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Photoactive bimetallic framework for direct aminoformylation of nitroarenes

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A bimetallic catalyst, AgPd@g-C_3N_4, synthesized by reducing silver and palladium salts over the graphitic carbon nitride (g-C_3N_4), performs concerted reductive formylation of aromatic nitro compounds under photo-chemical conditions using formic acid which serves the dual role as hydrogen source and formylating agent.

Introduction:

The synthesis of amines and their conversion to *N*-formyl derivatives is an important reaction in organic synthesis due to its extensive application in natural product synthesis and drug discovery.[1] Conventionally, amino-formyl derivatives have been synthesized from nitro compounds in two separate steps involving nitro reduction followed by *N*-formylation.[2] Most of the earlier developed processes in the reduction of nitro group use stoichiometric amount of reagents. The heightened awareness surrounding climate change and the growing importance of pollution prevention have resulted in the dramatic shift to use catalytic reagents instead. In general, the catalytic variant developed for the reduction of nitro compounds often requires high hydrogen pressure and elevated temperature; [3] safety being a worrisome concern for high pressure hydrogenation on industrial scale. Alternative protocols have been advanced by employing *in-situ* generated hydrogen along with a precious metal catalyst. Most of these procedures require vigorous stirring in aqueous media under a carbon monoxide atmosphere; [4] a hazardous and toxic contaminant. Formic acid, available from biomass resources, has been introduced as a safer alternative for the transfer hydrogenation of nitro compounds to generate aryl amines.[5] The formylation of amine has to be carried out subsequently in a separate step. Rutile-supported gold catalyst has achieved such direct conversion of nitro compounds to *N*-formylamines.[6] However, this reaction is temperature dependent. At elevated temperatures, it leads to the formation of *N, N*-demethylation whereas slight variation towards lower side (~ 60 °C) doesn't allow the formylation of reduced products.[7] In addition, it requires an inert atmosphere along with the use of organic solvents. Magnetically retrievable palladium catalyst has also been used for the conversion of nitro-arenes to the corresponding *N*-formyl derivatives; complexity of the catalyst preparation and its higher loading are the main limitations of this method. [8] Iron metal in combination with corresponding carboxylic acid has been introduced but the lower product yields and heating over extended period of time renders this an unproductive and tedious method.[9] This prompted us to develop a simple and sustainable catalyst which can accomplish this transformation in aqueous media under ambient conditions. In continuation of our ongoing efforts to develop sustainable methods[10] that aim for reduction in chemical waste generation, [11] we have designed a bimetallic AgPd@g-C_3N_4 photoactive heterogeneous catalyst system for the direct transformation of aromatic nitro compounds to *N*-formylamines.

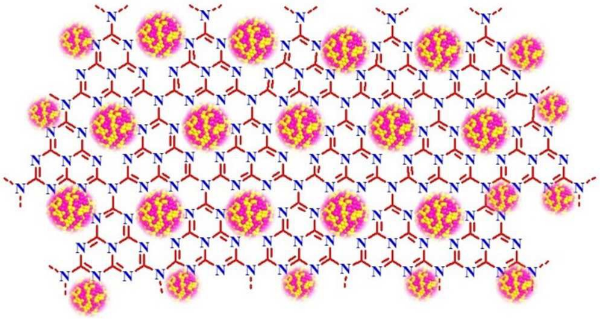

Figure 1 Structure of AgPd@g-C_3N_4

Synthesis and characterization

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See

Graphitic carbon nitride (g-C_3N_4) was synthesized by heating urea in a furnace at 500 °C and the ensuing pale yellow solid was dispersed in water by sonicating over a period of 15 mins.[12] The silver and palladium salts ($AgNO_3$ and $Pd(NO_3)_2$) were sequentially added and the reaction mixture was stirred for 12 hours. The reaction temperature was raised to 50 °C and the silver and palladium salts were reduced to Ag(0) and Pd(0) nanoparticles using excess of sodium borohydride ($NaBH_4$). The reaction temperature was cooled to ambient temperature, centrifuged and the solid was washed with methanol and vacuum dried at 50 °C. The AgPd@g-C_3N_4 catalyst (Figure 1) was isolated as a fine solid powder.

The catalyst was characterized using transmission electron microscopy, scanning electron microscope, X-ray photoelectron spectroscopy, X-ray diffraction and Inductive coupled plasma atomic emission spectroscopy (ICP-AES).

TEM spectra of the catalyst endorse the formation of single phase silver and palladium nanoparticles with spherical morphology (Figure 2). The SEM image of AgPd@g-C_3N_4 and its EDX confirm the immobilization of silver (Ag) and palladium (Pd) nanoparticles over the surface of g-C_3N_4 (Figure 3). The concentration of Ag (4.67%) and Pd (4.55%) were found using ICP-AES analysis. The XPS (Figure 4) analysis of AgPd@g-C_3N_4 corroborated the formation of palladium and silver nanoparticles on the surface of graphitic carbon nitride (Figure 3) which was further supported by XRD (Figure 5).

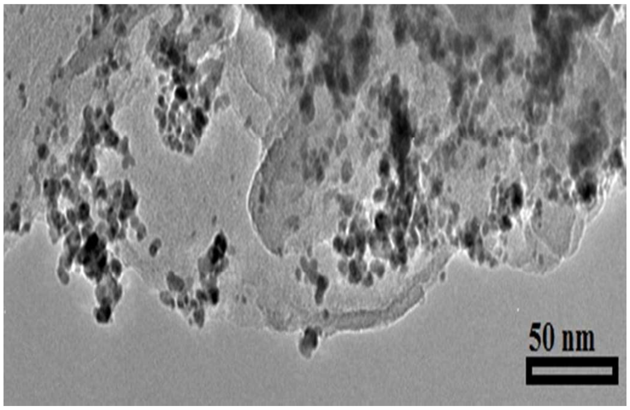


Figure 2 TEM image of AgPd@g-C_3N_4 catalyst

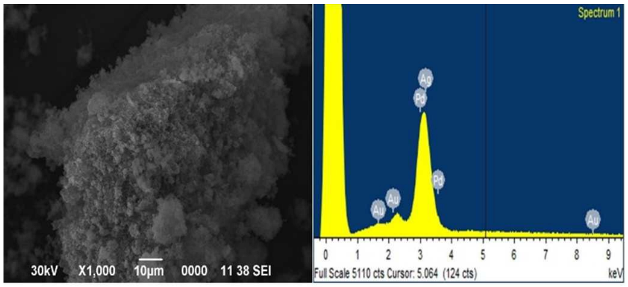


Figure 3 SEM and EDX data of AgPd@g-C_3N_4 catalyst

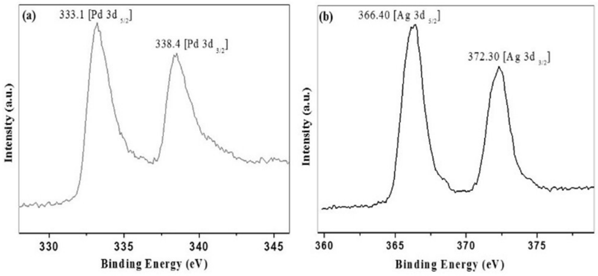


Figure 4 XPS spectra of AgPd@g-C_3N_4; a) Pd 3d XPS spectra; b) Ag 3d XPS spectra

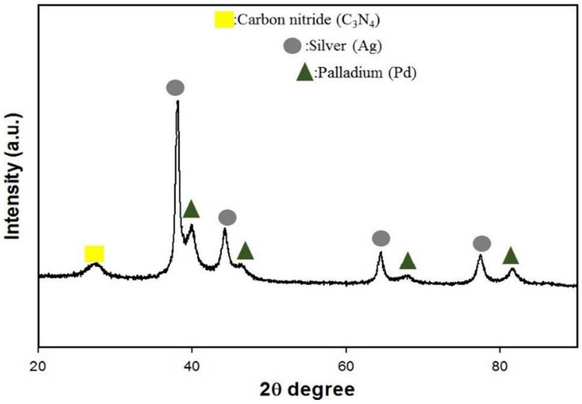


Figure 5 XRD spectra of AgPd@g-C_3N_4 catalyst

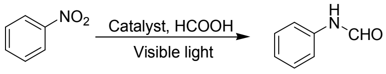
Result and discussion

The most important step in the development of the active catalyst was the design and synthesis of catalytic system for the direct conversion of nitro compounds to *N*-formylamine derivatives, preferably using visible light to derive this reaction. In view of the known prowess of graphitic carbon nitride (g-C_3N_4) as a photo active support,[13] we pursued this approach using formic acid as the reducing as well as a formylating agent in presence of bimetallic catalyst.

First, Pd (10 mol %) was immobilized on g-C_3N_4 and tested for the aqueous reductive formylation of the nitro group using formic acid as an hydrogen source; the formation of 47% of desired product after 12 hours of exposure to visible light (Table, entry 1) was encouraging. Increasing palladium load (Table 1, entry 2) did not improve catalytic activity whereas low-loading decreased the yield to 30% (Table 1, entry 3).These results suggested that the Pd@g-C_3N_4 was not sufficiently active to accomplish this transformation. We sought to enhance its activity by adding a catalytic promoter, preferably an abundant material such as copper. Consequently, copper-palladium CuPd@g-C_3N_4 catalysts were synthesized and used which afforded higher yields (65%) of the desired product (Table 1, entry 4). Various amounts of copper and palladium loadings were next examined (Table 1, entries 5-6). The CuPd@g-C_3N_4 catalyst with 10% Cu and 5% Pd (Table 1, entry 5) gave the desired product in 55% yield, whereas CuPd@g-C_3N_4 catalyst with 5% Cu and 10% Pd gave 69% of product. A recent report on the use of Ag-Pd system on an ultrathin support, [14] encouraged us to explore the use of silver as co-catalyst partner, and therefore we synthesized AgPd@g-C_3N_4 framework. The reaction of nitrobenzene with formic acid in the presence of bimetallic AgPd@g-C_3N_4 gave a quantitative yield of N-formyl aniline (Table 1, entry 7, 2 h). The variation in Ag and Pd concentration in the catalyst played a crucial role in the reductive formylation of the nitro group. The catalyst with 10% Ag and 5% Pd loading required 5 h for the completion of reaction (Table 1, entry 8). On the other hand, the catalyst system comprising 5% Ag and 10% Pd gave a quantitative yield of the desired product within 2 h (Table 1, entry 9). Further reduction in silver concentration led to an increase in reaction time and decrease in the product yield (Table 1, entry 10). The reaction with silver alone, Ag@g-C_3N_4, did not show any evidence of reductive formylation product even after 24 hours (Table 1, entry 11).

After establishing the ideal reaction conditions for the catalyst, it was imperative to evaluate the performance of AgPd@g-C_3N_4 with a wide variety of substrates. Accordingly, an array of nitro derivatives were subjected to reductive formylation reaction (Table 2, entries 1-9); all the substrates bearing electron donating (Table 2, entries 2-3) and electron withdrawing substituents (Table 2, entries 4-9) were converted to the corresponding amino formyl derivatives. It was difficult to corroborate the reactivity pattern in line with the nature of the substituents and electronic behavior as most of the reactions were completed within 2 hours.

Tabele 1 Screening of catalysts for *N*-formylation

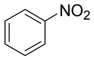
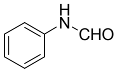
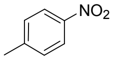
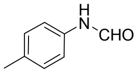
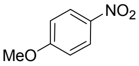
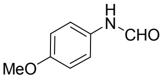
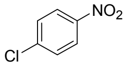
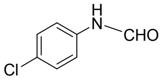
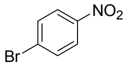
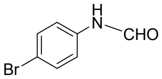
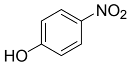
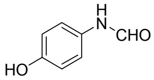
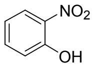
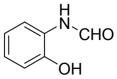
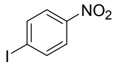
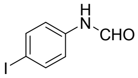
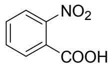
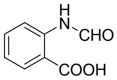
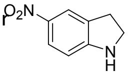
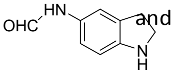
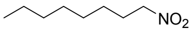


Entry	Catalyst	Time	Yield[a, b]
1	Pd@g-C_3N_4 (10% Pd)	12 h	48 %
2	Pd@g-C_3N_4 (20% Pd)	12 h	49%
3	Pd@g-C_3N_4 (5% Pd)	12 h	31%
4	CuPd@g-C_3N_4 (10%Cu : 10% Pd)	12 h	65 %
5	CuPd@g-C_3N_4 (10%Cu : 5% Pd)	12 h	55 %
6	CuPd@g-C_3N_4 (5%Cu : 10% Pd)	12 h	69 %
7	AgPd@g-C_3N_4 (10%Ag : 10% Pd)	2 h	99 %
8	AgPd@g-C_3N_4 (10%Ag : 5% Pd)	5 h	88 %
9	AgPd@g-C_3N_4 (5%Ag : 10% Pd)	2 h	99 %
10	AgPd@g-C_3N_4 (2%Ag : 10% Pd)	5 h	85 %
11	Ag@g-C_3N_4 (10% Ag)	24 h	-

a) Reaction conditions: 1 mmol of nitrobenzene; Formic acid (2 mmol); Water (1.0 mL); Catalyst (25 mg); 40 watt domestic bulb; b) Isolated yield

The recyclability of the catalyst in terms of practical and sustainable use were established using recycling experiments for the reductive formylation of nitrobenzene. After the completion of the first reaction, AgPd@g-C_3N_4 was recovered and reused for the reductive formylation of fresh batch of nitrobenzene. AgPd@g-C_3N_4 was found to be stable and could be reused several times without losing its activity (ESI, S2); even after 6th cycle, the nitrobenzene was efficiently converted into *N*-formyl aniline. The reactivity and stability of the catalyst could be attributed to the graphitic carbon nitride (g-C_3N_4) which holds Ag and Pd nanoparticles tightly. The metal leaching in the AgPd@g-C_3N_4 catalyst was studied using ICP-AES analysis of the reaction solvent and the recycled catalyst before and after the reaction. The absence of metals in the mother liquor and the percentage of Ag (4.65%) and Pd (4.54%) in recycled catalyst confirmed that g-C_3N_4 holds the metals tightly. The trifling metal leaching may be attributed to high porosity and polarity of the g-C_3N_4 support which holds these metals *via* non-covalent interactions.

Table 2 *N*-formylation of nitroarenes catalyzed by AgPd@g-C_3N_4 [a]

Entry	Reactant	Product	Time	Yield[b]
1			2h	99 %
2			2h	98 %
3			2h	96 %
4			2h	97 %
5			2h	97 %
6			2h	97 %
7			2h	96%
8			2h	97 %
9			2h	96 %
10			3h	76 %
11		-	12h	-

a) Reaction conditions: Nitroarenes (1 mmol); Formic acid (2 mmol); Water (1.0 mL); Catalyst (25 mg); 40 watt domestic bulb; b) Isolated yield

Conclusions

The silver and palladium were immobilized by reducing their salt forms over g-C_3N_4 (graphitic carbon nitride) surface. The synthesized AgPd@g-C_3N_4 catalyst was used for the direct amino formylation of aromatic nitro group under photo chemical condition using visible light as a source of energy and formic acid as a reducing as well as formylating agent. The bimetallic catalyst is highly effective in decomposing formic acid into hydrogen and using it as a formylating agent in a concerted process.

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Disclaimer

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