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Selective Deposition of Gold Nanoparticles on or Inside Carbon Nanotubes and Their Catalytic Activity for Preferential Oxidation of CO

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Gold nanoparticles have been deposited on three kinds of carbon nanotubes (CNTs), including nitrogen-doped CNTs, by three different methods, namely, impregnation, organometallic decomposition, and deposition–precipitation. The choice of the gold precursor, the support, and the preparation procedure is critical for the control of the size and location (on or inside the nanotubes) of the gold nanoparticles. These

catalysts were tested for the selective oxidation of CO in a hydrogen-rich atmosphere. We have shown that the use of nitrogen-doped CNTs as a support permits one to reach much higher activity and selectivity at low temperature than with the other CNT supports. This catalyst also shows a good stability under reaction conditions without detectable sintering.

Introduction

Hydrogen-containing gas mixtures for polymer-electrolyte-membrane fuel cells (PEMFCs) should be free of CO to avoid poisoning of the Pt-based PEMFC catalyst. Preferential oxidation (PROX) of CO has been recognized as one of the most direct and efficient methods to achieve acceptable CO concentrations, typically below 100 ppm.^[1] In an H₂-rich atmosphere, H₂ and CO compete to react with O₂, thus leading to a decreased hydrogen yield. In addition, CO can consume additional H₂ by undergoing hydrogenation, which should be avoided unless the CO concentration in the reactant stream is low enough, because it consumes relatively large amounts of hydrogen. To develop PEMFC for practical applications, it is thus necessary to find catalysts that can be used to remove CO selectively in an H₂-rich system by oxidizing CO to CO_2 , while at the same time being inactive for hydrogen oxidation. Typical catalysts used in this reaction are gold or platinum nanoparticles

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(NPs) supported on oxides. Additionally, some researchers have suggested that factors such as the choice of the support or the metal particle size, which might be influenced by the catalyst preparation method, play an important role in the CO oxidation reaction.^[2]

Carbon nanotubes (CNTs) constitute a new class of support that, due to their remarkable properties, may play an active role in catalytic activity (including oxidation reactions),^[3] which should permit one to reach higher catalytic activity and stability than with conventional supports.^[4] Thus, CNTs constitute an interesting alternative to conventional supports due to (i) their high purity that can avoid self-poisoning; (ii) the improved mechanical properties, high electrical conductivity, and thermal stability of these materials; (iii) the high accessibility of the active phase and the absence of any microporosity, which eliminates diffusion and intraparticle mass transfer in the reaction medium; (iv) the possibility of macroscopic shaping of this support; (v) the specific metal-support interactions that can directly affect catalytic activity and selectivity; (vi) the possibility of chemical modification of their surface by doping (for example, with nitrogen) or grafting; and (vii) the possibility of confinement effect in their inner cavity.^[5–7]

Since CNTs are chemically inert, a pretreatment of the surface is needed for metal anchoring that involves oxidation of the CNTs by a strong oxidizing acid, or tedious metal-catalyst synthetic procedures.^[8] Commonly, the synthetic methods of metal catalysts involve citrate or borohydride reduction of higher-oxidation-state precursors, and only a few methods produce particles of uniform size.^[9–12] Jiang et al.^[13,14] selectively attached gold nanoparticles (by

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a cationic polyelectrolyte) to chemically functionalized CNTs. Covalent coupling of the activated CNTs with ionic liquids and subsequent anion exchange were used to achieve the assembly of controlled gold NPs on modified CNTs.^[15,16] Covalent coupling with (3-aminopropyl)trie-thoxysilane or polyethyleneimine was also reported.^[17–19] Gold NPs on CNTs present often a broad particle-size distribution, typically 12–20 nm.^[20] Theoretical studies have concluded that Au interactions with the graphite surface are weaker when compared to other metals.^[21]

Thus, to take advantage of all the potentiality of Au/ CNT catalysts, significant effort should be devoted to the synthesis of gold nanoparticles supported on CNTs, to the control of the morphology of nanostructures, and to factors that address these needs. In this paper we present different synthetic procedures for the design of high-performance Au/CNTs catalysts including (i) liquid-phase impregnation from preformed AuNPs; (ii) decomposition of a gold complex in the presence of modified CNTs so as to favor the dispersion of small AuNPs; and (iii) deposition-precipitation (DP) on functionalized and nitrogen-doped CNTs. Furthermore, we report the catalytic activity of AuNPs deposited on CNTs for selective CO oxidation in H2-rich streams. Characterization of the CNT supports and the Au/ CNT catalysts was performed by using nitrogen adsorption, TEM, infrared spectroscopy, thermogravimetric analysis (TGA), elemental analysis, chemical titration, and X-ray photoelectron spectroscopy (XPS). TEM has also been used to determine the spatial location (on or inside CNTs) of AuNPs in the different samples. The syntheses, structureproperty correlations, and relative catalytic activity of the systems are presented, with our attention focused on the influence of the size of the gold NPs on the catalytic activity and the interaction of these nanoparticles with the relevant support.

Results and Discussion

Synthesis and Characterization of the Supports

Commercial nanotubes CNT_P were segmented by ballmilling to open both their ends. The surface functionalization of segmented CNT_P and CNT_L (laboratory-grown CNT_S) with carboxylic groups, so as to provide good stability to the NPs, was achieved by nitric acid oxidation, thereby yielding CNT_{P2} and CNT_{L2} (Scheme 1). A simple and efficient method for the selective confinement of NPs in the inner cavity of CNTs is to use preformed NPs and CNT_S functionalized with a long alkyl chain.^[5] To graft long-chain alkyl-terminated moieties onto the CNT_P surface, CNT_{P2} was treated with thionyl chloride to produce acetyl chloride, and further treated with hexadecylamine (HDA) to produce the amide surface groups of CNT_{P3} (Scheme 1). Nitrogen-doped CNTs (CNT_N) were used without further functionalization.



Scheme 1. Procedures for the preparation of the catalytic systems.

Table 1 gives the Brunauer–Emmett–Teller (BET) surface-area characterization, mean pore diameter, mean diameter, and ash-content results for the different CNT supports used. The elemental and XPS analyses of the as-received and functionalized supports are given in Table 3.

Table 1. Textural properties of as-received CNTs.

Sample	$\begin{array}{c} BET\\ [m^2 g^{-1}]\end{array}$	Mean pore diameter [nm]	d _{ex} [nm]	d _{in} [nm]	Ash [%]
CNT _P	38	16	80	40	7
CNTL	180	13	14	7	8.9
CNT_{N}	292	10	52	25	7.5

As-received CNT_P and CNT_L present a small amount of surface oxygen functionalities (Table 2). Nitric acid treatment allows the introduction of polar hydrophilic surface groups, mainly -COOH but also phenol, carbonyl, and quinone.^[22] In the case of CNT_P, the duration of this treatment was limited to 3 h to avoid internal surface functionalization; this treatment produced 1 mmol of -COOH/g_{CNT} (determined by chemical titration^[23]) and an ash content of 7%, as evidenced by the results of elemental analysis (Table 2). CNT_L was functionalized with nitric acid treatment for 8 h. The concentration of surface -COOH groups in CNT_{L2} is 0.011 mmol g⁻¹, which points to a lower reactivity of CNT_L surface compared to CNT_P. The bulk quantitative (elemental analysis) and surface semiguantitative (XPS) analyses confirm the functionalization of CNT_{P2} , CNT_{P3}, and CNT_{L2} and the presence of the incorporated nitrogen in doped CNT_N.

The effective functionalization of CNT_{P2} and CNT_{L2} , and the grafting of the long alkyl chain on the CNT_{P3} surface were also checked by IR spectroscopy (Figure 1). The band at 1580 cm⁻¹ is due to CNT skeletal in-plane vibration, and that at 1721 cm⁻¹ is assigned to v_{asym} (COOH) of the carboxylic groups (from hydrolysis of some acetyl chloride groups in the case of CNT_{P3}). CNT_{P3} shows a band at 1635 cm⁻¹ that is consistent with the amide function, and the aliphatic C–H stretching bands located between 2850 and 2950 cm⁻¹ are also present.

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Table 2. Elemental and XPS analyses of as-received and functionalized CNTs.

	XPS [atom-%]	Elemental analysis [wt%]				
	С	Ο	Ν	C	0	Ν
CNT _P	98.6	1.4	_	93.3	0.4	0.6
CNT _{P2}	86.1	13.9	_	83.2	8	0.5
CNT _{P3}	89.2	9.8	1	88.8	3.3	1.1
CNT _L	95	0.6	_	94	_	_
CNT _{L2}	87.3	4.6	_	91.4	7.6	_
CNT_N	91.8	5.5	3.7	89.5	2.1	2.6



Figure 1. Infrared spectra (KBr pellets) of (a) CNT_P and (b) CNT_L.

Preformed Nanoparticles

Gold(I) complexes that bear alkynyl and isocyanide ligands with long alkyl or alkoxy chains were used as precursors for the nanoparticles. The new complex [Au(C=C- $C_6H_4-C_{14}H_{29})(C\equiv N-C_6H_4-O-C_2H_5)$] (Au¹) was prepared by reaction of [C=N-C₆H₄-O-C₂H₅] with [Au(C=C- $C_6H_4-C_{14}H_{29})$]_n. As reported for similar systems,^[24] it displays liquid-crystal behavior and shows a smectic A mesophase (SmA) in the temperature range 415–433 K.

Gold nanoparticles were obtained by thermal decomposition of Au¹ in toluene at 383 K. Figure 2 shows the TEM images of preformed AuNPs by using Au¹ as precursor. The nanoparticles average diameter is (18.7 ± 0.5) nm. The IR spectra of the nanoparticles show a weak v(C=N) absorption at 2195 cm⁻¹, which has been reported as characteristic of *p*-alkoxyphenyl isocyanides bonded to gold nanoparticles,^[25] thereby suggesting that these nanoparticles are stabilized by coordination of the isocyanide ligand.



Figure 2. TEM images of preformed Au¹NPs and histogram with the size distribution of the preformed AuNPs.

Synthesis and Characterization of the Supported Catalysts

Three synthetic routes were applied for the preparation of Au/CNT samples (Table 3 and Scheme 1). The first method was a simple impregnation (IP) procedure of preformed NPs from complex Au¹ on CNT_{P3} in THF, an organic solvent that presents a low surface tension (26 mNm⁻¹) and that should wet and penetrate inside the CNT_{P3}. The sample prepared in this way was named Au¹/ CNT_{P3}. The second method consists of the thermal decomposition (DC) at 373 K of the complexes Au² or Au³ in the presence of CNT_{P3} , thereby giving rise to Au^2/CNT_{P3} and Au^{3}/CNT_{P3} . This method is known to favor the dispersion of small AuNPs on and in CNT_{P3}. The third route consists of the synthesis by deposition-precipitation (DP) starting from a water/methanol (15:1) solution of Na[AuCl₄] that is added to CNT_{L2} or CNT_N; the resulting precipitate was dried at 373 K in air overnight. The corresponding catalysts were labeled Au/CNTL2 and Au/CNTN.

Table 3. Nomenclature and characteristics of the catalysts.

Support	Method	Sample
CNT _{P3}	IP DC	Au ¹ CNT _{P3} Au ² /CNT _{P3}
CNT _{L2} CNT _N	DC DP DP	Au ³ /CNT _{P3} Au/CNT _{L2} Au/CNT _N

TEM was performed to determine dispersion, particle size, and spatial location of gold NPs in the different CNT samples. Figures 3, 4, 5, and 6 show TEM images of synthesized AuNPs on and in CNTs.



Figure 3. TEM micrograph and histogram with the size distribution of Au²/CNT_{P3}.



Figure 4. TEM micrograph and histogram with the size distribution of Au $^3/CNT_{P3}$.

Au²/CNT_{P3} compounds show very small AuNPs of 1.25 nm anchored on or inside CNT_{P3} (Figure 3). The confinement of AuNPs is clearly nonselective, and most of the NPs are visible on the external CNTs surface. The presence of gold nanoparticles inside CNTs cannot be excluded since 3D TEM has not been done to quantify precisely the ratio of confined particles to those on the surface.^[5,7] However, XPS data (see Table 4) indicate that most of the gold is on the external surface. The very small mean particle size can be attributed to stabilization by the support and by the organic species formed upon ligand dissociation.



Figure 5. TEM micrograph and histogram with the size distribution of Au¹/CNT_{P3}.



Figure 6. TEM micrograph and histogram with the size distribution of Au/CNT_N .

Table 4. Catalyst characterization.

Sample	Loading ^[a] (wt%)	Au NP size ^[b] [nm]	Surface Au mass ^[c] [%]	Au 4f _{7/2} [eV]
Au ² /CNT _{P3}	7	1.25	3	84.4
Au ³ /CNT _{P3}	5	7	5	85.2
Au ¹ CNT _{P3}	6	18	nd ^[d]	nd ^[d]
Au/CNTL ₂	1	3.5	nd ^[d]	nd ^[d]
Au/CNT _N	5	11	2	84.2

[a] Determined by TG measurements. [b] Determined by TEM. [c] Determined by XPS measurements. [d] Not detected.

For Au³/CNT_{P3}, larger AuNPs (7 nm) are nicely dispersed on CNT_{P3} (Figure 4).

The use of preformed AuNPs with controlled-surface CNT_{P3} lead to confined large NPs of $d_m = 18.1$ nm inside the functionalized CNT_{P3} (Figure 5).

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Finally, for Au/CNT_N (Figure 6), in which the bamboo structure does not allow the confinement, AuNPs with a mean diameter of 11 nm are located on the external surface.

Table 4 shows the characterization data of the gold catalysts. Thermogravimetric analyses (SI1 in the Supporting Information) performed in air provide the determination of the gold content (Table 4). The CNT_P compounds show the lowest gasification temperature because of their low crystallinity and higher defect content. Surface semiguantitative (XPS) analyses (Table 4) allowed us to determine the Au loading on the CNT surface and the location of the NPs.^[5,6,26] The differences in the gold loading obtained from TGA (bulk analysis) and XPS (surface analysis) can be understood as a consequence of the confinement of AuNPs inside CNTs. Since XPS is a surface-analysis technique, the XPS data confirm the nonselective confinement of Au²NPs inside CNT_{P3} and the selective confinement of Au¹NPs in the inner cavity of CNT_{P3}. The XPS spectra (SI2 in the Supporting Information) detect Au 4f7/2 with binding energies over 84 eV (Table 4). These are typical values for Au⁰,^[27] thereby indicating the formation of metallic AuNPs on the side walls of CNTs.

The XRD diffractograms of Au/CNTs (SI3 in the Supporting Information) show typical peaks at $2\theta = 25^{\circ}$ that can be assigned to CNT (002 plane), and the peak 2θ values at 38.4, 44.6, and 64.8° are assigned to gold. The peak intensity of (002) decreases for CNT_P thus indicating lower nanotube crystallinity. The broad peaks in the XRD pattern in the case of Au² indicate that AuNPs are too small to yield XRD signals. In the case of Au³ (average size 7 nm as determined by TEM), the broadening of the peaks could be due to the presence of the organic stabilizer (diffraction peaks at low 2θ values). For higher particle size (Au¹), the presence of the ligand has no effect on the XRD diffractograms.

Catalytic Activity

The catalytic performance of Au^1/CNT_{P3} , Au^2/CNT_{P3} , Au^3/CNT_{P3} , Au/CNT_{L2} , and Au/CNT_N was evaluated for the preferential oxidation of CO in an H₂-rich stream.

Figure 7 shows the CO oxidation performance of the catalysts at constant gas velocity. Au¹/CNT_{P3} and Au/CNT_{L2} exhibited almost no catalytic activity toward CO oxidation. For Au¹/CN_{P3}, this is attributed to its large particle size. For Au/CNTL₂, in which AuNPs are mostly confined in the CNT cavity, it is difficult to predict the reactivity,^[6] and its low activity might be due to the combined effects of confinement and the low Au loading (1% w/w). In fact, the study of Au catalysts on different supports^[28] has confirmed that the catalytic activity of supported Au depends on the size of AuNPs^[2] and is influenced by the interaction between Au and the support.

 Au/CNT_N exhibited high catalytic activity and high stability; the catalytic performances remained unchanged after 48 h. It is thus established that CNT_N must play an essential



Figure 7. CO transformed (below) and selectivity to CO_2 among possible reactions of O_2 (above) versus temperature.

role in the high activity of AuNPs. CNT_N contains nitrogen in different forms including pyridinic, pyrrolic, and quaternary species, which improve the electronic density and the basicity of the carbon nanotubes. It was earlier shown that these nitrogen atoms act as an important promoter of Ru nanoparticles and increase their activity in the ammonia decomposition reaction.^[29] In this sense, modification of the electronic structure of CNTs to include electron-donor states near the conduction-band edge was reported for CNT_N synthesized by pyrolyzing ferrocene/melamine mixtures.^[30] Gong et al.^[31] have recently observed that the incorporation of electron-accepting nitrogen atoms appears to impart a relatively high positive-charge density. Dommele et al.^[32] demonstrated that nitrogen-containing carbon nanotubes display basic properties. For Au/CNT_N, even though the mean particle size is quite large (11 nm), it contains a significant population of AuNPs < 6 nm that could explain the high activity.

Finally, the results of the catalytic oxidation of CO from Au^2/CNT_{P3} are surprising in the light of the very small particle size measured for this sample. Indeed, it is known that very small gold nanoparticles are particularly active at low temperature for this reaction.^[2] This lack of reactivity is perhaps due to the presence of an organic stabilizer coating the gold particles. At higher temperatures, after thermal decomposition of this stabilizer, the NPs should start to become more active.

TEM images (Figure 8) obtained for Au²/CNT_{P3} after reaction provide evidence of the sintering process between neighboring NPs due to the thermal decomposition of the stabilizer during the reaction process. Interestingly, the sintering is more pronounced for AuNPs located inside CNT_{P3} than on their external surface. In the case of AuNPs on CNT_N, no sintering was observed after reaction.



Figure 8. TEM micrographs of Au^2/CNT_{P2} after reaction.

At room temperature, the selectivity of Au/CNT_N and Au/CNT_{L2} reached 100%. At higher temperatures, both conversion and selectivity decreased due to competition between CO and H₂ oxidation. In contrast to this behavior, the catalysts prepared with CNT_{P3} as support show higher conversion and selectivity at 420 K. Thus, the oxidation rate of H₂ is not independent of the support materials and the nature of the gold precursor. The organometallic precursors that contain long alkyl or alkoxy chains, which produce upon decomposition organic stabilizing species, yield catalysts that show higher CO selectivity at higher temperature.

Conclusions

Until now, the techniques used for depositing AuNPs on activated carbon or CNTs required tedious procedures, and only a few methods produce particles of uniform size. We have investigated three methods (impregnation, decomposition, and deposition–precipitation) to control the loading of gold NPs with a narrow particle-size distribution and to conveniently attach AuNPs onto the walls of CNTs. The use of preformed AuNPs with controlled surface leads to NPs confined inside the functionalized CNTs. This is an efficient method for the selective confinement in CNTs.

Our results also show that bamboo-like nitrogen-doped carbon nanotubes present interesting potential for the deposition of AuNPs by the deposition–precipitation method.^[33] Additionally, we have shown that CNTs doped with nitrogen are a promising support material for gold-catalyzed low-temperature CO oxidation. Finally, the competition between CO and H₂ oxidation depends on the nature of both the support and the gold precursor.

Experimental Section

Preparation of Carbon Nanotube Supports: The pristine multiwalled nanotubes CNT_p were obtained from Applied Science (Pyrograph III, 98% purity, 2% remaining iron catalysts), which were segmented $(0.1-1 \,\mu\text{m})$ by a ball-milling technique. Multiwalled nanotubes CNT_L (98% purity, 2% iron catalyst) were synthesized by chemical vapor deposition according to previously reported procedures.^[34] Nitrogen-doped nanotubes CNT_N have been produced in a fluidized bed reactor by catalytic chemical vapor deposition on Fe/SiO₂ catalysts from acetylene/ammonia mixtures at 1023 K;^[29] they present a bamboo-like structure with graphene layers perpendicular to the CNT axis. CNTP and CNTL were functionalized on the surface with carboxylic acids by nitric acid oxidation to yield CNT_{P2} and CNT_{L2}; according to reported procedures^[5] CNT_P were also functionalized with amide long-alkylchain-terminated groups. A typical preparation is as follows: carbon nanotubes functionalized on the surface with carboxylic acid groups (CNT_{P2}) were treated with thionyl chloride to produce the corresponding acetyl chloride derivative, and further treated with hexadecylamine (HDA), thereby giving rise to the amide surface groups of the carbon nanotubes (CNT_{P3}).

Gold Precursors: H[AuCl₄]·3H₂O was purchased from Sigma-Aldrich. Literature methods were used to prepare [AuCl(tht)]^[34] (tht = tetrahydrothiophene), $[HC \equiv CC_6H_4 - C_{14}H_{29}]$,^[35] $C \equiv NC_6H_4(4-C_{14}H_{29})$ OC_2H_5), $[Au(C \equiv C - C_6H_4 - C_8H_{17})(C \equiv N - C_6H_4 - O - C_{10}H_{21})]$ (Au²), and $[Au(C \equiv C - C_6H_4 - C_{10}H_{21})(C \equiv N - C_6H_4 - O - C_2H_5)]$ (Au³).^[24] $[Au(C \equiv C - C_6H_4 - C_{14}H_{29})(C \equiv N - C_6H_4 - O - C_2H_5)]$ (Au¹), not previously reported, was prepared as the analogous Au³, starting from $[HC = CC_6H_4 - C_{14}H_{29}]$. It was isolated as a white solid. Yield: 0.55 g, 84%. ¹H NMR (CDCl₃): δ = 7.45 (d, J = 8.7 Hz, 2 H, $C \equiv NC_6H_4O_{-}$), 7.40 (d, J = 7.9 Hz, 2 H, $C \equiv CC_6H_4$), 7.06 (d, J =7.9 Hz, 2 H, C=CC₆H₄), 6.94 (d, J = 8.7 Hz, 2 H, C=NC₆H₄O), 4.08 (c, J = 7.0 Hz, 2 H, C=NC₆H₄OCH₂-), 2.57 (t, J = 7.0 Hz, 2 H, C=CC₆H₄CH₂), 1.56 (m, 2 H, C=CC₆H₄CH₂CH₂), 1.44 (t, J =7.0 Hz, 3 H, C=NC₆H₄OCH₂CH₃), 1.26 (m, 24 H, acetylide alkyl chains), 0.89 [t, J = 6.6 Hz, 3 H, CH₃ (acetylide)] ppm. IR (KBr): $\tilde{v} = 2215 \text{ cm}^{-1} \text{ (C=N)}; \text{ (CH}_2\text{Cl}_2): \tilde{v} = 2214 \text{ cm}^{-1} \text{ (C=N)}.$ C31H42AuNO (641.65): calcd. C 58.03, H 6.60, N 2.18; found C 58.06, H 6.43, N 2.20. DSC/transition, K [kJmol⁻¹] (C = crystal phase; Sm = smectic phase; I = isotropic liquid): $C-C^1$, 352 (19.9); C1-C2, 364 (3.0); C2-SmA, 415 (32.8); SmA-I (dec.), 433 (microscopy data).

Synthesis of Preformed Gold Nanoparticles: Complex Au¹ (0.046 g, 0.072 mmol) was dissolved in toluene (6 mL), and the colorless solution was heated at 383 K for 14 h to give a red solution. Then the solvent was removed under vacuum to give a brown solid. IR (KBr): $\tilde{v} = 2195 \text{ cm}^{-1}$ (C=N).

Preparation of Supported Gold Catalysts: Three methods were used (see Table 3 and Scheme 1). **Method A (Impregnation Procedure, IP):** A red solution of AuNPs (obtained from 0.046 g of Au¹) in tetrahydrofuran (1 mL) was poured slowly into a flask that contained CNTs (0.05 g). The resulting pasty mixture was stirred for 30 min and then sonicated for a further 30 min. Both steps, stirring and subsequent sonication, were repeated three times. Then the mixture was stirred overnight and the solvent evaporated under vacuum. The sample prepared was labeled Au¹/CNT_{P3}. **Method B** (Decomposition Procedure, DC): A mixture of Auⁿ (n = 2, 3; 0.072 mmol) and CNT_{P3} (0.05 g) in tetrahydrofuran (1 mL) was successively stirred and sonicated as described in Method A. After 3 h of alternating stirring and ultrasonic treatment at room temperature, the mixture was stirred overnight and then dried at 373 K in air to give Auⁿ/CNT_{P3}. **Method C (Deposition Proceipitation Pro**

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cedure, DP): A solution of [HAuCl₄] in a mixture of water/methanol (15:1) was treated with an aqueous solution of Na₂CO₃ (0.2 M) until the pH reached 11. After stirring for 1 h, the solution was added to CNT_{L2} or CNT_N . After 4 h of alternating stirring and ultrasonic treatment at room temperature as described above, the precipitate was collected by filtration and washed with deionized water until no Cl⁻ was detected. The samples were dried at 373 K in air overnight; the corresponding catalysts were labeled Au/ CNT_{L2} and Au/ CNT_N .

Instrumentation and Measurements: The BET surface area of the support was measured from the nitrogen-adsorption isotherm with an ASAP instrument. TEM images were measured with a JOEL 1011 electron microscope operated at 110 kV. At least 200 particles were used to determinate the mean diameter of the Au-particle NPs. XRD patterns were obtained with a scanning Seifert XRD 3000P diffractometer. XPS analysis was performed with an ESCA-PROBE P (Omicron) spectrometer by using nonmonochromatized Mg-K radiation (1253.6 eV). IR spectra were recorded with a Perkin-Elmer FT BX instrument and ¹H NMR spectra (room temp., CDCl₃) with Bruker AC 300 or ARX 300 instruments. Combustion analyses and mesophase identification were made as reported elsewhere.^[36] The catalytic experiments for CO oxidation were carried out with a continuous-flow fixed-bed reactor with 0.05 g of catalyst {contact time (w/F) [w = weight (catalyst); F = flow rate (feed stream)] of 19 g_{cat}/hmol_{CO}}. The gas mixture consisted of 1% CO, 1% O₂, and 40% H₂ in He at 1×10^{-2} cm³ min⁻¹, and the products were analyzed by gas chromatography using a carboxen 1000 column. The selectivity and conversion values were calculated according to Equations (1) and (2), in which X and S are percentages of conversion and selectivity, respectively, and F is the inlet and outlet molar flow of the indicated gas.

$$X_{\rm CO} = (F_{\rm CO}^{\rm in} - F_{\rm CO}^{\rm out}/g_{\rm Au}) \tag{1}$$

$$S_{\rm CO_2} = [(F_{\rm CO}^{\rm in} - F_{\rm CO}^{\rm out})/2(F_{\rm O_2}^{\rm in} - F_{\rm O_2}^{\rm out})]100$$
(2)

Supporting Information (see footnote on the first page of this article): Thermogravimetric, XPS and XRD analyses of selected samples.

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