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Article (Special Column on New Porous Catalytic Materials)

Size-control growth of thermally stable Au nanoparticles encapsulated within ordered mesoporous carbon framework

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ARTICLE INFO

Article history:

Received 3 March 2015

Accepted 8 May 2015

Published 5 January 2016

Keywords:

Gold nanoparticles

Size

Carbon

Mesoporous

ABSTRACT

Simultaneously controlling the size of Au nanoparticles and immobilizing their location to specific active sites while hindering migration and sintering at elevated temperatures is a current challenge within materials chemistry. Typical methods require the use of protecting agents to control the properties of Au nanoparticles and therefore it is difficult to decouple the influence of the protecting agent and the support material. By functionalizing the internal surface area of mesoporous carbon supports with thiol groups and implementing a simple acid extraction step, we are able to design the resulting materials with precise control over the Au nanoparticle size without the need for the presence of any protecting group, whilst simultaneously confining the nanoparticles to within the internal porous network. Monodispersed Au nanoparticles in the absence of protecting agents were encapsulated into ordered mesoporous carbon at various loading levels via a coordination-assisted self-assembly approach. The X-ray diffractograms and transmission electron microscopy micrographs show that the particles have controlled and well-defined diameters between 3 and 18 nm at concentrations between 1.1 and 9.0 wt%. The Au nanoparticles are intercalated into the pore matrix to different degrees depending on the synthesis conditions and are stable after high temperature treatment at 600 °C. N₂ adsorption-desorption isotherms show that the Au functionalized mesoporous carbon catalysts possess high surface areas (1269–1743 m²/g), large pore volumes (0.78–1.38 cm³/g) and interpenetrated, uniform bimodal mesopores with the primary larger mesopore lying in the range of 3.4–5.7 nm and the smaller secondary mesopore having a diameter close to 2 nm. X-ray absorption near extended spectroscopy analysis reveals changes to the electronic properties of the Au nanoparticles as a function of reduced particle size. The predominant factors that significantly determine the end Au nanoparticle size is both the thiol group concentration and subjecting the as-made materials to an additional concentrated sulfuric acid extraction step.

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1. Introduction

Au catalysts have attracted significant attention since being reported as exhibiting high catalytic activity by Haruta, Hutch-

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This work was supported by the State Key Basic Research Program of China (2013CB934102), the National Natural Science Foundation of China (21322308, 21173149), the Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT-IRT1269), the Research Fund for the Doctoral Program of Higher Education (20123127110004), and Shanghai Science & Technology and Education Committee (11JC1409200, DZL123, S30406).

DOI: 10.1016/S1872-2067(15)60917-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 1, January 2016

ings and co-workers [1–3]. Such Au catalysts have found applications in areas such as selective oxidation [4–6], hydrogenation [7–10], epoxidation [11,12] and coupling reactions [13, 14]. Correlation of catalytic activity to the resulting particle size and the catalyst-support interface is crucial when considering their design and therefore isolating the Au nanoparticles to a desired location and increasing dispersion is a prerequisite for improved catalysis [15–18].

Activated carbon has been recently reported as scaffolds for Au nanoparticles [19,20], because of their many superior advantages to their oxide counterparts, such as stability in both acidic and basic environments and thermal stability up to 900 °C under inert atmospheres [21]. Additionally, activated carbon supports do not strongly interact with Au nanoparticles, which may take advantage of the particle size effect while minimizing the interface interaction effect for Au and oxide. Research publications related to Au supported on carbon lacks numbers when compared with Au supported on oxides, possibly because of the diverse origin of carbon, the redox properties and the ease in reducing Au(III) precursors resulting in, for example, the formation of large metallic aggregates. A colloidal deposition method was first developed by Rossi and co-workers to obtain 3-nm Au particles on activated carbon [22]. Protecting groups are always used [23–25]. It has been established that both the carbon support and the protecting agents can influence the overall activity of Au catalysts [21,26–29]. For example, particle size can be governed by the functionality of the protecting agent and thus alterations in both steric hindrance and the electronic properties of the Au nanoparticles results. Therefore, it remains a challenge to decouple the influences of the carbon supports' textural properties, the surface functionality—to include the protecting groups—which are highly related to the diffusion of liquid reactants and the properties intrinsic to the Au catalyst such as particle size and metal surface area [21]. Another problematic route leading to the rapid reduction of active sites is the occurrence of nanoparticle sintering during post-synthetic heat treatment of catalysts whereby the protective polymers are removed [30].

Compared with activated carbon possessing wide pore size distributions, ordered mesoporous carbons with well-defined mesoporous architectures and high surface areas are an example of an alternative support [31–35]. Nanocasting methods can be adopted to replicate Au-supported mesoporous carbon by using Au-containing functionalized SBA-15 silicates [36–40] as hard templates. However, the growth of nanoparticles from 2 to 7 nm occurs upon high-temperature treatment during the replication, which leads to low nanoparticle dispersion [33]. Additionally, the pore size from carbon that has undergone nanocasting is also difficult to tailor.

Intercalation of nanoparticles inside frameworks to improve stability is attractive [36–40]. For example, sulfur-containing silanes or silsesquioxanes are used to coordinate with Au species during triblock copolymer or surfactant self-assembly. The final products confine 2–7 nm Au nanoparticles in the walls of mesoporous (organo)silica. Very recently, our group developed a one-step coordination-assisted approach for the intercalation of monodispersed Au nanoparticles inside mesoporous carbon

walls [35]. The nanocatalysts show high activity and reusability in aerobic oxidation of alcohols. The limitation is however, that the nanoparticle size and the content are fixed to 9.0 nm and ~6.0 wt%, respectively. A pre-carbonization of the framework by sulfuric acid can yield Au nanoparticles with a size ~3.4 nm [41]. In this work, we demonstrate how to control both the size and density of the Au catalysts within the mesoporous carbon framework. By tuning the thiol functional group density with/without additional extraction of the template, stable Au nanoparticles in the absence of protecting agents, ranging from 3 to 18 nm in size and 0.01–0.09 g/g in concentration, are confined by the mesoporous carbonaceous frameworks upon carbonization at 600 °C. Nanoparticle aggregation is inhibited even at higher Au loadings. The reduction of the particle size results in changes to the electronic properties of the Au nanoparticles. As the resulting catalysts are stable at high temperature and are resistant to acid or base etching, the ability to tailor pore size and surface functionality retains the integrity of the nanoparticles and mesostructure. This allows for multiple tailoring of the catalyst properties for specific applications related to Au-supported mesoporous carbon catalysts.

2. Experimental

2.1. Synthesis of ordered mesoporous Au/C

In a typical synthesis of 9-Au(6)/C, Pluronic F127 (3.2 g; EO₁₀₆PO₇₀EO₁₀₆, M_w = 12600, Acros) was dissolved in an acidic ethanol solution (2.0 g of 0.2 mol/L HCl, 10.0 g of ethanol) at 40 °C prior to the addition of an ethanolic HAuCl₄ solution (6.3 mL, 48.5 mmol/L) under stirring. Thereafter, a mixture containing TEOS (2.08 g), (3-Mercaptopropyl)trimethoxysilane (MPTMS; 1.97 g) and ethanol (10.0 g) together with a solution containing preformed phenolic resins (2.0 g, prepared as described in references [34,35]) and ethanol (8.0 g) were added in sequence. After 2 h, the mixture was poured into dishes. The dishes were placed in a hood to evaporate ethanol at 40 °C for 5 h, and after to thermopolymerize at 100 °C for 24 h. The as-made films were ground into fine powders and termed: as-made 9-Au(6)/C. Removal of the block copolymer and carbonization of the as-made materials were achieved by calcination under N₂ via a temperature-controlled program from room temperature to 600 °C. Silica was removed from the composite by treatment with NaOH (1 mol/L). Specifically, the as-made 9-Au(6)/C sample was submerged for 12 h in a NaOH solution at 45 °C under stirring and repeated three times, each with a fresh alkaline solution. Finally, the mesoporous carbon-supported Au catalysts were washed with copious amounts of distilled water, and dried at 80 °C overnight under vacuum before activating the products by heat treatment at 150 °C for 4 h in air. The molar ratio for MPTMS/(MPTMS+TEOS) was tuned from 17% to 50% and Au incorporated into the final support within the range of 0.01–0.1 g/g. The detailed synthesis information was listed in Table 1. The final products were named as *x*-Au(*y*)/C, in which *x* represents the Au nanoparticle size of the Au/C catalysts and *y* represents Au content supported on the carbon. An optional sulfuric acid extraction step prior to high-temperature

Table 1

The detailed synthesis information in the sol-gel solution for ordered mesoporous Au/C.

Sample	HAuCl ₄ (mmol)	MPTMS (mmol)	TEOS (mmol)
3-Au(6)/C	0.31	10	10
9-Au(1)/C	0.05	10	10
9-Au(2)/C	0.10	10	10
9-Au(6)/C	0.31	10	10
9-Au(9)/C	0.49	10	10
14-Au(6)/C	0.31	6.65	13.3
18-Au(1)/C	0.05	3.30	16.7
18-Au(6)/C	0.31	3.30	16.7
100-Au(6)&C	0.31	0	20

treatment was performed on the as-made 9-Au(6)/C material. The composites were twice refluxed in 50 wt% sulfuric acid with mechanical stirring (typically 1.0 g of as-made material per 100 mL of 50 wt% sulfuric acid) at 90 °C for 24 h. The resultant materials were filtered, washed with distilled water and dried at 80 °C under vacuum overnight. This solid was designed as as-made 3-Au(6)/C. The following heating procedure and silica removal step are both exactly the same as above.

2.2. Characterization

The X-ray diffraction (XRD) measurements were recorded on a Rigaku Dmax-3C diffractometer using Cu K α radiation (40 kV, 20 mA, λ = 0.15408 nm). The metallic Au sizes were estimated according to the Scherrer formula on the basis of the 111 peak reflection from the wide-angle XRD diffractograms. N₂ adsorption-desorption isotherms were measured at –196 °C with a Micromeritics TriStar II 3020 analyzer. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}). By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branch of the isotherms. Transmission electron microscopy (TEM) analysis was conducted on a JEOL JEM 2100 microscope operated at 200 kV. Energy dispersive X-ray spectroscopy (EDX) was performed on a Philips EDAX instrument. Fourier transform infrared (FT-IR) spectra were collected on Nicolet Fourier spectrophotometer.

Thermal gravimetric analysis (TGA) curves were monitored on a Mettler Toledo 851e apparatus. X-ray photoelectron spectroscopy (XPS) measurements were recorded on a Perkin-Elmer PHI 5000CESCA system with a base pressure of 10^{–9} Torr. Au content was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian VISTA-MPX). The S content was measured on a Vario EL III elemental analyzer (Elementar, Germany). The temperature of the combustion tube was 1150 °C and the reduction tube at 850 °C. X-ray absorptions near extended spectra (XANES) at the Au L3 edge of samples were collected in fluorescence mode on the BL14W1 line of the Shanghai Synchrotron Radiation Facility (SSRF). Data were processed using the program ATHENA. All Extended X-ray Absorption Fine Structure (EXAFS) data were fitted using the program ARTEMIS.

3. Results and discussion

3.1. Characterization results

The first set of catalyst materials had a fixed Au content, while the density of the thiol groups protruding from the walls of the as-made material ranged from 1.55 to 3.06 mmol/g by tuning the addition of MPTMS from 3.30 to 10 mmol in the synthesis batch [42]. After carbonization and silica removal, the Au content for this set of Au/C catalysts is ~6 wt%, determined by ICP-AES (Table 2). TEM micrographs for 3-, 9-, 14-, 18-Au(6)/C show typical 2D hexagonal mesostructure. When the electron beam is perpendicular to the alignment of the pores, cylindrical pores are observed. With the incident beam is aligned parallel to the pores, the hexagonal ordering is clearly discernable. This is also true for the Au-free material establishing that the Au loading does not affect the overall long-range integrity of the mesostructure (Fig. 1). It is evident that mono-dispersed Au nanoparticles of tunable size are present on the carrier carbon supports. No observable large particles present outside the ordered mesopores clearly indicate that the thermally stable Au nanoparticles have been confined within the mesoporous carbonaceous matrix. In a previous report, HRSEM micrographs of the surface and cross section of the 9-Au(6)/C material, as well as the cross section after polishing were rec-

Table 2

Structural and textural properties of Au-supported mesoporous carbon catalysts.

Catalyst	Au content ^a (wt%)	a_0^b (nm)	S_{BET} (m ² /g)	V_t (cm ³ /g)	D_p (nm)	d_{Au}^c (nm)	d_{Au}^d (nm)
As-made 9-Au(6)/C	n.g.	12.7	—	—	—	—	—
As-made 3-Au(6)/C	n.g.	11.6	66	0.08	5.6	—	—
3-Au(6)/C	5.3	8.1	1269	0.79	3.4	3.4	3
9-Au(6)/C	5.8	8.0	1635	1.09	4.0	8.9	9
9-Au(1)/C	1.1	8.0	1634	1.06	3.8	8.5	9
9-Au(2)/C	1.8	8.1	1706	1.12	4.1	9.7	9
9-Au(9)/C	9.0	9.2	1529	1.01	4.0	9.9	9
14-Au(6)/C	6.0	9.0	1564	1.11	4.4	13.8	14
18-Au(1)/C	1.3	10.6	1349	1.11	5.6	18.4	18
18-Au(6)/C	5.7	10.4	1743	1.38	5.7	17.9	18
100-Au(6)&C	5.7	11.0	1331	1.23	6.0	150	50

^a Estimated by ICP-AES. ^b Cell parameter of the mesostructure. ^c Estimated from TEM analysis of average diameter. ^d Calculated from the Scherrer formula according to the (111) diffraction. n.g.—not given.

Fig. 1. TEM micrographs for Au-containing mesoporous carbon catalysts with varying particle sizes viewed along the (001) (a, c, e, g) and (110) (b, d, f, h) directions. (a, b) 3-Au(6)/C; (c, d) 9-Au(6)/C; (e, f) 14-Au(6)/C; (g, h) 18-Au(6)/C. Inset (b, d, f, h) is the corresponding metal particle size distribution histogram. Inset (c) is an expanded HRTEM micrograph of a Au nanoparticle. Inset (g) displays the EDX pattern.

ordered [35] and the Au nanoparticles can only be observed after cross section polishing, further indicating the intercalation of Au nanoparticles inside the framework rather than on the external surface of the mesostructured solids. In contrast to the 100Au(6)&C sample, synthesized in the absence of thiol func-

tional groups, a distinct phase separation between large Au nanoparticles (150 nm) and the ordered mesostructure domains is observed (not shown here).

The average nanoparticle size of 3.4 nm is observed for the 3-Au(6)/C catalyst, the nanoparticles each having a semiexposure morphology (Fig. 1(a, b)). The nanoparticles are part encapsulated with the carbon wall while the remainder protrudes out into the channels of the pore. In relation to the 9-Au(6)/C material, the nanoparticle size averages ~ 9.0 nm in size. Observation reveals that the particles span the entire width of the pore channels up to the adjacent pore walls, however, the nanoparticles do not penetrate into the carbon walls (Fig. 1(c, d)). The HRTEM micrograph of a representative Au particle in 9-Au(6)/C shows crystalline Au particles with the characteristic 0.24 nm Au{111} lattice fringe. With respect to the 14- and 18-Au(6)/C materials, the Au nanoparticle diameters exceed the pore width and hence penetrate the pore walls of the adjacent pore channels (Fig. 1(e–h)). Though the size of the Au nanoparticles, especially in 9-, 14-, and 18-Au(6)/C, is obviously larger than that of the pores, the integrity of the carbon network was not so severely damaged by the Au encapsulation. EDX analysis reveals the undetected S or Si (Fig. 1(g), the other materials display similar results, not shown). This result suggests that the functional groups have been volatilized during calcinations similar to Au-containing mesoporous silicates [38–40], and the silica components have been removed by NaOH etching.

The Fourier transform intensities of the k -weighted EXAFS functions are shown in Fig. 2(a) for the Au samples with varying nanoparticle sizes, and that of Au foil is also included for comparison. Similar higher-shell features to the Au foil are found, indicating the existence of clustered Au atoms, consistent with an *fcc*-structure retained in the Au nanoparticles. The Au clusters in the supported samples have a reduction in the Au-Au coordination number in the order of Au foil > 18-Au(6)/C > 9-Au(6)/C > 3-Au(6)/C (Table 3), possibly because of the decreasing particle size and therefore the enhanced surface area-to-volume ratio. The relative first nearest Au-Au length contraction and the Debye-Waller factor changes

Fig. 2. Fourier transform of EXAFS (a) and Au L3 edge XANES (b) spectra for ordered mesoporous Au supported carbon catalysts with different Au sizes along with that of Au foil. The inset in (b) is an expanded region of the intensity changes of the white line (within the dashed box). The legend in inset (b) is exactly the same in (a).

Table 3

Fit parameters of Au L3 edge EXAFS spectra for 100Au(6)/C, 18-Au(6)/C, 9-Au(6)/C and 3-Au(6)/C catalysts together with the reference Au foil.

Sample	Shell	N^a	R^b	σ^2^c ($10^{-3} \text{ \AA}^2$)	ΔE_0^d (eV)
3-Au(6)/C	Au-Au	8.6 ± 0.8	2.84 ± 0.01	9.9 ± 0.7	5.9 ± 0.6
9-Au(6)/C	Au-Au	10.1 ± 0.8	2.86 ± 0.01	8.9 ± 0.6	5.9 ± 0.5
18-Au(6)/C	Au-Au	10.3 ± 0.8	2.86 ± 0.01	8.6 ± 0.5	5.8 ± 0.5
100-Au(6)&C	Au-Au	10.4 ± 0.8	2.86 ± 0.01	8.3 ± 0.5	5.9 ± 0.4
Au foil	Au-Au	10.6 ± 0.8	2.86 ± 0.01	8.3 ± 0.5	5.2 ± 0.5

^a Coordination number. ^b Distance between absorber and backscatterer atoms. ^c Debye-Waller factor. ^d Inner potential correction.

as a function of the inverse Au-cluster diameter. Because mesoporous carbon does not strongly interact with the support, the contracted lattice is mainly attributed to the enhanced surface energy (nanosize effect) [43].

The normalized XANES spectra of the supported Au at the L3 edges is shown in Fig. 2(b), which probes the unoccupied densities of d states (the white line of L3-edge is mainly because of the $2p_{3/2} \rightarrow 5d$ dipolar transitions while the $2p_{3/2} \rightarrow 6s$ contribution is negligibly small). Similar three peak patterns are observed for the studied Au-containing mesoporous carbons as for the bulk Au foil within the first 40 eV above the edge, which are characteristic of an fcc structure in the nanoparticles. The mesoporous carbon-confined Au nanoparticles exhibit a noticeable decrease in the white line intensity as compared with Au foil in the order of 3-Au(6)/C < 9-Au(6)/C < 18-Au(6)/C. The ideal electron configuration of Au is $5d^{10}6s^1$; however, because of rehybridization, large clusters have an electron configuration of $5d^{10-x}6s^{1+x}$, with the d -band density of states closer to the Fermi level and increased holes in the d -band [44]. The smaller particles in 3-Au(6)/C with a shorter Au-Au distance and enhanced d - d interactions favor s - d rehybridization, narrow d -bands, lower d -orbital energy and increasing the d -electron count at the Au site in the nanoparticles [41,45,46].

The small-angle XRD patterns for all Au-containing mesoporous carbon materials show typical diffractions belonging to the ordered mesophase (Fig. 3(a)). With the decrease in Au nanoparticle size (S concentration increasing), the cell parameter reduces from 10.4 to 8.0 nm. By comparison, the Au-free

samples after carbonization with the initial S loading increasing from 1.55 to 3.06 mmol/g –SH show decreasing cell parameters from 12.4 to 11.0 nm [42]. These phenomena imply extended framework shrinkage by both smaller nanoparticles and the concentration of MPTMS in the as-made materials. Relatively diffused wide-angle attributed to fcc Au is detected, further confirming metallic Au nanoparticles. The Au sizes calculated by the Scherrer formula range from 3 to 18 nm (Fig. 3(b)), complementary to the TEM micrographs. The Au-containing mesoporous carbon materials display typical type-IV isotherms, revealing uniform mesopore distributions (Fig. 4, Table 2). Increased adsorption after the initial sharp capillary inflection shows the uptake of adsorbate at low relative pressures between p/p_0 of 0.01–0.3 implying the presence of an abundance of small pores in the region of 2 nm. A bimodal pore size distribution is observed for all Au/C catalysts. A similar phenomenon has been found in a Au-free mesoporous carbon material—formed from a carbon-silica composite—with a so-called “reinforced-concrete” pore wall, homogeneous in the carbon and silica distribution [35,47–49]. After etching away the silica component the emergence of small pores result in the distinct nitrogen adsorption at low relative pressures. Therefore, in the present Au/C catalysts, the large mesopores are generated by the removal of triblock copolymer and the small mesopores originate from the etched silica component inside the pore walls. High surface areas of 1269–1743 m²/g and large pore volumes of 0.79–1.38 cm³/g were achieved because of a large number of voids. The primary pore size reduces as a function of decreasing Au nanoparticle size, in the same order as the

Fig. 3. Small-angle (a) and wide-angle (b) XRD patterns of Au encapsulated ordered mesoporous carbon as a function of Au nanoparticle size. (1) 3 nm; (2) 9 nm; (3) 14 nm; (4) 18 nm.

lattice constant.

The XPS analysis is a surface-sensitive technique with a sampling volume that extends from the surface of the sample to a depth of 1–5 nm [50]. The Au catalysts 3-, 9-, and 18-Au(6)/C display diffused peaks with binding energies in the region of 84 and 88 eV, which can be assigned to Au $4f_{5/2}$ and $4f_{7/2}$ in the metallic state (Fig. 5). However, these two peaks are extremely weak. Compared with the Au concentration estimated from the ICP-AES analysis, the surface and near-surface concentration of metallic Au is distinctly low. Similar phenomena have been found in mesoporous carbon-supported Ni or Fe catalysts, in which metal or oxide nanoparticles are immobilized inside the mesopore carbon walls [51,52]. Therefore, the present Au-containing carbon materials also possess the intercalation of Au particles inside the pore walls, complementary to the electron microscopy analysis. Only Au, C, and O are detected, confirming the absence of any contamination from chlorine and sulfur for the catalyst.

The density of the thiol groups in the walls of the as-made materials was then fixed to 3.06 mmol/g, and the Au content tuned in the synthesis batch. Finally, materials displaying 1.1–9.0 wt% Au were loaded over carbon (9-Au(1)/C,

9-Au(6)/C, and 9-Au(9)/C).

These materials show similar XRD patterns and N_2 sorption isotherms with the as-made counterpart material synthesized with the same thiol group density (Fig. 6), indicating the retention of the monodispersed Au nanoparticles, ordered mesostructure, high surface areas, large pore volumes and uniform pore sizes, including the catalyst with the highest Au content (9.0 wt%). Interestingly, the TEM micrographs show that the Au nanoparticle size remains practically unchanged across this series of catalysts, only with a distinct increase in particle numbers (Fig. 7). This is in contrast to most heterogeneous catalysts, in which an increase in the loaded metal concentration would simultaneously lead to nanoparticle growth. Therefore, maintaining the same Au nanoparticle size across the loading level range after carbonization at 600 °C is possibly related to the thiol concentration in the as-made materials.

To further elucidate the effect of Au nanoparticle size as a function of thiol density in the as-made matrix, a sample of 18-Au(1)/C was synthesized with a reduced Au loading (1.3 wt%) with the same thiol concentration of 1.55 mmol/g. The TEM micrograph clearly shows the same particle size of 18 nm to that in 18-Au(6)/C. Furthermore, the ordered mesostructure

Fig. 4. N_2 adsorption-desorption isotherms (a) and pore size distribution curves (b) for Au nanoparticle supported mesoporous carbon. (1) 3-Au(6)/C; (2) 9-Au(6)/C; (3) 14-Au(6)/C; (4) 18-Au(6)/C.

Fig. 5. XPS spectra of 3-Au(6)/C (a), 9-Au(6)/C (b), and 18-Au(6)/C (c). (b) is the localized enlargement of the spectra in (a) in relation to the Au 4f peaks.

Fig. 6. Small-angle XRD (a), wide-angle XRD (b), N₂ sorption isotherms (c), pore-size distribution curves (d) for 9 nm Au and 18 nm Au containing ordered mesoporous carbon as a function of varying Au loadings. (1) 1.1 wt% for 9 nm Au; (2) 1.8 wt% for 9 nm Au; (3) 9.0 wt% for 9 nm Au, (4) 1.3 wt% for 18 nm Au.

is retained (data not shown here). The well-resolved XRD diffractograms in both the small-angle and wide-angle ranges demonstrate the ordered mesophase and *fcc* Au nanoparticles with an estimated size of approximately 18 nm. The type-IV

isotherms reveal the well-defined mesopores with a high surface area of 1349 m²/g, a pore volume of 1.11 cm³/g and a bimodal pore-size distribution centered at 5.6 nm and below 2 nm (Fig. 6). These results are in agreement with those related to 18-Au(6)/C.

3.2. Discussion

The pathway on the basis of a coordination-assisted triblock-copolymer self-assembly approach leading to the composites is shown schematically in Fig. 8.

The coupling agent of MPTMS containing reactive thiol groups was utilized as the inner wall component, which can react with preformed phenolic resins and co-condense with TEOS in the sol-gel resulting in the formation of a mesostructured framework with thiol functionality protruding from the walls [47]. The thiol functional group has an affinity to coordinate with a Au source, with a coordination number of two between the Au and S moieties, as analyzed by the Fourier transforms of EXAFS spectra [35]. The Au(III) species is reduced to Au(I) thiolate, similar to Au solutions stabilized by, for example, thiol-containing PTMP-PMAA ligands [53] and

Fig. 7. TEM micrographs for 9-Au(γ)/C with different Au loadings viewed along the (110) (a) and the (001) (b) directions. (a, b) 1.8 wt%; (c, d) 9.0 wt%. The inset shows the metal particle size distribution histogram.

Fig. 8. General scheme for the size-control synthesis of ordered mesoporous Au/C catalysts with Au nanoparticles intercalated to the carbon pore walls. From top to bottom: the thiol density ranges from 0.01 to 0.09 g/g, while the Au content remains constant. An additional sulfuric acid extraction step is performed for the 3-Au(6)/C material

p-HSCH₂(C₆H₄)C(CH₃)₃ [54]. The phenomenon is different with the Au(III)-Cl coordination in both the reference HAuCl₄ solution and the thiol-free synthetic solution. Therefore, the interaction among the Au, silane, and resins are strengthened in the synthesis solution. Triblock copolymer assembly at the interface is induced by the hydrogen-bonding interaction between the hydrophilic EO segments and the hydroxyl groups of the resins and silicates followed by solvent evaporation to increase the polymer concentration above the critical micellar concentration (CMC).

In the preceding step, the assembling mesostructured inorganic-organic hybrid composite is thermopolymerized at 100 °C to form flaxen as-made films. The FT-IR spectrum for the as-made 9-Au(6)/C material exhibits several bands at 3400, 3000–2800, 1610, 1460, 1350, 1100, and 950 cm⁻¹ corresponding to the characteristic stretching modes of phenolic resins, silicate and the triblock copolymer F127 (data not shown here), indicative of the organic-inorganic composite [41]. The C-S stretching mode at 690 cm⁻¹ suggests the presence of a S-containing functional group [55]. However, the thiol group in IR is invisible under the current conditions [55,56]. The S and Au signals are under the limit of detection in the XPS spectrum for the as-made 9-Au(6)/C sample, possibly because of the encapsulation of the thiol group and Au species in the framework and the triblock copolymer deep within the crystal.

Upon carbonization at 600 °C and the removal of silica, the carbon-based Au catalysts are obtained. The TGA curve for as-made 9-Au(6)/C material shows two predominant weight losses at 200–400 and 400–900 °C (not shown here). The weight losses are related to the decomposition of the triblock copolymer and the organosiloxane and the polymerization of carbon, which results in a significant weight loss of small molecules, for example, CH₄, and CO. Sulfur content successively decreases from 3.06, 0.98, 0.45 to ~0 mmol/g as the pyrolysis temperature increases from room temperature to 250, 350, and 600 °C (determined by elemental analysis). This result

demonstrates the simultaneous elimination of sulfur and pyrolysis of the polymeric framework with almost complete exclusion of sulfur residue in the final products.

Two key issues need to be addressed when tailoring the size of the metallic Au in the as-made material. The first factor to consider is the thiol density. In the absence of thiol functionality, phase separation of large Au nanoparticles (~150 nm) and the ordered mesoporous carbon support take place [35,41]. The lack of S-Au coordination results in an agglomeration of Au nanoparticles which proceed to grow outside of the porous ordered mesostructure domains. Increasing the thiol group loading in the as-made matrix from 1.55, to 2.21 and finally to 3.06 mmol/g results in the nanoparticle size continuously reducing from 18 to 14 and then to 9 nm, regardless of the Au concentration.

The reduction of Au ions to metallic Au is inhibited by the strong coordination with the thiol group. At elevated temperatures, the thiol moieties are gradually removed. Au species, once in the absence of the thiol functionality—and hence having no coordination—are reduced and dramatically aggregate together because of the low-melting point. Simultaneously, the “soft” polymeric framework becomes “rigid”. As a consequence, if the S species concentration is too low to stabilize the Au before the formation of the relatively “rigid” carbonaceous framework, the coagulation of Au nanoparticles inside mesopore channels is feasible with the possibility of penetration into the pore walls. At much higher S: Au ratios (ranging from 10.9 to 32.7), practical coordination in solution is necessary for the stabilization of the Au species in the solid during high temperature treatment. Stabilization hinders agglomeration until the “rigid” framework is fixed (at this stage, S-containing species should not be completely decomposed and the S-Au bond should remain), because the crystal growth energy in the solidified pore walls is high. As particle growth is confined by the framework, the particles remain homogeneously dispersed in the matrix. For example, Au nanoparticles grow to 18 nm in 18-Au(6)/C—which incorporates a low thiol loading of 1.55 mmol/g in the sol-gel—and therefore occupies two lattice cells. Increasing the thiol group loading protruding from the walls would strengthen the coordination and therefore, inhibit the reduction, mobility and aggregation of Au nanoparticles upon elevated temperatures. The sample 9-Au(6)/C which contains 3.06-mmol/g S in the as-made material can finally confine 9-nm nanoparticles in the matrix. The nanoparticles size is predominantly larger than the pore size but similar to the lattice constant for the mesophase. In these cases, the simultaneous formation of Au nanoparticles and relatively rigid silica-carbon framework favors the intercalation of monodispersed Au in the pore walls with no sign of any loss of integrity to the ordered mesopore arrays. Once the thiol concentration is fixed in the as-made material, the tuning of Au content shows negligible effect in the Au particle sizes within a defined range. For example, the samples 9-Au(y)/C, with the same S content as in the starting composite but having varying Au loadings between 1.8 and 9 wt%, possess similar particle sizes. The 18-Au(1)/C with a low Au content of 1.3 wt% has a similar large particle of approximately 18 nm to 18-Au(6)/C. It should be noted that in

this present study, the S: Au ratio in the as-made materials should be higher than 10 to achieve high loadings of monodispersed Au.

The second factor to consider is the additional concentrated sulfuric acid treatment [41]. We attribute this step as pre-carbonization, which is normally adopted for nanocasting mesoporous carbon [57, 58]. After sulfuric acid extraction, the IR spectrum for the as-made 3-Au(6)/C material shows a reduction in the vibration intensities at 1610, 1460 and 1350 cm^{-1} for phenolic resins, and in the C–H vibrations between 3000 and 2800 cm^{-1} and the C–O vibrations at 1100 cm^{-1} for the triblock copolymer when compared with the initial composite 9-Au(6)/C. This demonstrates further polymerization of the framework and partial removal of Pluronic F127 [34,42,49]. Concentrated sulfuric acid has also been reported as an alternative agent to remove triblock copolymers [42]. The C–S stretching mode at 690 cm^{-1} can be maintained, implying the protection of thiol functional groups. The comparison for S $2p_{3/2}$ XPS spectra between Au-free and as-made 3-Au(6)/C samples clearly demonstrate the formation of Au–S interactions and the residual unreacted –SH in the latter. The accessibility of –SH to Au facilitates the coordination (Fig. 9) [41, 42]. Additionally, the XPS spectrum exhibiting a doublet with binding energies of 84.7 and 88.5 eV were similar to those of Au(I) in an alkanethiolate complex for Au $4f_{7/2}$ and $4f_{5/2}$, confirming the stabilization of Au species by thiol groups [41]. The as-made 3-Au(6)/C sample displays a much smaller weight loss in the TGA curve than the 9-Au(6)/C material, in particular in the range below 400 °C, because of the extraction of the block copolymer (data not shown here). On one hand, the partially condensed framework may favor the formation of a rigid framework at lower temperatures compared with the starting matrix, and thereafter, the fixing of Au nanoparticles after their reduction. Conversely, materials that liberate less heat during the decomposition of the organics also favor the stabilization of Au particles because heat is the main driving force for the mobility of nanoparticles. As a result, the immobilized Au nanoparticles are approximately 3 nm in size, much smaller than those in the direct carbonized sample with the same Au and thiol loadings (~9 nm). Following this pre-carbonization idea,

two additional samples were also synthesized. Beginning with the starting composite of 14-Au(1)/C, the catalyst synthesized with the additional acid extraction step together with subsequent carbonization at elevated temperatures exhibited well-resolved diffraction peaks at low-angle two theta values in addition to an un-resolved peak at higher two theta angles, similar to the mesoporous carbon 3-Au(6)/C material. This result indicates that the catalyst possesses similar Au nanoparticle size of approximately 3 nm and retains a highly ordered mesostructure (Fig. 10). The BET surface area, pore volume and pore size of this catalyst is 1321 m^2/g , 0.86 cm^3/g and 3.8 nm, respectively. The second sample is derived from 18-Au(6)/C via the two-step carbonization. Interestingly, this sample also exhibits analogous XRD patterns to 3-Au(6)/C in both small-angle and wide-angle ranges, indicating the restriction of the Au nanoparticle growth to ~3 nm in the ordered carbon mesostructure (Fig. 10). These results show the importance of the pre-carbonized “rigid” framework by acid extraction to inhibit particle aggregation during the subsequent heating stage.

The final Au-containing mesoporous carbon materials have high surface areas, large pore volumes, interpenetrated, uniform bimodal mesopores. The pores are essential for diffusion and can therefore enhance the accessibility of the Au nanoparticles, which if the textural properties are not suitable, can minimize diffusion because of pore blockage by Au nanoparticles. Further investigation on the mass transfer effect is currently being studied.

Finally, the complete elimination of the coordination agent may show negligible effect on any catalytic performance for Au-containing mesoporous carbon catalysts. The coordination-assisted self-assembly approach adopted may establish a protocol that allows for the control of both the particle size and density of metal in porous carbon supports.

4. Conclusions

In summary, tailoring of the size and concentration of encapsulated Au nanoparticles supported on mesoporous carbon in the absence of protecting agents have been controlled by a

Fig. 9. XPS spectra for as-made Au-free (a) and 3-Au(6)/C (b) composites in the S $2p$ (A) and Au $4f$ region (b).

Fig. 10. Small-angle XRD (a), wide-angle XRD (b), N_2 sorption isotherms (c), and pore-size distribution curves (d) for the 3-nm Au-containing mesoporous carbon derived from as-made 14-Au(1)/C (1) and as-made 18-Au(6)/C (2) via the two-step carbonization process.

coordination-assisted self-assembly approach. Au nanoparticles with controlled sizes between 3 and 18 nm and contents of 1.1–9.0 wt% are thermally stable and do not sinter to large particles or migrate to the external surface of the carbon mesostructure upon high temperature treatment at 600 °C. The increase of thiol group loading together with subjecting the as-made supports to an additional pre-carbonization step before pyrolysis reduces the Au nanoparticle size. The reduction of the particle size results in the modifications to the electronic properties of the Au nanoparticles. The supported nanogold catalysts exhibit high BET surface areas of $> 1200 \text{ m}^2/\text{g}$, large pore volumes $> 0.8 \text{ cm}^3/\text{g}$ and bimodal pore sizes with the larger mesopore in the range of 3.4–5.7 nm and smaller secondary pore at 2 nm, showing potential applications in mass transfer, catalysis, adsorption and sensors.

References

- [1] G. J. Hutchings, *J. Catal.*, **1985**, 96, 292.
- [2] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.*, **1987**, 405.
- [3] M. Haruta, *Nature*, **2005**, 437, 1098.
- [4] M. McEntee, W. Tang, M. Neurock, J. T. Yates Jr., *J. Am. Chem. Soc.*, **2014**, 136, 5116.
- [5] W. Zhu, Y. J. Zhang, H. Zhang, H. Lv, Q. Li, R. Michalsky, A. A. Peterson, S. Sun, *J. Am. Chem. Soc.*, **2014**, 136, 16132.
- [6] Z. Y. Zhang, Y. Wang, X. Li, W. L. Da, *Chin. J. Catal.*, **2014**, 35, 1846.
- [7] S. Fountoulaki, V. Daikopoulou, P. L. Gkizis, I. Tamiolakis, G. S. Armatas, I. N. Lykakis, *ACS Catal.*, **2014**, 4, 3504.
- [8] G. Li, D. E. Jiang, S. Kumar, Y. X. Chen, R. C. Jin, *ACS Catal.*, **2014**, 4, 2463.
- [9] G. Li, R. C. Jin, *J. Am. Chem. Soc.*, **2014**, 136, 11347.
- [10] H. Wei, X. Wei, X. Yang, G. Yin, A. Wang, X. Liu, Y. Huang, T. Zhang, *Chin. J. Catal.*, **2015**, 36, 160.
- [11] V. I. Sobolev, K. Y. Koltunov, *Appl. Catal. A*, **2014**, 476, 197.
- [12] W. S. Lee, M. C. Akatay, E. A. Stach, F. H. Ribeiro, W. N. Delgass, *J. Catal.*, **2014**, 313, 104.
- [13] G. Li, D. E. Jiang, C. Liu, C. Yu, R. Jin, *J. Catal.*, **2013**, 306, 177.
- [14] S. Shabbir, Y. Lee, H. Rhee, *J. Catal.*, **2015**, 322, 104.
- [15] X. Feng, X. Duan, G. Qian, X. Zhou, D. Chen, W. Yuan, *J. Catal.*, **2014**, 317, 99.
- [16] S. Gil, N. Cuenca, A. Romero, J. L. Valverde, L. Sánchez-Silva, *Appl. Catal. A*, **2014**, 472, 11.
- [17] N. T. Khoa, S. W. Kim, D. H. Yoo, E. J. Kim, S. H. Hahn, *Appl. Catal. A*, **2014**, 469, 159.
- [18] G. R. Zhang, B. Q. Xu, *Chin. J. Catal.*, **2013**, 34, 942.
- [19] A. Goguet, C. Hardacre, I. Harvey, K. Narasimharao, Y. Saih, J. Sa, *J. Am. Chem. Soc.*, **2009**, 131, 6973.
- [20] H. Zhang, B. Dai, W. Li, X. Wang, J. Zhang, M. Zhu, J. Gu, *J. Catal.*

Graphical Abstract

Chin. J. Catal., 2016, 37: 61–72 doi: 10.1016/S1872-2067(15)60917-2

Size-control growth of thermally stable Au nanoparticles encapsulated within ordered mesoporous carbon framework

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Thermally stable gold nanoparticles with sizes of 3–18 nm and free of protecting agent have been loaded onto ordered mesoporous carbon via a coordination-assisted self-assembly approach.

- 2014**, 316, 141.
- [21] L. Prati, A. Villa, A. R. Lupini, G. M. Veith, *Phys. Chem. Chem. Phys.*, **2012**, 14, 2969.
- [22] L. Prati, M. Rossi, *J. Catal.*, **1998**, 176, 552.
- [23] T. Yokamotorn, S. Yamazoe, R. Takahata, J. Nishigaki, A. Thiravasasith, J. Limtrakul, T. Tsukuda, *ACS Catal.*, **2014**, 4, 3696.
- [24] C. Fernandes, C. Pereira, A. Guedes, S. L. H. Rebelo, C. Freire, *Appl. Catal. A*, **2014**, 486, 150.
- [25] F. Porta, L. Prati, M. Rossi, S. Coluccia, G. Martra, *Catal. Today*, **2000**, 61, 165.
- [26] C. L. Bianchi, S. Biella, A. Gervasini, L. Prati, M. Rossi, *Catal. Lett.*, **2003**, 85, 91.
- [27] M. L. Toebe, Y. H. Zhang, J. Hajek, T. A. Nijhuis, J. H. Bitter, A. J. van Dillen, D. Y. Murzin, D. C. Koningsberger, K. P. de Jong, *J. Catal.*, **2004**, 226, 215.
- [28] R. Y. Zhong, K. Q. Sun, Y. C. Hong, B. Q. Xu, *ACS Catal.*, **2014**, 4, 3982.
- [29] R. Y. Zhong, X. H. Yan, Z. K. Gao, R. J. Zhang, B. Q. Xu, *Catal. Sci. Technol.*, **2013**, 3, 3013.
- [30] M. T. Bore, H. N. Pham, E. E. Switzer, T. L. Ward, A. Fukuoka, A. K. Datye, *J. Phys. Chem. B*, **2005**, 109, 2873.
- [31] K. K. R. Datta, B. V. S. Reddy, K. Ariga, A. Vinu, *Angew. Chem. Int. Ed.*, **2010**, 49, 5961.
- [32] S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.*, **2000**, 122, 10712.
- [33] F. Kerdi, V. Caps, A. Tuel, *Microporous Mesoporous Mater.*, **2011**, 140, 89.
- [34] Y. Meng, D. Gu, F. Q. Zhang, Y. F. Shi, H. F. Yang, Z. Li, C. Z. Yu, B. Tu, D. Y. Zhao, *Angew. Chem. Int. Ed.*, **2005**, 44, 7053.
- [35] S. Wang, Q. Zhao, H. Wei, J. Q. Wang, M. Cho, H. S. Cho, O. Terasaki, Y. Wan, *J. Am. Chem. Soc.*, **2013**, 135, 11849.
- [36] E. Besson, A. Mehdi, C. Reye, R. J. P. Corriu, *J. Mater. Chem.*, **2009**, 19, 4746.
- [37] L. Chen, J. Hu, R. Richards, *J. Am. Chem. Soc.*, **2009**, 131, 914.
- [38] B. Lee, H. Zhu, Z. Zhang, S. H. Overbury, S. Dai, *Microporous Mesoporous Mater.*, **2004**, 70, 71.
- [39] P. Wu, P. Bai, Z. Lei, K. P. Loh, X. S. Zhao, *Microporous Mesoporous Mater.*, **2011**, 141, 222.
- [40] H. Zhu, B. Lee, S. Dai, S. H. Overbury, *Langmuir*, **2003**, 19, 3974.
- [41] S. Wang, J. Wang, Q. Zhao, D. Li, J. Q. Wang, M. Cho, H. Cho, O. Terasaki, S. Chen, Y. Wan, *ACS Catal.*, **2014**, 4, 797.
- [42] X. Zhuang, Q. Zhao, Y. Wan, *J. Mater. Chem.*, **2010**, 20, 4715.
- [43] A. Balerna, S. Mobilio, *Phys. Rev. B*, **1986**, 34, 2293.
- [44] I. Coulthard, S. Degen, Y. J. Zhu, T. K. Sham, *Can. J. Chem.*, **1998**, 76, 1707.
- [45] L. F. Mattheiss, R. E. Dietz, *Phys. Rev. B*, **1980**, 22, 1663.
- [46] J. T. Miller, A. J. Kropf, Y. Zha, J. R. Regalbuto, L. Delannoy, C. Louis, E. Bus, J. A. van Bokhoven, *J. Catal.*, **2006**, 240, 222.
- [47] X. Zhuang, Y. Wan, C. Feng, Y. Shen, D. Zhao, *Chem. Mater.*, **2009**, 21, 706.
- [48] Y. Wan, H. Wang, Q. Zhao, M. Klingstedt, O. Terasaki, D. Zhao, *J. Am. Chem. Soc.*, **2009**, 131, 4541.
- [49] R. Liu, Y. Shi, Y. Wan, Y. Meng, F. Zhang, D. Gu, Z. Chen, B. Tu, D. Zhao, *J. Am. Chem. Soc.*, **2006**, 128, 11652.
- [50] S. Suzer, *Appl. Spectrosc.*, **2000**, 54, 1716.
- [51] A. H. Lu, J. J. Nitz, M. Comotti, C. Weidenthaler, K. Schlichte, C. W. Lehmann, O. Terasaki, F. Schüth, *J. Am. Chem. Soc.*, **2010**, 132, 14152.
- [52] W. Wang, H. Y. Wang, W. Wei, Z. G. Xiao, Y. Wan, *Chem. Eur. J.*, **2011**, 17, 13461.
- [53] A. B. Laursen, K. T. Hojholt, L. F. Lundegaard, S. B. Simonsen, S. Helveg, F. Schueth, M. Paul, J. D. Grunwaldt, S. Kegnoes, C. H. Christensen, K. Egeblad, *Angew. Chem. Int. Ed.*, **2010**, 49, 3504.
- [54] P. M. Arnal, M. Comotti, F. Schueth, *Angew. Chem. Int. Ed.*, **2006**, 45, 8224.
- [55] S. Ungureanu, M. Birot, G. Laurent, H. Deleuze, O. Babot, B. Julián-López, M. F. Achard, M. I. Popa, C. Sanchez, R. Backov, *Chem. Mater.*, **2007**, 19, 5786.
- [56] K. Wilson, A. F. Lee, D. J. Macquarrie, J. H. Clark, *Appl. Catal. A*, **2002**, 228, 127.
- [57] M. Choi, R. Ryoo, *Nat. Mater.*, **2003**, 2, 473.
- [58] R. Ryoo, S. H. Joo, S. Jun, *J. Phys. Chem. B*, **1999**, 103, 7743.

尺寸可控、高热稳定性有序介孔碳Au催化剂的合成

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摘要: 纳米Au催化剂被认为是具有商业价值的用于醇选择氧化的第二代催化剂。这是因为Au氧化还原电势高, 化学稳定性好, 可抑制易使Pt族元素中毒的胺等的毒化; 其次, 对于一些特定选择氧化和还原反应而言, 具有较优的反应选择性。目前较多的研究集中在调变Au纳米颗粒与氧化物载体的相互作用, 获得协同效应。例如, 利用CeO₂纳米晶为载体, 沉积Au纳米颗粒(约3 nm), 使CeO₂部分还原为非计量比的催化材料, 活化氧并获得高选择氧化性能。碳是相对惰性的载体, 与Au相互作用力弱, 因此可被用于研究Au纳米颗粒本征催化性能。但负载碳金催化剂在焙烧甚至还原过程中易团聚, 且在反应中易流失, 可能导致活性下降。利用胶体沉积法可获得介孔碳负载纳米Au催化剂, 对葡萄糖选择氧化具有很高的催化活性和选择性。但是, 制备中使用的保护剂残留经常被忽略。由于立体效应或电子结构调变作用, 保护剂可能影响Au催化剂活性或稳定性。

我们前期建立了反应单体参与的自组装技术合成功能化介孔碳路线, 一步在介孔碳骨架中掺杂氧化物纳米催化剂。本文从介孔催化材料的结构出发, 设计“镶嵌”在碳骨架中的纳米Au颗粒。采用配位作用辅助表面活性剂自组装技术, 以苯酚和甲醛为碳前体, 引入含巯基硅烷偶联剂, 通过配位作用稳定金离子, 获得尺寸可控介孔碳限域纳米Au催化剂。低温炭化中, 由于巯基-金的配位作用阻抑金属移动或团聚, 高温下聚合物炭化为相对刚性的碳骨架。此时, Au纳米颗粒被相邻介孔孔墙限制。硅烷偶联剂可除去, 不影响碳载体, 并可产生丰富二级孔道, 获得多级孔道介孔碳材料。

X射线衍射和透射电镜结果显示, 所合成的催化剂中Au颗粒的尺寸可控, 为3–18 nm, 且具有单分散性, 均匀地分散在整个介孔碳骨架中, 其含量为1.1–9.0 wt%。金碳催化剂具有有序的二维六方介孔结构。能量散射谱(EDX)也证明了催化剂只含有C、O和Au元素, 没有S和Si元素的残留。X射线光电子能谱(XPS)结果显示催化剂表面的Au含量远远低于ICP的测试结果, 也证明了Au纳米颗粒分布在介孔碳骨架内, 同时只含有C、O和Au元素也与EDX相符。X射线近边吸收谱结果表明, 随着颗粒尺寸的减小, Au表面电子性质发生改变。N₂吸附脱附等温线显示, 有序介孔碳金催化剂具有典型的第IV型曲线, 说明孔径分布范围较窄, 主孔道尺寸为3.4–5.7 nm。值得注意的是, 低压力段吸附量显示明显突跃, 暗示其具有一套约为2 nm的次级介孔。所有的催化剂都具有高的比表面积(1269–1743 m²/g)和大的孔体积(0.79–1.38 cm³/g)。Au纳米颗粒具有高的热稳定性, 在惰性气氛中, 即使在600 °C也未见明显聚集长大。

进一步讨论了合成中影响金纳米颗粒尺寸的重要影响因素。(1)巯基含量: 通过调节巯基组分的含量, 可以调控催化剂中Au纳米颗粒的尺寸(9–18 nm)。需要强调的是, Au纳米颗粒尺寸与巯基在新合成材料中的浓度有关, 当巯基含量在所研究的范围中时(1.55–3.06 mmol/g), Au纳米颗粒尺寸仅仅与巯基浓度有关, 而与Au浓度无关。(2)硫酸预炭化处理: 新合成的材料经过一步硫酸预炭化处理, 可以得到尺寸为3 nm的有序介孔碳金催化剂。表征结果证明, 经过硫酸预炭化处理, 大量表面活性剂被除去, 同时聚合物载体发生部分炭化, 有助于在后续高温炭化中保护3 nm金颗粒不团聚。尺寸可控、高热稳定性、无配体保护的有序介孔碳负载Au催化剂有望应用在催化和传感器等领域。

关键词: 金纳米颗粒; 尺寸; 碳; 介孔

收稿日期: 2015-03-03. 接受日期: 2015-05-08. 出版日期: 2016-01-05.

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基金来源: 国家重点基础研究发展计划(973计划, 2013CB934102); 国家自然科学基金(21322308, 21173149); 教育部创新团队发展计划(PCSIRT-IRT1269); 教育部高等学校博士学科点基金(20123127110004); 上海市科委和教委基金(11JC1409200, DZL123, S30406).

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