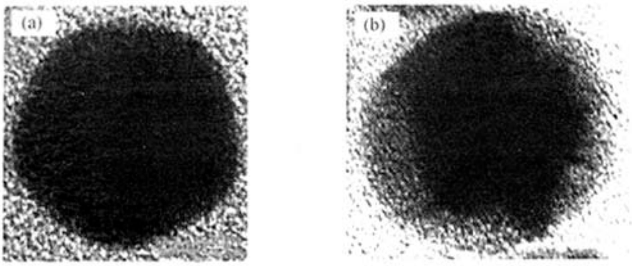

Fig.7 High-resolution TEM image

(a)—one of the gold particles; (b)—one of the Au core-Ag shell particles

3.4 Preparation and growth of rodlike Au nanoparticles

The photochemical method not only was used for the preparation of the monodispersed spherical gold nanoparticles and bimetallic Au-Ag composite nanoparticles, but also could be gone for the synthesis of one-dimensional nanorods by the cationic surfactant as the soft template. K. Esumi*et al*. reported first a preparing anisotropic gold particles method by 253.7 nm UV irradiation in rodlike micellar solution formed with cationic surfactant of haxdecyltrimethylammine chloride (CTAC)[54]. The more recent photochemical research showed that a small amount of silver addition is critical for the formation of one-dimensional gold rods in the aqueous solution of hexadecyltrimethylammonium bromide (CTAB)[53]. The previous method can obtain rodlike colloidal gold particles with larger aspect ratio under conditions of higher surfactant concentration and increasing irradiation time and for the later the largest aspect ratio obtained by controlling the concentration of gold and long time irradiation is 5. However, these anisotropic gold nanorods take on randon orientation distribution in the both cases.

We proposed a new photochemical reduction method of preparing gold nanorods. In this route, gold nanorods were synthesized in the aqueous solution medium of N,N-dimethylformamide (DMF), using rodlike miceller formed with CTAC as template and acetone as photosensitive agent. By changing the volumetric ratio of DMF and H2O, the miceller template shape is transformed from spherical to rodlike due to the change of solvent polarity and the micelle aggregation number. As a result, rodlike gold nanoparticles with different aspect ratios were obtained. We investigate the influence of the concentrations of HAuCl4 and

CTAC as well as irradiation time on the growth of nanoparticle self-organization. It has been noted that higher concentration of CTAC is adverse to the formation of nanorods, however long time irradiation is favorable to the growth of nanorods. The UV-Vis spectra showed one transversal surface plasma maximum absorption peak at 542.5 nm and longitudinal one at 775 nm. Under optimal conditions, the nanorods with a diameter of 20 to 22nm and a length of 1 to 3 μm were obtained (Fig.8). Moreover the orientation of nanorods is consistent. Simultaneously, the mechanism of the growth of gold nanoparticles in rod-shaped micelle was discussed by means of selected area electron diffraction and XDS analysis. It is suggested that rodlike particles between two micelles contact head to head and grows along (111) crystallographic facets with the lowest energy. This conclusion agrees with that in the literature[79].

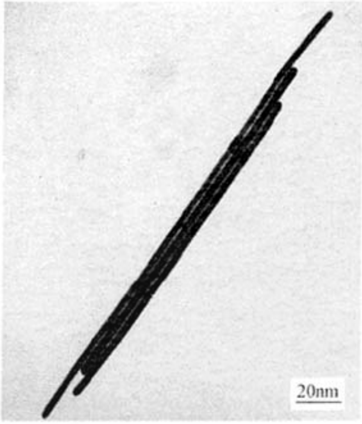

Fig.8 TEM images of Au nanoparticles

3.5 The synthesis by indirect photochemical method

As above mentioned, in recent years all investigations of the photochemical preparation of colloidal gold nanoparticles were carried out by the direct photoreduction reaction. In our works, except for utilizing direct photochemical reduction method, a new strategy idea of synthesizing gold nanoparticles, i.e. the indirect photochemical preparation was proposed for the first time[80].

This method is based on a sensitive photochemical reduction reaction of Fe(III)-EDTA/Fe(II)-EDTA complex system in chloracetic acid-sodium acetate buffer solution. Owing to lower reduction potential for Fe(III)-EDTA/Fe(II)-EDTA system and higher oxidation potential for Au(III)/Au(0) couple, a rapid redox reaction can occur between Fe(II)-EDTA complex and Au(III) ions in the buffer solution. Thereupon, the photochemical reaction of Fe(III)-EDTA/Fe(II)-EDTA complex system was used for indirect synthesis of gold nanoparticles. The experimental results showed that the Fe(II)-EDTA complex to act as a reducing reagent is easy generated by UV irradiation. Simultaneously, Au(III) ions were rapidly reduced, producing gold atoms to aggregate forming small nanoparticles which were stabilized by EDTA or foreign protective agent, such as PVP, PVA or citrate etc.

In the presence of citrate in particular, when the molar ratio of citrate to Au(III) was definite, the gold nanoparticles with an average diameter of 6.7 nm and narrower size distribution were synthesized in the complex buffer solution. It is possible to obtain smaller size gold nanoparticles by increasing the concentration of citrate.

In this indirect photochemical synthesis, Fe(III)-EDTA/Fe(II)-EDTA complex system plays a medium role of photoelectron transition. The charge transfer mechanism on the excited state of Fe(III)-EDTA coordination complex and the formation of gold nanoparticles can probably be described in Fig.9.

4 Au nanocatalyst prepared by Au sol and its application

The research and application for gold nanocatalysis, such as showing in Fig.1, are one of more important areas for gold nano-technology. There have introduced in a lot of reviews for this field in detail[9-12,81]. Twice successful international conferences of the 'Catalytic Gold' held in Cape Town, South Africa in April 2001 and the 'Gold 2003' held in Vancouver, Canada in September 2003 have shown the developing direction and research findings of the gold catalysis. Currently, the investigation on the gold catalysis is mainly fo-

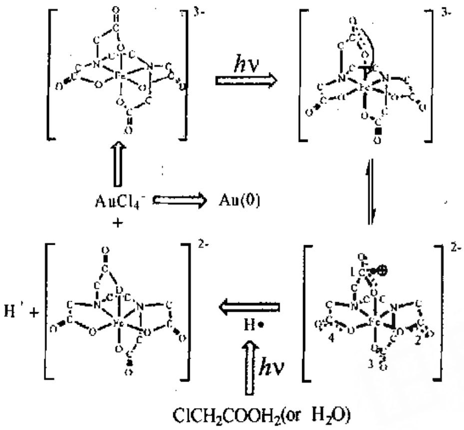

Fig. 9 The illustration of photochemical reaction mechanism of Fe(III)-EDTA/Fe(II)-EDTA complex

cused on pollution control, innovations in chemical processes and fuel cells etc. The paper published by Corti *et al*.[9] gave the number of patents related to gold catalysis and application distributing area of the patents in recent yeas (Fig. 10).

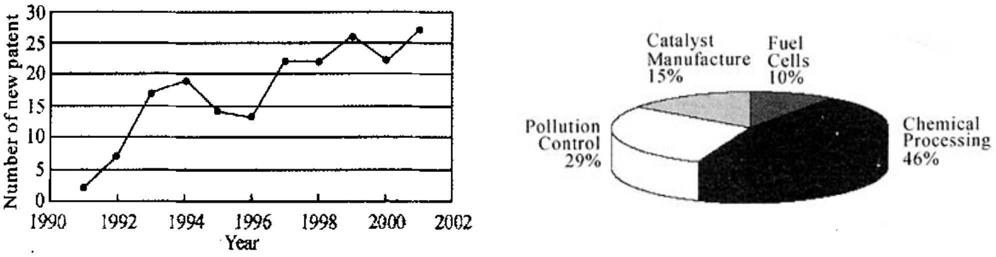

Fig. 10 The number of patents related to gold catalysis and application distributing area of the patents

As regards the preparation of gold catalyst, with various metal oxides as supports the method of the coprecipitation or deposition-precipitation of $Au(OH)_3$ is widely used. When active carbon is used for the carrier, the impregnation method of colloidal gold nanoparticles is simple and efficient. However it is difficult to deposit gold nanoparticles on metal oxide supports by this method, because gold nanoparticles has lower melting point and lower affinity to metal oxides. In addition, the gold nanocatalyst can be also prepared by Au(III)-acetylacetonate compound decomposition or vacuum deposition method.

Herein we mainly focus on the preparation, characterization and catalytic application of gold catalysts obtained by immobilizing the sols on carbon. In this aspect, a series of researches were carried out by Prati and co-workers[82-86]. The colloidal gold solution was prepared by chemical reductants such as hydrazine, sodium borohydride, using PVP or PVA as protective agent, and then immobilized on active carbon. Gold catalyst obtained was used for selective liquid phase oxidation reaction of diols. The research results showed that the catalytic activity of Au/C catalyst for liquid phase oxidation reaction depends obviously on the size of gold nanoparticles and gold exposure on the carbon surface. These two factors are also connected to the nature of activated carbon. The curves shown in Fig. 11 indicated the relationship between catalytic activity and the diameter of Au particles on two supports[86].

On the basis of literatures, we studied the preparation and characterization of Au/C catalyst and applied this catalyst to catalyze liquid phase oxidation reaction of glucose[87]. However, it is different from previous investigation that the colloidal gold solution was prepared by citrate reduction or photochemical reduction method, and then was impregnated with activated carbon. The dimension of gold particles was controlled by changing the molar ratio of citrate to Au(III), resulting in high active Au/C catalyst. The characterization with TEM indicated that after impregnation the size of the colloidal gold particle does not change; the average diameter of the particles on the surface of activated carbon is 9.92 nm under optimum preparing conditions. For liquid phase oxidation reaction of D-glucose, the dependence of the conversion on the diameter of Au particles was shown in Fig.12.

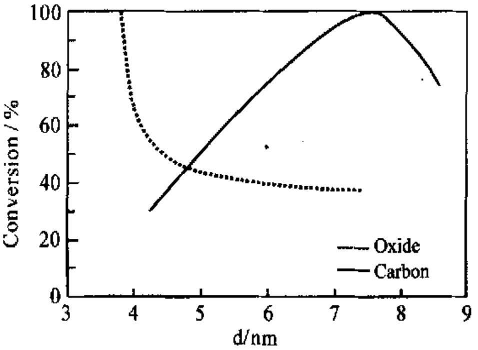

Fig.11 Dependence of catalytic activity of Au/Al_2O_3 and Au/C catalysts for the oxidation of glycols on the diameter of Au particles

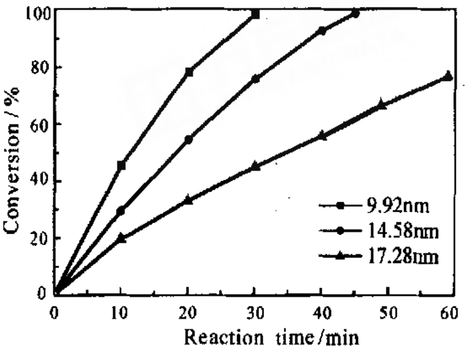

Fig.12 Dependence of the conversion on the diameter of Au particles for D-glucose oxidation

Obviously, the catalytic activity of Au/C catalyst decreases with increasing gold particle size. The catalyst obtained by impregnating about 10 nm gold particles on activated carbon has higher catalytic activity. This result is agreement with the literature[85] in which the catalytic activity of the catalyst with 7—8 nm gold particles is the highest.

In order to obtain the information of the lattice structure and chemically bond state of gold nanoparticles on actived carbon surface, the fresh prepared and used catalysts were characterized with XRD and XPS technology, respectively. It has been found that the half-peak width of XRD peak of gold particle for used catalyst has narrowing tendency, indicating the lattice structure of the particle trend towards the perfection. For XPS energy spectrum, the fine structure of Au4*f* photoelectron spectrogram was obtained by high resolution linear fitting method (Fig.13).

It can be seen from Fig.13(a) that the corresponding Au4$f_{7/2}$ splited into two peaks: 83.93 eV and 84.76 eV for the fresh prepared catalyst. The former was agreement with binding energy of Au(0) located on Au4*f*7 84.0 eV and the latter shifted +0.76 eV. The change of the binding energy means to form a new chemically bond state. However, for the used catalyst no split Au4*f*7 peak was observed after linear fitting (Fig.13(b)). Based on comparing the fine structures of the O1s energy spectra for fresh prepared and used catalysts (Fig.14), thereupon, it is assumed that an $Au^{\delta+}-O^{\delta-}$ chemically bond state exists on the surface of fresh prepared catalyst. Perhaps, this $Au^{\delta+}-O^{\delta-}$ chemically bond state just about led to high catalytic activity reason of Au/C catalyst.

Acknowledgement

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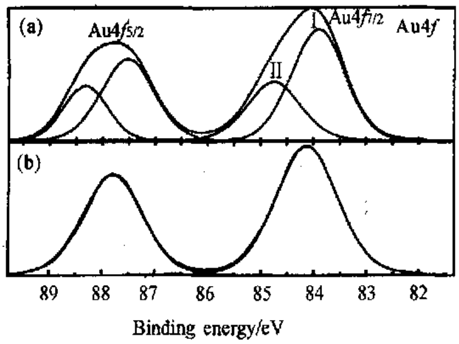

Fig.13 The Au4f XPS fitting curves of Au/C catalyst

(a)—fresh; (b)—used

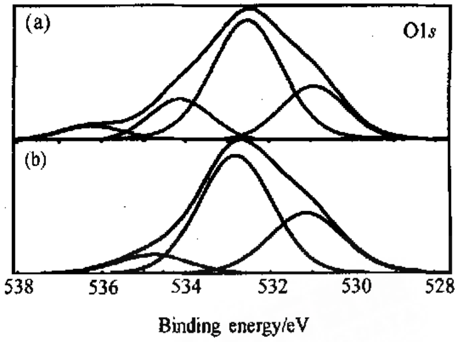

Fig.14 The O1s XPS fitting curves of Au/C catalyst

(a)—fresh; (b)—used

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