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Nanoparticle Catalysts

Gold Nanoparticles Embedded in a Mesoporous Carbon Nitride Stabilizer for Highly Efficient Three-Component Coupling Reaction**

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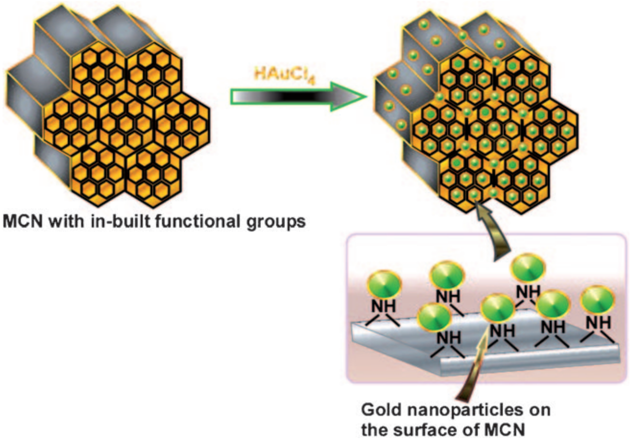
Metal nanoparticles have attracted much attention in the fields of catalysis, separation, magnetism, optoelectronics, and microelectronics owing to their unique physical and chemical properties.[1–7] However, the overall performance of these metal nanoparticles is dependent on the size, shape, crystal structure, and the textural parameters.[8] Several methods, including hydrogen reduction, porous support matrix, self-assembly, and surfactant-assisted processes, have been used for controlling the size and shape of the nanoparticles.[9–16] Among the methods used, the fabrication of the nanoparticles on the surfaces of porous supports with high surface area, in particular mesoporous matrixes, and various pore diameters and structures is quite attractive as these systems offer well-ordered pores with controllable size, high surface area, and large pore volume.[17] The ordered mesopores dictate the size and shape of the nanoparticles as they are formed in the confined matrix, and the high surface area and large pore volume help the formation of a high degree of homogeneously dispersed nanoparticles on the surface of the support. Although the size of the nanoparticle can be controlled by a mesoporous support strategy, stabilization and reduction of the particles on the porous surface after their formation is quite challenging.

Generally, organic functional groups anchored or grafted on the surface of a porous matrix are used for the stabilization and reduction of the nanoparticles.[11] However, functionalization of the mesoporous support involves multiple steps, which is a time-consuming process, may poison the catalytic active sites of the support and the particles, and can sometimes even damage the structure and the textural properties of the supports. Thus, it is highly imperative to look for an alternative mesoporous support with inbuilt functional groups and excellent textural characteristics for the fabrication of highly stable nanoparticles. Recently, Vinu et al.[18] reported the synthesis of mesoporous carbon nitride (MCN) with ordered pores and controlled textual parameters through a simple polymerization reaction between carbon tetrachloride and ethylenediamine by using SBA-15 as a sacrificial template; MCN has inbuilt -NH_2 and -NH groups on the mesoporous walls which can provide a platform for the generation of metal and metal oxide nanostructures. Herein, we demonstrate for the first time the fabrication of highly dispersed Au nanoparticles with a size of less than 7 nm on the the inner surface of an MCN support, which acts as stabilizing, size-controlling, and reducing agent without the need for any external agent or surface modification (Scheme 1). We also demonstrate that the Au nanoparticles embedded in MCN are a highly active, selective, and recyclable catalyst in the three-component coupling reaction of benzaldehyde, piperidine, and phenyl acetylene for the synthesis of propargylamine, which is an intermediate for the construction of nitrogen-containing biologically active molecules and for the synthesis of polyfunctional amino derivatives.[19]



Scheme 1. Encapsulation of gold nanoparticles over MCN with in-built functional groups without any external stabilizing agent.

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The fabrication of nanosized gold nanoparticles on the mesoporous surface of a carbon nitride matrix without any stabilizing agent is shown in Scheme 1. The mesopore-directed growth of Au nanoparticles with the help of a support with inbuilt groups as a stabilizing agent is unique in controlling the size and shape and avoiding agglomeration of the nanoparticles. As can be seen in Scheme 1, auric chloride ions were adsorbed within the pores of MCN by means of sonication. The mesopores of the carbon nitride control the size of the Au nanoparticles as they grow within the restricted environment of the pore channels, and inbuilt functional groups such as NH_2 or NH groups present on the wall structure of the carbon nitride act as a stabilizing agent by providing an anchoring and heterogeneous surface and allow the formation of highly dispersed Au nanoparticles without any agglomeration. The presence of functional amine groups on the MCNs helps the reduction of the Au nanoparticles inside the mesopores. The reduction of chloro auric salt is further enhanced by the addition of a small amount of reducing agent.

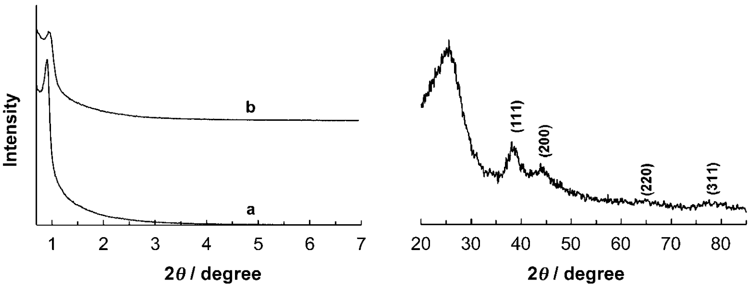


Figure 1. Left: powder XRD patterns of: a) pure MCN and b) Au nanoparticle encapsulated MCN. Right: wide-angle powder XRD pattern of Au nanoparticle encapsulated MCN.

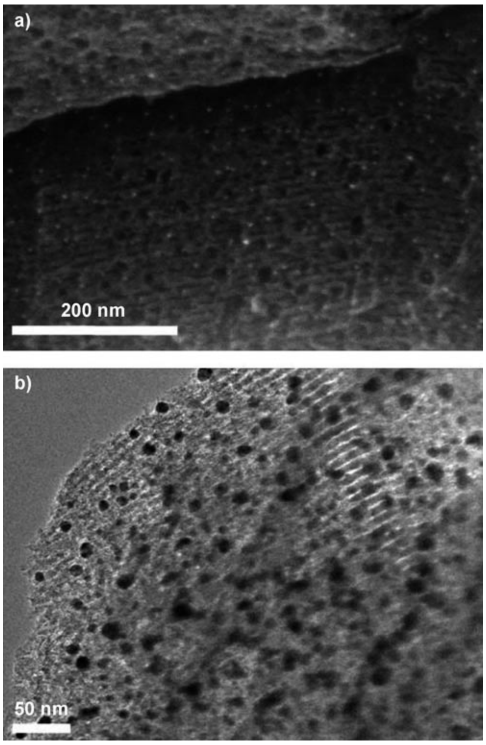


Figure 2. a) FE-HRSEM and b) HRTEM images of Au nanoparticle encapsulated MCN.

The material was characterized by powder XRD measurements to check the structure of the MCN before and after the encapsulation of Au nanoparticles. Figure 1 shows the lower-angle powder XRD pattern of MCN before and after the incorporation of Au nanoparticles. Both samples show a sharp peak at lower angle, indicating that the hexagonally ordered porous structure of the MCN remains intact even after the encapsulation and stabilization of Au nanoparticles. A significant decrease in the intensity of the lower-angle peak was observed for MCN loaded with Au nanoparticles. This result can be attributed to filling of the pores with Au nanoparticles, which are formed along the channels of the carbon nitride, confirming that Au nanoparticles are indeed formed inside the nanochannels of the carbon nitride.[20] The unit cell constant of the sample before and after the encapsulation of Au nanoparticles remains almost the same. The wide-angle X-ray diffraction pattern of Au nanoparticle loaded MCN exhibits four peaks, which could be indexed as the (111), (200), (220), and (311) reflections of the face-centered-cubic structure of crystalline Au^0 (Figure 1, right). Among the peaks observed, the intensity of the (111) peak is the highest, indicating that (111) plane was the predominant crystal facet. The peaks are very broad and weak, suggesting the formation of ultrasmall nanocrystalline Au particles inside the pore channels of carbon nitride. The absence of large and intense peaks at higher angles further confirms that no large particles were formed on the external surface of the support. These results reveal the pore-size-controlled growth of the nanoparticle in the confined matrix.

The structure and morphology of the Au nanoparticles inside MCN were examined by scanning electron microscopy (Figure 2a). White colored dots, which correspond to the gold nanoparticles, are uniformly distributed and anchored along the heterogeneous mesoporous surface of the rodlike particles of carbon nitride with the inbuilt functional groups (Figure 2a). All the particles are uniform in size and shape and densely packed inside the nanochannels of carbon nitride. No agglomeration of the Au nanoparticles was observed in the HRSEM image, revealing that the inbuilt functional groups in the MCN firmly anchor the formed nanoparticles. The size of the particles obtained from the HRSEM image was approximately 7 nm, which is similar to the size of the pore diameter of MCN.

An HRTEM image of Au nanoparticle encapsulated MCN is shown in Figure 2b. A regular arrangement of dark spherical spots, which correspond to Au nanoparticles, is clearly observed along the nanochannels of the support. Interestingly, a linear arrangement of mesochannels, which are arranged in regular intervals, is also clearly seen, suggesting that the mesostructure of the support is stable even after the formation of Au nanoparticles. The average size of the Au nanoparticles obtained from the HRTEM image was approximately 7 nm, which is quite consistent with the data obtained from the HRSEM image. It should be noted that the size of the particles that are formed on the external surface of the support, as seen in the HREM image and anchored by the terminal functional groups, is slightly larger than that of the particles formed inside the mesochannels. Figure 3 shows the energy-dispersive X-ray (EDX) pattern and the elemental mapping of the Au nanoparticles encapsulated on the MCN. Peaks for the elements C, N, and Au are clearly seen in the EDX spectrum. There is no peak for Cl in the EDX spectrum, indicating the high purity of the Au nanoparticles. The amount of Au present in the sample is 0.05 at.%, which matches well with results from inductively coupled plasma mass spectrometry (ICP-MS) analysis. Elemental mapping reveals that the Au atoms are uniformly distributed in the samples, and no trace of agglomeration is found in the sample (Figure 3, inset).

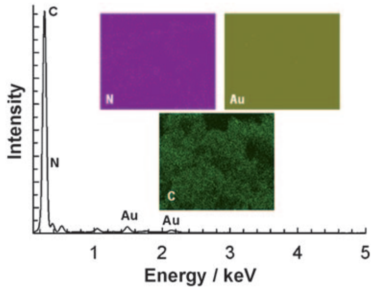


Figure 3. EDX pattern of Au nanoparticle encapsulated MCN. The inset shows the elemental mapping of the same sample.

The encapsulation of the Au nanoparticles over the mesochannels of the MCN stabilizer has made a significant change in the textural parameters of the materials. Figure 4 shows the nitrogen adsorption–desorption isotherms of the MCN before and after the encapsulation of the Au nanoparticles. The isotherms of both samples are of type IV with an H1 hysteresis loop, which are typically observed for mesoporous materials. The pore size distributions for the two samples reveal that the pores are highly ordered and have a narrow pore size distribution (not shown). In addition, the shape of the isotherm and the hysteresis loop of the two samples are almost identical. These results reveal that the highly ordered structure is maintained even after the encapsulation of Au nanoparticles. A small change in the specific surface area and the specific pore volume of the sample after Au encapsulation is observed. The specific surface area was found to decrease from 580 $m^2 g^{-1}$ for pure MCN to 508 $m^2 g^{-1}$ for Au nanoparticle encapsulated MCN, and the specific pore volume decreases from 0.74 to 0.63 $cm^3 g^{-1}$ for the same samples. This result could be mainly due to the formation of the nanoparticles inside the pores. The absence of an abrupt change in the pore volume and surface area of the support after Au encapsulation further confirms that pores of the support are not blocked by Au particles larger than the pore size of the support, revealing that the inbuilt basic sites or groups on the support materials do not allow the agglomeration or migration of the nanoparticles but instead stabilize or anchor them on the pore wall structure. However, the size of the nitrogen adsorbate molecule is small enough to penetrate inside the pore channels of the support encapsulated with the metal nanoparticles through the microporous channels connected between the primary mesopores of the support. Thus, it is also possible that the reduction of the textural parameters of the support may originate from blockage caused by the encapsulated nanoparticles with sizes similar to that of the pore size of the support.

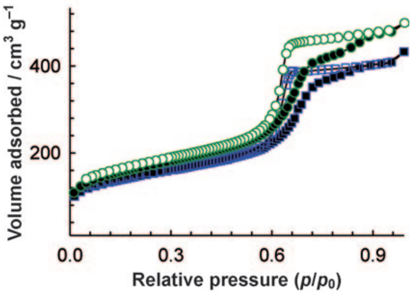


Figure 4. Nitrogen adsorption–desorption isotherms of (●) pure MCN and (■) Au nanoparticle encapsulated MCN.

To clarify the stabilizing role of the inbuilt amine or basic sites, we conducted a control experiment with pure mesoporous carbon without any nitrogen atoms in the wall structure. Mesoporous carbon CMK-150 with a pore size of 6.5 nm was used as the support for the encapsulation of the Au nanoparticles. A series of Au nanoparticles with sizes ranging from 20 to 140 nm (see the Supporting Information), which in turn are made of smaller Au nanoparticle units, was formed. Most of the particles were formed on the external surface of the mesoporous carbon but not inside the mesoporous channels owing to agglomeration. These results reveal the vital role of nitrogen in the MCN matrix in preventing the aggregation of nanoparticles and stabilizing the formed nanoparticles inside the mesoporous channels (Scheme 1).

The synthesis of propargylamines has received much attention in modern pharmaceutical, biological, and synthetic chemistry, as they are synthetically versatile key intermediates for the preparation of biologically active compounds and drugs.[19] Propargylamines are generally prepared by a three-component coupling reaction of an aldehyde, an alkyne, and an amine, commonly called A^3 coupling, by using strong bases such as butyllithium, organomagnesium reagents, or lithium diisopropylamide (LDA) and exploiting the relatively high acidity of the terminal acetylene to form alkynyl metal compounds.[21] However, this process becomes less attractive because of the need of stoichiometric quantities of the reagents and their high sensitivity to moisture. Recently, metal nanoparticles, especially gold nanoparticles, have been exploited to activate the C−H bond of the terminal alkyne and offer high surface to volume ratio.[22] However, metal nanoparticles in their pure form tend to agglomerate, which limits their efficiency in the catalytic process.

Herein, we used for the first time highly dispersed Au nanoparticles encapsulated over MCN (Au-MCN) stabilizer as the catalyst for the synthesis of propargylamines by an A^3 coupling reaction. The catalytic efficiency of Au-MCN was tested in the three-component coupling of aldehyde, amine, and alkyne. Initially, benzaldehyde, piperidine, and phenylacetylene were mixed with CN-Au-150 (20 mg) in toluene. Although the reaction proceeded smoothly in toluene at 100 °C, a low yield of the product was obtained even after 24 h. Interestingly, the yield of the final product increases significantly with increasing loading of the catalyst from 20 to 50 mg. Hence, further experiments were carried out with a catalyst weight of 50 mg for the treatment of benzaldehyde, piperidine, and phenyl acetylene. The reaction was completed in 24 h with a yield of the final product of almost 96 %, as analyzed by gas chromatography. These results prompted us to study the substituent effects on the aromatic ring. Interestingly, electron-deficient aromatic aldehydes such as *p*-nitrobenzaldehyde also gave reasonable conversion under similar conditions. Even halo-substituted benzaldehydes, for example, *p*-chlorobenzaldehyde, furnished the desired product in good yield. The results are summarized in Table 1. No conversion was found in the absence of catalyst or by using only pure MCN catalyst under identical conditions. These results clearly indicate the importance of the encapsulation of the Au nanoparticles inside the mesochannels of the MCN stabilizer.

Table 1: Catalytic activity of Au nanoparticle encapsulated MCN in the A^3 coupling reaction for the synthesis of propargylamines.

Substrate	Conversion [%]		Selectivity [%]	
	12 h	24 h	12 h	24 h
benzaldehyde	63.8	96.2	79.2	64.4
p-nitrobenzaldehyde	40.7	55.6	70.3	76.7
p-chlorobenzaldehyde	25.5	35.7	47.3	60.0

In conclusion, we have demonstrated a simple approach for the encapsulation of Au nanoparticles over highly ordered MCN with inbuilt functionalities that acts as a stabilizing, reducing, and pore-size-controlling agent without addition of any external agent or surface modification of the wall structure of the support. The ultrasmall Au nanoparticles are highly dispersed and anchored firmly on the functional moieties in the surface of the MCN, which helps the formation of the particle by an in situ reduction process as well as avoids the agglomeration of the particle on the porous surface. We also demonstrated that the Au nanoparticle encapsulated MCN can be used as a highly active, selective, and recyclable heterogeneous catalyst for coupling benzaldehyde, piperidine, and phenylacetylene for the synthesis of propargylamine. This method is quite simple and the strategy can be extended for the fabrication of various other metal and metal oxide nanoparticles over MCN with different structure and pore diameters, which could have many potential applications in separation, hydrogen storage, drug delivery, electrode materials for fuel cells, and catalytic organic transformations.

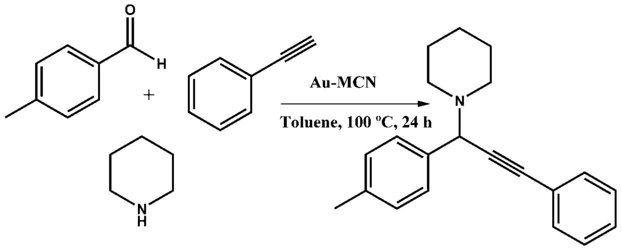
Experimental Section

Preparation of MCN: MCN material was prepared by the following method. In a typical synthesis, calcined SBA-15-150 (0.5 g),[18] prepared at a synthesis temperature of 150 °C, was added to a mixture of ethylenediamine (1.35 g) and carbon tetrachloride (3 g). The resultant mixture was heated at reflux with stirring at 90 °C for 6 h. The obtained dark-brown solid mixture was placed in a drying oven for 12 h and then ground into a fine powder. The template carbon nitride polymer composites were then heat treated in a nitrogen flow of 50 mL per minute at 600 °C for 5 h with a heating rate of 3.0 °C per minute and kept under these conditions for 5 h to carbonize the polymer. The MCN was recovered after dissolution of the silica framework in 5 wt % hydrofluoric acid, filtration, several washings with ethanol, and drying at 100 °C.

Preparation of Au nanoparticles within MCN: $HAuCl_4$ was used as a metallic salt precursor for the preparation of Au nanoparticles. Typically, MCN (20 mg) was dispersed in water (2 mL) by mild sonication for 2 min. $HAuCl_4$ solution (1.5 mL; 2 mM) and then $NaBH_4$ (1 mL; 0.1 M) were added to this suspension. The obtained mixture was washed thoroughly with distilled water and finally dried in a vacuum oven at 60 °C.

Control experiment with mesoporous carbon: CMK-3 150 (20 mg) was added to a sample vial along with distilled water (2 mL) under sonication for 5 min. $HAuCl_4$ solution (1.5 mL; 2 mM) and then $NaBH_4$ (1 mL; 0.1M) were added to this suspension. The obtained mixture was washed thoroughly with distilled water and finally dried in a vacuum oven at 60 °C.

Catalysis with Au nanoparticle encapsulated MCN (A^3 coupling reaction): In a typical experiment, Au nanoparticle encapsulated MCN (50 mg) was added to a mixture of aldehyde (1 mmol), amine (1.2 mmol), and alkyne (1.3 mmol) in toluene (2.0 mL). The resulting mixture was allowed to stir in toluene at 100 °C over a period of 12–24 h (Scheme 2). After complete disappearance of aldehyde as monitored by TLC, the mixture was diluted with toluene and centrifuged to obtain a clear solution, which was analyzed by GC. The desired product was isolated by silica gel column chromatography using a gradient mixture of ethyl acetate/*n*-hexanes (1:9) as eluent. The product thus obtained was characterized by ^1H NMR spectroscopy.



Scheme 2. Catalytic activity of Au nanoparticle encapsulated MCN in the three-component coupling reaction of benzaldehyde, piperidine, and phenylacetylene for the synthesis of propargylamine.

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Keywords: heterogeneous catalysis · nanoparticles · mesoporous materials · nitrides

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