A facile synthesis strategy to couple porous nanocube of CeO_2 with Ag nanoparticles: An excellent catalyst with enhanced reactivity for 'click reaction' and carboxylation of terminal alkynes

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Supporting Information SI-1

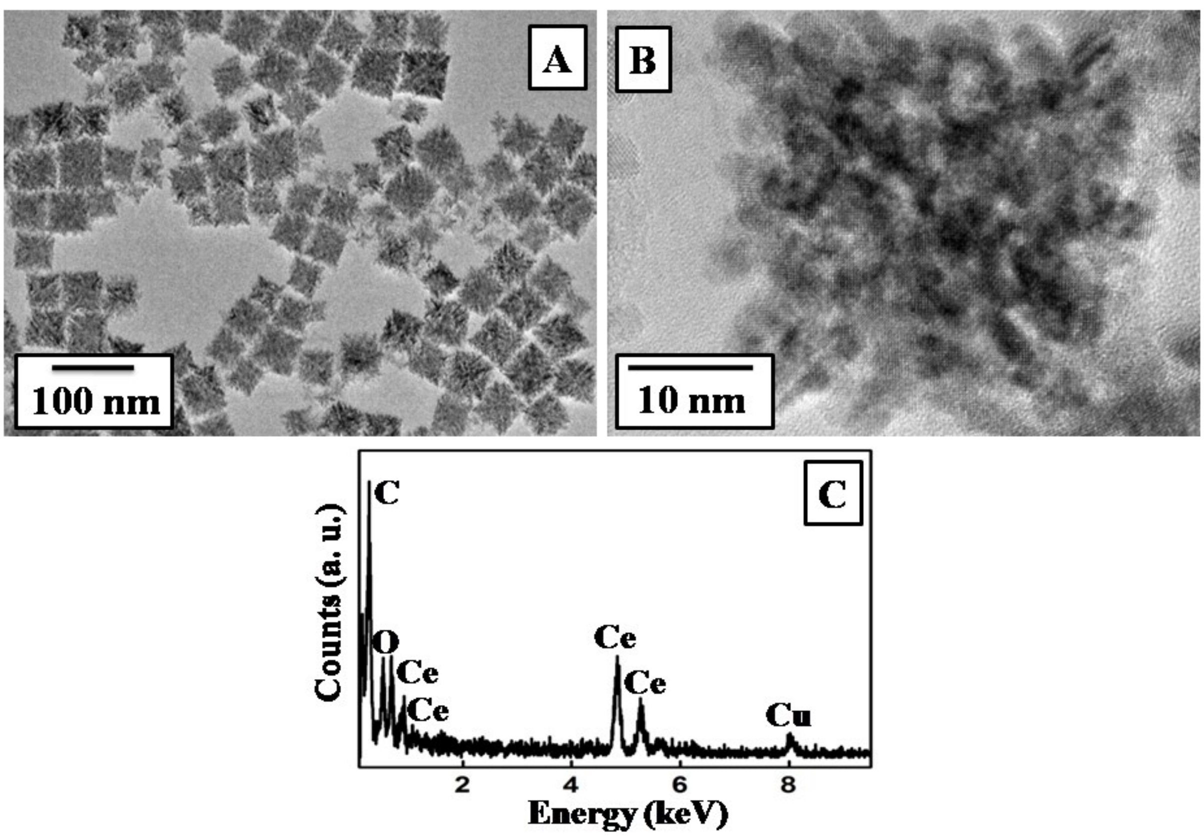


Figure SI-1. TEM images of 3-D porous CeO_2 nanocube prepared by hot injection method at (A) low magnification, (B) high magnification and (C) the corresponding EDX.

Supporting Information SI-2

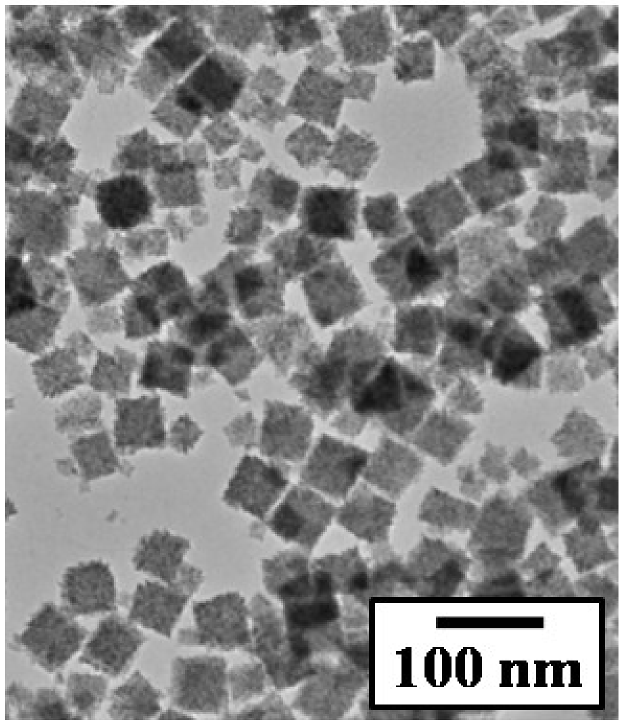


Figure SI-2. TEM image of DMP-modified CeO_2 nanocubes. No deformation due to surface modification with DMP.

Supporting Information SI-3

Table SI-1 Synthesis of 1, 4-disubstituted-1, 2, 3-triazole in the presence of different catalyst in the model reaction.

Entry	Catalyst	Time (h)	Yield[b] (%)
1	CeO_2-Ag nanocomposites	3	98
2	CeO_2	12	15
3	Ag-nps	8	44
4	Ag-HCP	6	68
5	Ag-MPTiO_2	6	75
6	AgCl	12	23
7	$AgNO_3$	12	18

[a]Reaction conditions: phenyl acetylene (1.2 equiv); aromatic amine (1equiv); Water (10 ml); catalyst (20 mg), room temperature. [b]Isolated yields.

Supporting Information SI-4

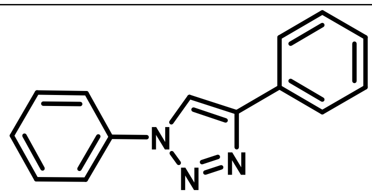
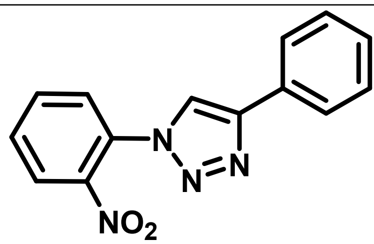
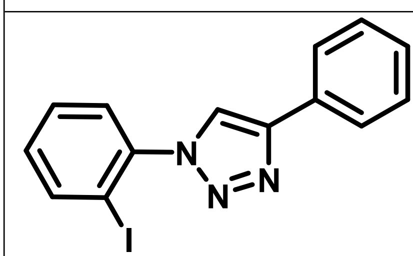
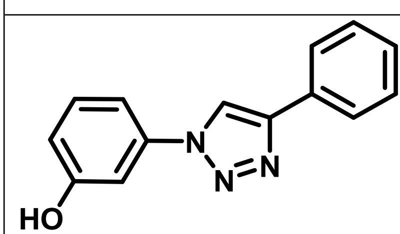
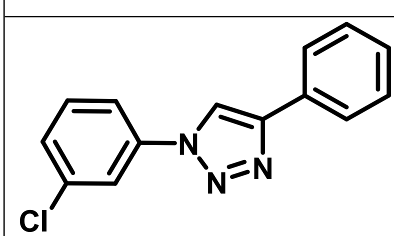
Table SI-2 Optimization of the solvent for the formation of 1, 4-disubstituted-1, 2, 3-triazole.

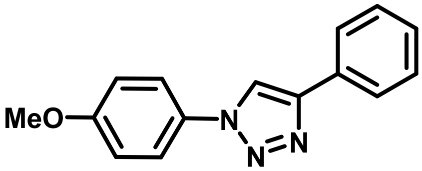
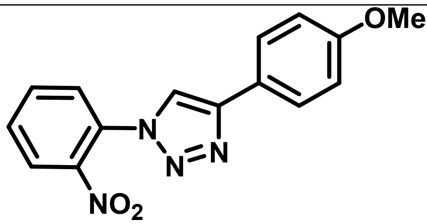
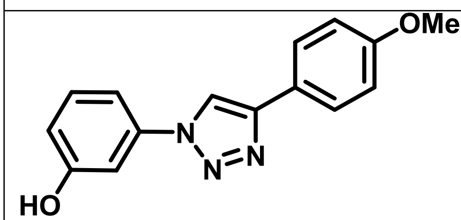
Entry	Solvent	Time (h)	Yield[b] (%)
1	Toluene	6	12
2	DMF	3	88
3	DMSO	3	80
4	THF	5	68
5	ACN	6	47
6	Water	3	98

[a]Reaction conditions: phenyl acetylene (1.2 equiv); aromatic amine (1equiv); solvent (10 ml); CeO_2-Ag nanocomposites catalyst (20 mg), room temperature. [b]Isolated yields.

Supporting Information SI-5

Table SI-3. ^{1}H NMR data of isolated 1, 4-disubstituted 1, 2, 3-triazoles.

	The product was separated by easy recrystalisation technique by ethanol.**^{1}HNMR (400 MHz, $CDCl_3$):** δ 7.32-7.36 (m, 1H), 7.37-7.45 (m, 3H), 7.48-7.54 (m, 2H), 7.72-7.78 (m, 2H), 7.85-7.88 (m, 2H), 8.20 (s, 1H) ppm.
	The product was separated by easy recrystalisation technique by ethanol. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.18-7.44 (m, 1H), 7.49-7.52 (m, 2H), 7.73-7.77 (m, 2H), 7.84-7.87 (m, 1H), 7.94-7.96 (d, 2H), 8.12 (s, 1H), 8.15-8.17 (d, 1H) ppm.
	The product was separated by easy recrystalisation technique by ethanol. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.21-7.26 (m, 2H), 7.33-7.37 (m, 1H), 7.43-7.53 (m, 4H), 7.88-7.93 (m, 2H), 7.96-7.98 (m, 1H), 8.10 (s, 1H) ppm.
	The product was separated by easy recrystalisation technique by ethanol. **^{1}H NMR (400 MHz, DMSO-d_6):** δ 6.94 (s, 1H), 7.33-7.44 (m, 4H), 7.48-7.54 (m, 2H), 7.93-7.96 (d, 3H), 9.25 (s, 1H) ppm.
	The product was separated by easy recrystalisation technique by ethanol. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45-7.47 (d, 1H), 7.51-7.58 (m, 4H), 7.75-7.78 (m, 1H), 7.91-

	7.93 (m, 1H), 7.95-7.99 (m, 2H), 8.25 (s, 1H) ppm.
	The product was separated by easy recrystalisation technique by ethanol. **[1]H NMR (400 MHz, $CDCl_3$):** δ 3.93 (s, 3H), 7.07-7.12 (m, 2H), 7.41-7.45 (m, 1H), 7.51-7.54 (m, 2H), 7.72-7.76 (m, 2H), 7.91-7.96 (m, 2H), 8.15 (s, 1H) ppm.
	The product was separated by easy recrystalisation technique by ethanol. **[1]H NMR (400 MHz, $CDCl_3$):** δ 3.96 (s, 3H), 7.19-7.48 (m, 1H), 7.52-7.55 (m, 2H), 7.75-7.84 (m, 2H), 7.88-7.90 (m, 1H), 7.94-7.99 (d, 2H), 8.12 (s, 1H), 8.17-8.19 (d, 1H) ppm.
	The product was separated by easy recrystalisation technique by ethanol. **[1]H NMR (400 MHz, DMSO-d_6):** δ 3.94 (s, 3H), 6.96 (s, 1H), 7.35-7.46 (m, 3H), 7.53-7.57 (m, 2H), 7.96-7.98 (d, 3H), 9.30 (s, 1H) ppm.

Supporting Information SI-6

Table SI-4 Effect of various reaction parameters on carboxylation of 1-phenylethyne.

Entry	**Base**	**Solvent**	**Temperature (^0C)**	**Time (h)**	**Yield[b] (%)**
1	Na_2CO_3	DMF	80	12	23
2	K_2CO_3	DMF	80	12	49
3	Cs_2CO_3	DMF	80	12	98
4	DBU	DMF	80	12	34
5	DBN	DMF	80	12	37
6	Et_3N	DMF	80	12	Trace
7	KO^tBu	DMF	80	12	11
8	Cs_2CO_3	DMSO	80	12	62
9	Cs_2CO_3	THF	80	12	44
10	Cs_2CO_3	Dioxane	80	12	28
11	Cs_2CO_3	Toluene	80	12	No reaction
12	Cs_2CO_3	DMF	25	12	12
13	Cs_2CO_3	DMF	50	12	39
14	Cs_2CO_3	DMF	70	12	81
15	Cs_2CO_3	DMF	90	12	98
16	Cs_2CO_3	DMF	80	4	24
17	Cs_2CO_3	DMF	80	8	52
18	Cs_2CO_3	DMF	80	10	78
19	Cs_2CO_3	DMF	80	14	98

[a]Reaction conditions: alkyne (1.0 mmol), 30 mg of CeO_2-Ag nanocomposites, base (1.5 mmol), CO_2 (1.0 atm), solvent (5 ml), [b]GC Yield.

Supporting Information SI-7

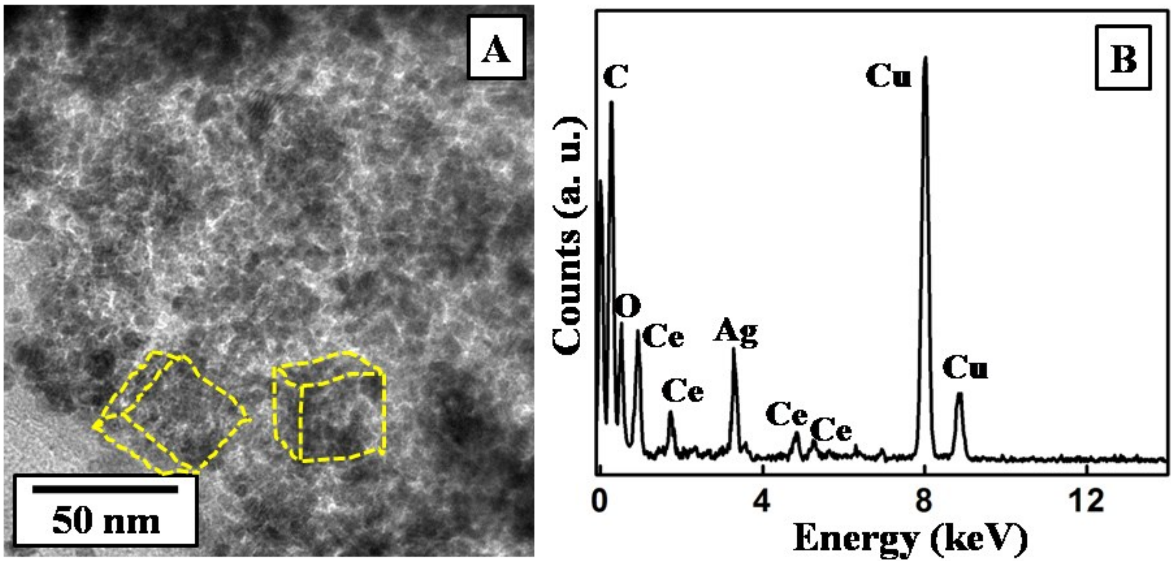


Figure SI-3. (A) TEM and (B) EDX analysis of CeO_2-Ag nanocomposite catalyst recovered after 5 cycles.

Supporting Information SI-8

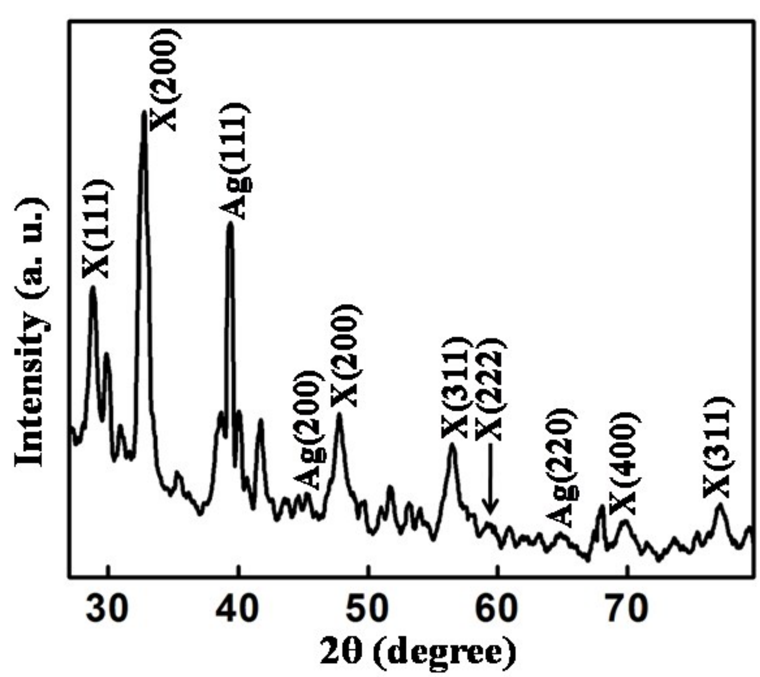


Figure SI-4. XRD of CeO_2-Ag catalyst recovered after 5 cycles. X (hkl) denotes the (hkl) plane of CeO_2.

Supporting Information SI-9

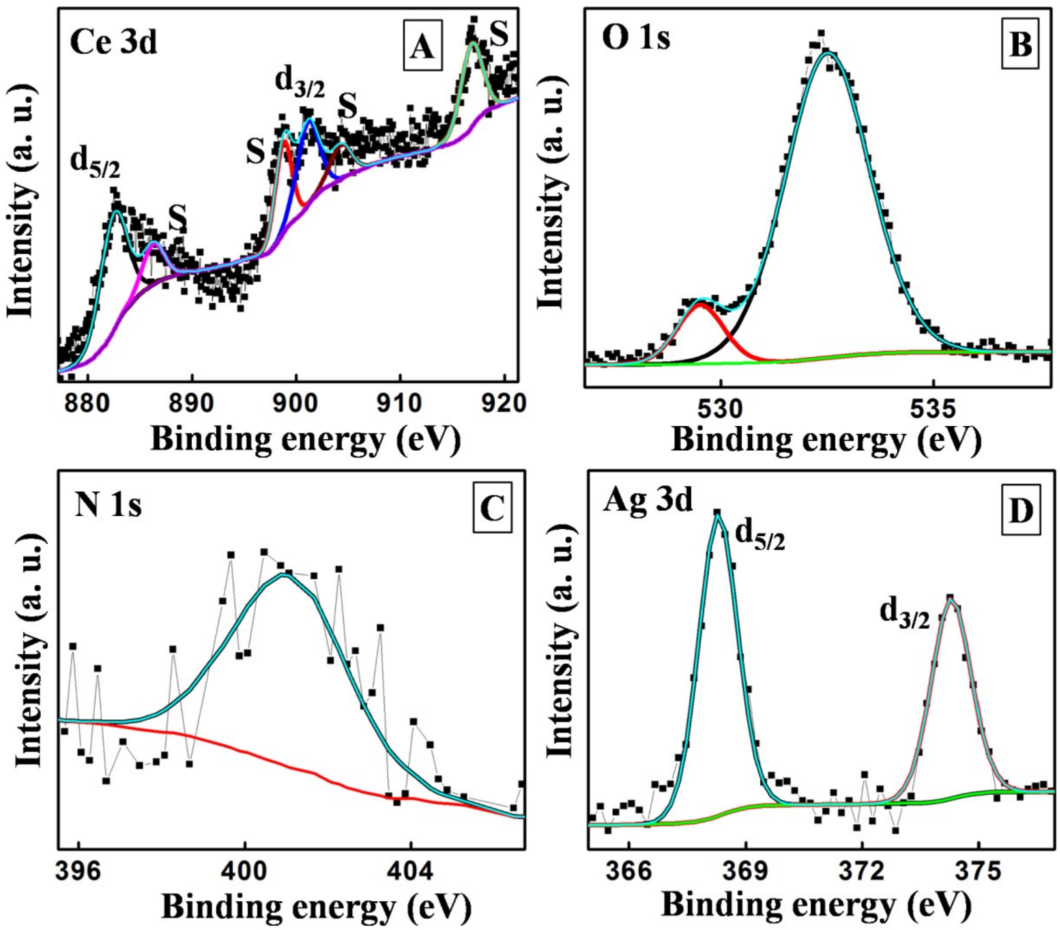


Figure SI-5. XPS spectra of (A) Ce 3d, (B) O 1s, (C) N 1s and (D) Ag 3d from CeO_2-Ag catalyst recovered after 5 cycles.