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The graphical abstract for

"Deoxygenative coupling of nitroarenes to synthesize aromatic azo compounds with CO using supported gold catalysts"

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A simple ligand- and additive-free gold catalyst system that enables the CO-mediated reductive coupling of nitroarenes has been identified.

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COMMUNICATION

Deoxygenative coupling of nitroarenes to synthesize aromatic azo compounds with CO using supported gold catalysts †

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A facile and efficient catalytic system based on mesostructured ceria-supported gold (Au/meso-CeO₂) catalyst was developed for the synthesis of various aromatic azo compounds by reductive coupling of the corresponding nitroaromatics, using ¹⁰ CO as the sole deoxygenative reagent, under additive-free and mild reaction conditions.

Azo compounds constitute one of the largest classes of industrially synthesized organic compounds and are important intermediates for dyes, food additives, radical reaction initiators, and ¹⁵ therapeutic agents because of their widespread and diverse biological activities.¹ Especially, those with aromatic substituents are known to serve as useful precursors to various products that have found numerous applications in material science.² Despite many known methods,³ there is an ongoing interest in ²⁰ the development of convenient and general protocols for the

- synthesis of these compounds. Hence, novel approaches such as copper-catalyzed oxidation of aromatic amines and a two-step, one-pot conversion of nitro compounds via the intermediacy of the corresponding anilines have been recently developed.⁴ Des-
- ²⁵ pite all these achievements, the direct reductive coupling of readily available nitroarenes represents the most straightforward route to this class of compounds. In this resgard, H₂ gas is undoubtly one of the most attractive and popular means to effect reduction, thereby leading to a number of catalytic hydrogena-
- ³⁰ tive coupling procedures of nitroarenes.⁵ However, it should be noted that the use of H_2 is not perfectly atom-economical as it might seem, given that current industrial production of H_2 relies overwhelmingly on fossil fuels and the fact the associated emissions have led to a net increase in atmosphere CO₂ levels.⁶
- ³⁵ Moreover, the necessity of special handling of highly flammable H_2 gas and/or the requirement of external base additives to achieve an acceptable level of selectivity have diminished the ultimate appeal and utility of these procedures.

So far, much less attention has been paid to the direct reduc-40 tive coupling of nitroarenes to give azo compounds by exploi-

- ting carbon monoxide (CO) as an effective reagent. As one of the cheapest C_1 sources in the chemical industry, CO is now heavily used in a number of highly selective syntheses of a wide range of chemicals and fuels.⁷ Aside from being a very useful
- ⁴⁵ C₁ building block, CO is also known to act as a reductant.⁸ The use of CO instead of hydrogen gas or other hydrogen donar agents is particularly interesting in light of the fact that CO is

produced in multiton quantities as a byproduct of the steel industry and thus represents an abundant source for chemical reduc-

- ⁵⁰ tion. ^{9,10} However, most of such reductions proceed by the water- gas shift reaction (CO + $H_2O = H_2 + CO_2$) and therefore utilize hydrogen as the terminal reductant.¹¹ While conceptually more attractive in the context of without using an external hydrogen source, the potential of using CO as the sole reductant ⁵⁵ to obtain aromatic azo compounds from corresponding nitroar-
- enes remains largely unexplored. In an early research on the interaction of CO with nitrocompounds in the absence of a catalyst, the conversion of nitroarenes into azo derivatives with yields up to 97.5% was achievable, but an exceptionally high
- ⁶⁰ CO pressure (3000 atm) was required.¹² A subsequent followup study in the 1960s showed that the reductive coupling of nitroarenes can take place in anhydrous benzene at 200 °C and a CO pressure of 200 atm by employing Fe(CO)₅ as the catalyst.¹³ However, this system is not adequately effective and not very ⁶⁵ selective since only moderate yields of the corresponding azo derivatives in the range of 40-80% can be attained.

There is considerable current interest in developing more benign organic synthesis facilitated by supported gold nanoparticles (NPs), which have emerged over the last decade as a pro-70 mising new class of green catalytic materials to meet the everincreasing demand for clean and resource-efficient chemical synthesis.¹⁴ As part of our continuing investigation into reduction chemistry by supported Au NPs, we recently reported the outstanding catalytic ability of Au NPs for the deoxygenation 75 of nitroaromatics to anilines as well as epoxides to their corresponding olefin compounds using CO/H2O as a reducing reagent.^{11b,11e} In such deoxygenation, a Au-hydride species was generated in situ from the reaction of H₂O with CO, which led to the highly chemoselective reduction. Being aware of the advan-⁸⁰ tages of adopting the Au-based deoxygenation protocols and also utilizing the excellent catalytic activity of supported gold toward CO activation and related transformations,¹⁴ we envisaged that the selective deoxygenation of nitroaromatics accompanied by the formation of the azo linkage in the reduced prod-85 ucts would be plausible via gold-catalyzed deoxygenative couplings under CO atmosphere and anhydrous conditions.

Herein we report the first demonstration of the efficient catalytic reductive coupling of nitroarenes under mild CO pressures, facilitated by a Au catalyst supported on mesostructured CeO₂ 90 (meso-CeO₂) featuring high redox capacities. The present cataChemComm Accepted Manuscript

lytic system is highly effective in that turnover numbers (TONs) of up to ~ 2000 can be achieved, and is workable on a large scale. Even under atmospheric conditions, the catalytic activity of the meso-CeO₂ supported Au is much greater than those of $\frac{12}{3}$

- ⁵ previously reported systems requiring high CO pressures.¹³ In addition, this new process works under mild conditions and enables the selective deoxygenative coupling of a wide range of functionalized nitroarenes while leaving other reducible or thermally labile functional groups intact.
- To assess the viability of the proposed reaction, we first explored the conversion of nitrobenzene (1a) under mild processing conditions, i.e., 5 atm of CO pressure in toluene at 150 °C. We initially examined the reduction of 1a over a benchmark Au/TiO₂ catalyst (average Au particle size ~ 2.8 nm, Figure 15 S1a), which has been widely studied and proven to be highly active for a large variety of functional group transformations.^{11b}, ^{11e-11g} It is not surprising that aniline (4a) formation competes
- with the desired reductive coupling in standard nondry toluene solvent (Table 1, entry 1). However, the use of freshly distilled toluene minimises the formation of **4a** (entry 2), appreciable formation of azobenzene (**2a**) and azoxybenzene (**3a**) with the overall yield being a modest 25% can be attained. This result was encouraging and led us to further examine a series of gold
- deposited on other mineral supports such as Fe₂O₃, Al₂O₃, ZnO,
 ²⁵ ZrO₂ and hydrotalcite (HT, layered double Mg-Al hydroxide). These catalysts, however, were not found to be particularly active, and in most cases the unwanted **3a** being obained predominantly (entries 3-7). Interestingly, when applying a commercial ultrafine ceria (Evonik Adnano 50) supported gold ³⁰ catalyst (Au/CeO₂-50, average Au particle size ~3.3 nm, Figure S1b), appreciable levels of reductive coupling activity was observed, thus furnishing the desired **2a** in a favorable selectivity of approximately 58% at full **1a** conversion (Table 1, entry 8). A systematic study of the catalyst was then accomplished w-
- ³⁵ **Table 1** Deoxygenative coupling of nitrobenzene to azobenzene with CO in the presence of various catalysts.^{*a*}

	at., CO bluene	_й N-	+	-N N-	<	
	0.41.4	T.	0		1 1 (0/)	4a
Entry	Catalyst	(h)	$(0/a)^b$	2-	2-	4-
10	A /TT'O	(II)	(%)	<u>2a</u>	<u>3a</u>	4a 21
1-	Au/11O ₂	5	27	24	45	31
2	Au/TiO_2	5	26	34	64	2
3	Au/Fe ₂ O ₃	5	17	17	81	2
4	Au/Al_2O_3	5	28	86	10	4
5	Au/ZnO	5	37	77	18	5
6	Au/ZrO_2	5	8	14	83	3
7	Au/HT	5	12	11	88	1
8	Au/CeO ₂ -50	5	100	58	40	2
9	Au/CeO ₂ -90	5	100	84	15	1
10	Au/meso-CeO ₂	5	100	99	0	1
11^{d}	Au/meso-CeO ₂	5	100	14	85	1
12^e	Au/meso-CeO ₂	11	100	98	0	2
13 ^f	Au/meso-CeO ₂	5	8	8	92	0
14^g	meso-CeO ₂	5	67	4	96	0

^{*a*}Reaction conditions: 2.0 mmol **1a**, anhydrous toluene (5 mL) and Au 0.5 mol% at 150 °C under 5 atm of CO. ^{*b*} GC analysis using *tert*-butylbenzene as an internal standard. ^{*c*} As-received toluene from Aldrich. ^{*d*} 120 °C. ^{*e*} 1 atm of CO. ^{*f*} 5atm of N₂ instead of CO. ^{*g*} 250 mg meso-CeO₂ was used. ith a set of Au/CeO₂ samples with varied ceria specific surface area ranging from 50 to 140 m²·g⁻¹ (entries 8-10). To our delight, ⁴⁰ it was found that an excellent yield of **2a** of about 99% can be attained with a catalyst composed of gold deposited on meso-CeO₂ (S_{BET} ~ 139 m²·g⁻¹, Figure S2) (entry 10).

In a scaled-up reaction at gram quantity (1a, 20 mmol), the Au/meso-CeO₂ catalyst provided a high isolated yield (96%) of 45 the corresponding azo product (see Scheme S1). In this case, a TON as high as 2000 was achieved, a value which is significantly higher than those obtained with previously reported system requiring high CO pressure (Fe(CO)₅¹³: TON 20). These results indicated that Au/meso-CeO2 constituted a practical 50 catalyst for the deoxygenative coupling of nitroarenes produce azobenzenes amenable to gram-operations. After the reaction, the Au/meso-CeO₂ sample could be easily recovered by filtration using toluene as a solvent. Inductively Coupled Plasma (ICP) analysis confirmed that no Au was present in the ss filtrate (detection limit: <7 ppb), indicating that the observed catalysis is truly heterogeneous. Furthermore, the recovered Au/meso-CeO₂ can also be reused at least five times without an appreciable loss of activity(see ESI⁺), thus further demonstrating the utility of Au/ meso-CeO₂ for achieving reductive coup-60 ling of nitro compounds, with catalyst loadings that are orders of magnitude lower than that have previously been employed for this transformation under additive-free conditions. In addition, the X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) confirmed almost no change in the disper-65 sion of the Au or metallic state of Au before and after reuse (see ESI[†]). These results are in good agreement with an excellent

retention of the activity of this catalyst. Consistent with the case identified for catalytic deoxygenation of nitroarenes to anilines using CO/H₂O,^{11b,11e-11g} we found 70 that gold is exceedingly active for reductive coupling of nitroarenes with CO compared with other noble metals (Table S1, entry 1-5). Subsequent experiments focused on the effect of the reaction temprature revealed that under otherwise identical reaction conditions the Au/meso-CeO₂ exhibited dramatically 75 diminished production of 2a at 120 °C (Table 1, entry 11). Upon solvent screening it was found that the reaction catalyzed by Au/meso-CeO₂ proceeded efficiently in a variety of solvents, with the highest rate reached in anhydrous toluene (Table S2). Furthermore, it is revealed that the reaction can proceed smoo-⁸⁰ thly even at atmospheric pressure, although a longer reaction time was required (entry 12). The reaction also proceed under an inert atmosphere of N₂, although the reaction rate decreased significantly with 3a being formed as the major product (entry 13). In contrast, when replacing CO with H₂, 4a is formed pre-⁸⁵ ferentially even at low **1a** conversion levels (Table S3).¹⁵ We also tested other gold-based precursors or materials such as HAuCl₄, Au₂O₃ and bulk Au⁰ powder (mean particle size, ca. 150 nm), but all of them gave no conversion (Table S1). At this juncture, it is interesting to note that Au-free meso-CeO₂ can 90 deliver appreciable reduction of 1a, despite the fact that only the intermediate product of 3a was formed predominantly (entry 14). Taken together, these results show that the combination of CO and Au NPs strongly associated with meso-CeO2 is essential for achieving a high catalytic activity for selective 95 reductive coupling of 1a into 2a under mild conditions.

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$R \stackrel{\text{II}}{\square} \xrightarrow{\text{NO}_2} \frac{\text{Au/meso-CeO}_2}{5 \text{ atm CO, 150 °C}} R \stackrel{\text{II}}{\square} \xrightarrow{\text{N}_1} R$							
Entry	Products	Time (h)	Yield. $(\%)^b$				
1	Ns _N 2a	5	99 (95)				
2	F Ns _N 2b	33	74 (70)				
3		15	91 (86)				
4	Br Ns N 2d Br	28	85 (79)				
5	CI N N CI 2e	5	91 (85)				
6		28	74 (68)				
7	Br	16	86 (81)				
8		20	86 (79)				
9	N°N 2i	15	79 (73)				
10	N _N 2j	22	86 (79)				
11	N _N N _N 2k	8	92 (85)				

Table 2 Au/meso-CeO₂ catalyzed deoxygenative coupling of nitroare-

nes to give symmetric azo compounds.^a

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^{*a*} Reaction conditions: 2 mmol substrate, anhydrous toluene (5 mL), Au/meso-CeO₂ (Au 0.5 mol%) at 150 °C under 5 atm of CO. ^{*b*} GC yield using *tert*-butylbenzene as an internal standard. Numbers within parentheses refer to yields of isolated products.

⁵ With these promising results in hand, a variety of simple and readily available nitrobenzenes were further examined to demonstrate the general applicability of this novel CO-mediated catalytic system (Table 2). Both steric and electronic properties of the substituents in nitroarenes affect the coupling reac-¹⁰ tion significantly. Generally, nitrobenzenes containing a substi-

Scheme 1 Proposed mechanism for deoxygenative coupling of nitrobenzene with CO in the presence of Au/meso-CeO₂ as catalyst.

tuent on the aromatic ring mostly require a longer reaction time. ¹⁵ The yields of *m*-substituted azo arenes were somewhat higher than those for the corresponding *o*- or *p*-substituted nitroarenes (Table 2, entries 3-7). The nitroaromatics bearing electronwithdrawing groups are converted smoothly and selectively into the desired products with good to excellent yields (74-91%) ²⁰ (entries 2-9). Electron-donating substituted nitroaromatics, such as 1-methyl-4-nitrobenzene and 1-methyl-3-nitrobenzene, also formed the corresponding azo compounds in good yields after 22 and 8 hours, respectively, of reaction (entries 10, 11). Furthermore, asymmetrical aromatic azo compounds, having a ²⁵ high value as key intermediates for prodrugs and liquid crystals, could also be synthesized with moderate yields upon using two different substituted nitroarenes as the reactants (Table S5).¹⁶

Taking into account the previous mechanisctic investigation on related systems¹⁷ and our experimental observations, a pro- $_{30}$ posed surface-redox reaction pathway involving Ce⁴⁺/Ce³⁺ couple through cooperation between gold and the CeO₂ support is depicted in Scheme 1. The first step involves fast CO-induced catalyst reduction via abstraction of the lattice oxygen at the Au /CeO₂ perimeter interface to produce an oxygen vacancy. Sub-35 sequent deoxygenative coupling of the nitro group of 1a occured on the resultant vacancy sites provides the azoxybenzene, which then undergoes a further deoxygenation to give the azobenzene species,^{15,18} thereby completing the catalytic cycle. This redox-coupling route is well supported by the following 40 results: 1) An evaluation of the material redox behavior by COtemperature-programmed reduction (CO-TPR) measurements revealed that the reactive removal of surface oxygen from Au/ CeO2 occurred at much lower temperatures than other Au-based catalysts (Figure S5), thus verifying the distinguished deoxyge-45 nation activities of the Au/CeO₂ samples. 2) By monitoring the deoxygenation of 1a with reaction time, we established that the reaction proceeds via the intermediacy of azoxy compound, ¹⁹ indicative of a sequential deoxygenation pathway (Figures S6).

3) A systematic study of the influence of the support surface areas in the Au/CeO_2 -based materials showed an excellent correlation between the oxygen storage capacity (OSC) and corresponding activity for selective **3a** deoxygenation (Figure **C**7) and **b** and **b** are a finite formula of the selective **3a** between the formula of the selective **3b** and **b** are a finite formula of the selective **3b** and **b** are a finite formula of the selective **3b** and **b** are a finite formula of the selective **3b** and **b** are a finite formula of the selective **3b** are a finite formula of the selective **3b** are a finite formula of the selective **3b** and **b** are a finite formula of the selective **3b** are a finite formula of the selective **3b** are a finite formula of the selective **3b** and **3b** are a finite formula of the selective **3b** are a finit

5 S7), thus underscoring the importance of the greater surface oxygen mobility in facilitating the crucial CO-induced reductive coupling via a redox-mediated pathway.

In conclusion, we have successfully developed a facile and efficient gold-catalyzed approach for the synthesis of aromatic ¹⁰ azo compounds directly from reductive coupling of the corresponding nitroarenes by using CO as the sole reductant. The reaction is very mild, general, scalable, and tolerant of various functionalities. This reductive coupling method, using a robust and reusable gold catalyst with inexpensive and abundatly ¹⁵ available CO as the appealing reductant under mild conditions, can make a significant contribution not only to reveal the synthetic potential of supported gold catalysts but also to establish

a more benign and industrially viable process.

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Notes and references

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 † Electronic Supplementary Information (ESI) available: Chemicals and 30 materials, catalyst characterization, catalyst preparation and activity test. See DOI: 10.1039/b000000x/

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