Supporting Information

2	Visible-light driven reaction of CO ₂ with alcohols using Ag/CeO ₂ nanocomposite:
3	First photochemical synthesis of linear carbonates under mild conditions
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1 1.0 Synthesis of Ag/CeO₂ photocatalyst

The Ag/CeO₂ composite with different loading of silver nanoparticles (Ag NPs) was 2 synthesized by precipitation method through minor modification to the previously reported 3 method using AgNO₃ followed by the heat treatment as shown in Scheme S1. In a typical 4 synthesis of active photocatalyst AC-5 (5wt% Ag/CeO₂), 5.8 mmol (2.52 gm) of 5 Ce(NO₃).6H₂O in 100 ml deionized H₂O was added, and the resulting mixture was stirred for 6 15 min. Then, 0.44 mmol (0.075 gm) of AgNO₃ was added to the solution, stirred for 15 7 min., and 7 ml of aqueous ammonia (25%) was added as a reducing agent and the resulting 8 9 suspension was stirred for 30 minutes. After that, the mixture was aged at 120 °C for 1 h and then allowed to cool at room temperature. The cooled mixture was centrifuged at 4000 rpm 10 for 5 min and washed with distilled water and ethanol. The obtained solid was dried at 60 °C 11 for 24 h to give light brownish-colored material (1.2 gm).¹ 12



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1 2.0 Characterization Techniques

The crystalline structure of the samples was determined by powder X-ray diffraction (PXRD) 2 with Rigaku Smart Lab diffractometer using CuK α radiation ($\lambda = 1.5406$ Å) at a scan rate of 3 4°/min. X-Ray diffraction (XRD) patterns of all the samples were collected at room 4 temperature between 0° to $80^{\circ} 2\theta$ values with a 0.02° angle step. Morphology of the materials 5 was determined by FE-SEM on FEI, Quanta instrument. High-resolution TEM (HR-TEM) 6 was performed on JEOL, JEM 2100, with 200 kV accelerating voltage. The sample for HR-7 TEM analysis was prepared by dissolving it in ethanol followed by ultrasonication for 10 min 8 to make a suspension. The one drop of the prepared suspension was added onto a copper/ 9 lacey carbonalloy grid. The chemical composition and binding energies in the synthesized 10 materials was determined by XPS analysis using K-alpha, Thermo Scientific Corp. XPS 11 instrument with monochromatized X-ray Mg Ka radiation. The surface properties such as 12 surface area, pore size and pore volume of the samples were investigated with a nitrogen 13 sorption isotherm on Micromeritics ASAP 2020 plus, USA chemisorption unit. The samples 14 were degassed at 250 °C for 4h before the analysis. Thermogravimetric analysis of the 15 samples was done on EXSTAR TG/DTA6300 instrument under N2 at flow rate of 100 ml/ 16 min and a heating rate of 10°C/min. The FTIR spectra were collected on the Nicolet FT-IR 17 spectrophotometer at room temperature. PEC measurements (PEC) such as Mott-Schotkey, 18 EIS and CV analysis were performed on Versatat-4 potentiostat in CO₂ saturated 0.1 M 19 20 aqueous KHCO₃ solution using Pt as a counter and Ag/AgCl as a reference electrode. The material coated on the FTO plate was used as a working electrode. During the analysis, the 21 active surface area of the working electrode was taken as 1 cm². The metal content in the 22 active photocatalyst (AC-5) was determined by using an Inductively coupled plasma atomic 23 emission spectrometer (ICP-AES, DRE, PS-3000UV, Leeman Labs Inc, USA). ¹H and ¹³C 24

NMR spectra of the products (linear carbonates) were collected at 500 MHz by using Bruker
 Advance-II 500 MHz instrument.

3 2.1 Characterization of the photocatalysts

The textural properties of the synthesized materials were examined using the Brunauer-4 Emmett-Teller (BET) theory of multilayered adsorption and desorption of nitrogen (Figure 5 6 S1). The pure CeO₂ has shown the type IV isotherm with H3 hysteresis (according to IUPAC), and the BJH desorption curve confirms its mesoporous nature.² The surface area, 7 pore size, and pore volume of bare CeO₂ is found to be 51.18 m²/g, 11.16 nm, and 0.14 8 cm³/g, respectively. After the doping of Ag NPs onto the CeO₂, the isotherms remain same as 9 type IV with H3 hysteresis in all the synthesized nanocomposites. However, the surface 10 properties such as surface area, pore size and pore volume are found to be changed with 11 increasing the loading of Ag NPs in the nanocomposite. The textural properties of the CeO₂ 12 and its Ag doped nanocomposites are shown in Table S1. 13





S.No.	Sample Code	SurfaceArea (m ² /g)	Pore Size (nm)	Pore Volume (cm ³ /g)	Crystalline size± (nm)
1.	CeO ₂	51.18	11.16	0.14	6.11
2.	AC-1	51.23	10.65	0.13	6.44
3.	AC-2.5	60.74	8.65	0.13	7.35
4.	AC-5	69.24	8.62	0.12	7.18
5.	AC-7.5	56.23	9.12	0.14	6.46

1 Table S1. Bulk properties of the synthesized materials

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[±]*The crystalline size was calculated by using the Scherrer equation from the XRD data*

3 Among all the composites, the AC-5 photocatalyst possesses the highest BET surface area of 4 $69.24 \text{ m}^2/\text{g}$, the smallest pore size, and pore volume of 8.62 nm and 0.12 nm, respectively, 5 favouring its higher activity towards the photocatalytic reaction. It is assumed that the 6 variation in the surface properties on the loading of 1-7.5 wt% Ag NP might be due to the 7 accumulation of the Ag NP on the edges of the pores or the surface of CeO₂ rather than in 8 between of the pores. The BJH distribution curve showed that the synthesized materials are 9 mesoporous in nature.³

The nature of the functional groups in the prepared samples was probed by FTIR 10 11 spectroscopy as displayed in Figure S2. In all the samples, a broad band appeared at 3438 cm⁻ ¹ attributes to the O-H stretching vibration and band at 1628 cm⁻¹ ascribed to O-H bending 12 vibration of the adsorbed water molecules. In pure CeO2, a band at 488 cm⁻¹ attributes to the 13 deformation mode of the O-Ce-O bond.⁴ All the nanocomposites Ag/CeO₂ having variable 14 loading of silver NPs exhibited two new bands at 851 cm⁻¹ and 1052 cm⁻¹ correspond to the 15 non-bridging Ag-O stretching vibrations and the shifting of Ce-O band due to the 16 incorporation of Ag NPs.⁵ This slight shifting confirmed the interaction between both the 17 components in the Ag/ CeO₂ nanocomposites. 18



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Figure S2. FTIR spectra of CeO₂ and its derivatives

Figure S3 display the Raman spectra of pure CeO₂ and the most active AC-5 nanocomposite. 3 The Raman spectrum of CeO_2 exhibits two bands, in which the first band at 467 cm⁻¹ is 4 related to F2g vibrational mode corresponding to the elongation of the Ce-O bond. The second 5 and weak band at 1050 cm^{-1} is attributed to the asymmetric of the primary A_{1g} with small 6 contribution of symmetric $F_{2g} \mbox{ and } E_g \mbox{ mode.}^6$ The Raman spectrum of AC-5 exhibits three 7 bands, in which the band at 460 cm⁻¹ with red shift of 7 cm⁻¹ attributed to the F_{2g} mode of 8 9 CeO_{2.} This shifting in band value and lower intensity indicates that some of cerium atoms in CeO₂ have been replaced by the Ag atoms, creating a new framework having both silver and 10 CeO₂. The red shift indicates an effective interaction of Ag atoms with the oxygen atoms of 11 the $CeO_{2,}$ resulting to the elongated Ce-O bond. The broadening of the band at 460 cm⁻¹ 12 attributes to the hydrogen bonding in the AC-5 nanocomposite. The moderate band at 950 13 14 cm⁻¹ is due to the interaction of Ag-O bond in the CeO₂ while the band at 1339 cm⁻¹ attributes to the Ag-O-Ce-O bond.⁷ 15



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Figure S3. Raman spectra of CeO₂ and AC-5

The morphological features in the prepared materials were probed by high resolution 3 transmittance electron spectroscopy (HR-TEM). Figure 1b represents the HR-TEM of the 4 active photocatalyst AC-5 that has hexagonal morphology with particle size (~7.89 nm). The 5 value matches well to the crystalline size (~7.18 nm) as determined by using Scherrer 6 equation from XRD. The lattice fringes suggest that the material is highly crystalline in 7 nature. The d-spacing 3.13 Å and 2.51 Å corresponds to (111) and (200) planes of CeO₂ and 8 2.36 Å for Ag NP are in well agreement with the SAED pattern.⁸ Further, the SAED pattern 9 shows the concentric diffraction with bright dots clearly revealed the polycrystalline nature of 10 the material. Moreover, EDX shows the presence of all elements and elemental mapping 11 indicates the uniform distribution of all the elements Ag, Ce and O in Ag/CeO₂ photocatalyst 12 (Figure S4). 13



Figure S4. Element mapping of (a) Ce (b) O (c) Ag (d) SEM EDX pattern and (e) TEM EDX
pattern

4 Figure S5 display the HR-TEM image of pure CeO_2 that clearly indicates hexagonal 5 morphology having crystalline size (~ 6.19 nm). The lattice fringes indicate that the material 6 is high crystalline in nature. The d-spacing 3.1 Å and 2.49 Å corresponds to (111), (200) 7 planes of CeO₂, respectively.⁹ The SAED pattern clearly indicates the polycrystalline nature 8 of prepared CeO₂. Moreover, EDX shows the presence of all the elements i.e. Ce and O in 9 CeO₂ base material.



2 Figure S5. TEM Image of CeO_2 (a) at 100 nm (b) at 2 nm (c) 10 nm and (D) EDX pattern

X-ray photoelectron spectroscopy (XPS) used to determine the chemical properties and 3 nature of the constituted elements in the active AC-5 (Figure S6). The XPS spectra of Ce 3d 4 deconvoluted into three major peaks. The first peak of $3d_{5/2}$ deconvolutesd into four peaks i.e. 5 881.84 eV and 884.85 eV for Ce³⁺ and 883.97 eV and 888.42 eV for Ce⁴⁺. The second major 6 peak deconvoluted into four peaks i.e, at 897.90 eV contributed to $3d_{5/2}$ of Ce⁴⁺ and other 7 three peaks, in which the two peaks at 904.40 eV and 907.14 are due to the 3d $_{3/2}$ of Ce³⁺ 8 whereas a peak at 900.49 eV is for Ce^{4+} of $3d_{3/2}$. Third major peak deconvoluted into two 9 peaks at 916.28 eV and 919.14 eV corresponds to Ce4+. The XPS spectra confirmed the 10 existence of both Ce⁴⁺ and Ce³⁺ in AC-5. Furthermore, the difference of 18.5 eV between the 11 first and last peak of 3d_{5/2} confirm the presence of CeO₂ in AC-5 nanocomposite. The XPS 12 spectra of O-1s deconvoluted into three peaks, in which one peak at 528.81 eV represents the 13 lattice oxygen.² The replacement of Ce atoms by the Ag NP as confirmed by the XRD, FTIR, 14

and Raman spectroscopy, may change the lattice of nearby Ce-O bond, resulting in the 1 lowering of the binding energy for the lattice oxygen of CeO₂. However, the peak at 529.62 2 eV corresponds to the AgO_x and at 531.49 eV corresponds to the lattice defect in the ceria of 3 AC-5 nanocomposite. The XPS of Ag NP deconvoluted into four peaks, in which two peaks 4 at 367.76 eV and 373.75 eV corresponds to 3d5/2 and 3d3/2 of Ag⁰ whereas remaining two 5 peaks at 368.52 eV and 376.32 eV indicate Ag⁺ in AC-5.¹⁰ The XPS survey scan confirms the 6 existence of all the necessary elements i.e., Ag, Ce and O in AC-5. 7





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Figure S6. XPS spectra of (a) Ce (b) O (c) Ag and (d) XPS Survey of AC-5

1 For the comparison, the XPS spectra of base CeO_2 is shown in Figure S7 that shows all the 2 peaks related to 3d of Ce and survey scan indicates the presence of both Ce and O in the 3 material.



4

Figure S7. XPS spectra of (a) Ce, (b) O, and (c) XPS survey CeO₂

6 The optical and electronic properties of the synthesized samples were determined by using 7 ultraviolet visible spectroscopy. Pure CeO₂ exhibited a broad absorption band in the range of 8 200-380 nm, suggesting its activity in the UV region. After loading of silver NPs, the 9 absorption extended to the visible region. The observed absorption hump in the region 450-10 575 nm was due to the surface plasmonic resonance effect of Ag NP. The maximum 11 absorbance in AC-5 confirmed its higher photocatalytic activity.¹¹



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Figure S8. UV-Vis spectra of CeO_2 and its derivatives in range 200-800 nm

3 The band gap is one of the important properties of the semiconductors for the photocatalysis.
4 The band gap of the synthesized materials was calculated by using the tauc plot. The band
5 gap energy of the synthesized materials was calculated by using the equation:

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$$\alpha hv = A(hv - E_g)^{n/2}$$

7 Where α is the absorption coefficient, A is the proportionality constant, hv is the photonic 8 energy, E_g represents the band gap energy. Here "n" represent the transition mode having 9 values either 1 or 4, n=1 for the direct transition and n=4 for indirect transition in the excited 10 state. Since CeO₂ shows the indirect transitions, so the value of n for CeO₂ is 4.¹² The band 11 gap value was found to be decreased on increasing the loading of Ag NPs in the following 12 order: CeO₂>AC-1>AC-2.5>AC-5>AC-7.5.



Figure S9. Thermal behavior of CeO₂, AC-1, AC-2.5, AC-5, and AC-7.5 photocatalysts
 under N₂ atmosphere

The photoluminescence (PL) analysis was performed at 255 nm to demonstrate the charge 4 carrier separation efficiency of the synthesized materials. The highest intensity of the peak in 5 CeO₂ indicates the faster recombination of the charge carriers (e⁻/h⁺) and its lowest photo-6 efficiency. Doping of the Ag NPs in CeO2 improved the photo-efficiency that could be 7 further confirmed by the lower intensity of the PL band in all the Ag/CeO₂ nanocomposites 8 than pure CeO2.13 The lowest intensity of PL band in AC-5 represents the maximum charge 9 separation and minimum recombination of the photogenerated electrons and holes, 10 confirming its highest photocatalytic activity. 11



Figure S10. PL Spectra of CeO₂, AC-1, AC-2.5, AC-5 and AC-7.5

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4 To evaluate the photoelectrochemical properties of the synthesized materials, the cyclic voltammetry (CV) and linear sweap voltammetry (LSV) were performed under light 5 irradiation by scan rate of 20 mv. The CV and LSV of pure CeO₂ shows a strong reduction 6 potential at -1.2 eV with the moderate reduction current -0.75 mV. On doping of Ag NPs in 7 CeO₂ a significant change in the photocurrent and reduction potential was observed. Among 8 all the synthesized nanocomposites, AC-5 showed the reduction potential shifts from -1.2 eV 9 (CeO₂) to -0.4 eV (AC-5) with an increase in photocurrent from -0.75 mV (CeO₂) to -1.9 mV 10 (AC-5). This lowering in the reduction potential and increment in the reduction current 11 confirmed the higher reduction and strong absorption ability of AC-5 under visible light 12 irradiation. The higher activity of AC-5 as compare to the other composite materials was 13 confirmed by the higher current density at lower applied external potential under the visible 14 15 light.



Figure S11. CV and LSV of CeO₂, AC-1, AC-2.5, AC-5 and AC-7.5

Electrochemical impedance spectroscopy (EIS) determined the resistance in the movement of 3 the electrons, i.e., the charge transfer properties of the materials (Figure S12). The minimal 4 5 arc radius in the plot indicates the minimum resistance to the flow of the electrons, i.e., higher charge separation. Among the synthesized nanocomposites, CeO2 exhibits the largest arc, 6 whereas, AC-5 reveals smallest arc, further justifying the highest photocatalytic efficiency of 7 the AC-5.14 8

Mott-Schottky was used to determine the type of the semiconductor as well as the CB and 9 VB positions in the synthesized pure CeO₂ and most active nanocomposite AC-5. Both the 10 samples exhibit positive slopes, suggesting their n-type semiconductor behaviour. The base 11 CeO_2 has a flat band potential (E_{fb}) -0.79, while the active photocatalyst AC-5 has a flat band 12 potential (E_{fb}) -0.65. Notably, the flat band potential is used to calculate the band edge 13 potential of the semiconductor material through that the photocatalytic reaction mechanism 14 can be predicted. The conduction band of active AC-5 is calculated to be -0.55 eV which 15 16 matches well to the reduction potential of CO₂ to CO (-0.52 eV), confirming the activation of the CO₂ under the developed protocol.¹⁵ 17



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2 Figure S12. (a) EIS of CeO₂, AC-1, AC-2.5, AC-5 and AC-7.5 & (b) MS of CeO₂ and AC-5

The thermal stability of the samples was investigated by the thermogravimetric analysis 3 under nitrogen atmosphere ranging from 30-800 °C with a heating rate of 10 °C (Figure S13). 4 All the samples exhibited two major weight losses, the initial weight loss (8-10 %) in the 5 range of 150-200 °C is due to the evaporation of the solvent and other organic moieties. The 6 second weight loss is observed from 300-500 °C because of the degradation of the impurities 7 present in the sample, such as nitrate ions of the precursor. After that, the materials remain 8 stable without further mass loss up to 800 °C. The doping of Ag NPs enhanced the thermal 9 10 stability of the materials and among all the nanocomposites, AC-5 exhibit maximum thermal stability.16 11





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Figure S14. HR-TEM images of AC-5 (a,b) & AC-7.5 (c,d)

3 As experimentally observed that higher loading of Ag NPS affected the photocatalytic 4 activity adversely that can be further verified by comparing the HR-TEM images of AC-5 5 and AC-7.5 nanocomposites (Figure S14). As shown, the AC-7.5 material has more 6 accumulation of Ag NPs than AC-5. However, this data correlates well with the BET data of 7 AC-5 and AC-7.5 composition, where increased content of Ag resulted in decreased surface 8 area and increased pore volume and pore size. That is attributed to the accumulation of Ag 9 NPs over the surface of CeO₂ rather than inside the material's pores.



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Figure S15. Recyclability test of the recovered AC-5 photocatalyst

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4 Computational modeling and optimized geometries of the materials

5 Figure S16 shows the optimized geometries of the (100) surface of CeO₂ and Ag 6 doped CeO₂. For the Ag doped CeO₂ model, one of the surface Ce atoms was 7 substituted by Ag, and a (2 X 2 X 1) Monkost-Pack grid for the geometry optimization 8 of the Ag doped CeO₂ (100) surface was considered. Perfect CeO₂ (100) surface 9 shows a Ce-O bond distance of 2.373 Å which is in agreement with 2.352 and 2.340 Å 10 reported previously.^{17a,b} The Ag-O distance was found to be 2.382 Å and Ce-O 11 distance in the doped geometry was found to increase by 0.062 Å.



3 Figure S16. Typical optimized geometry of (100) surface of (a) CeO₂ and (b) Ag doped
4 CeO₂.

5 Figure S17 shows the charge distribution of perfect CeO₂ and Ag doped CeO₂. The 6 oxygen atoms maintain a negative charge of 0.335 e while Ce atoms maintain a 7 positive charge of 0.582 e throughout the surface. Introducing the Ag atom increases 8 the negative charge on O atom by 0.02 e. This is expected to improve the catalytic 9 tendency of the material since O atoms will assume more affinity for the adsorbed 10 reactant.¹⁸ On doping, Ce atoms become more positive in charge, rendering the Ce 11 atoms more reactive.



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13 Figure S17. Atomic Hirshfeld charges on (a) un-doped CeO_2 and (b) doped CeO_2 .

1 2.2 Spectral Data of the products (Linear carbonates)





















1 **References**

2	1.	M. Chernykh, N. Mikheeva, V. Zaikovskii, M. Salaev, L. F. Liotta and G. Mamontov,
3		Catalysts, 2020, 10, 580.
4	3.	P. K. Prajapati, S. Saini, N. Nandal and S. L. Jain, Journal of CO2 Utilization, 2021,
5		45 , 101402.
6	2.	P. K. Prajapati, A. Malik, N. Nandal, S. Pandita, R. Singh, S. Bhandari, S. Saran and
7		S. L. Jain, Applied Surface Science, 2022, 588, 152912.
8	3.	S. K. Meher and G. R. Rao, Journal of Chemical Sciences, 2014, 126, 361-372.
9	4.	M. S. Pujar, S. M. Hunagund, V. R. Desai, S. Patil and A. H. Sidarai, 2018.
10	5.	R. A. Ismail, S. A. Abid and A. A. Taha, Lasers in Manufacturing and Materials
11		Processing, 2019, 6, 126-135.
12	6.	A. Santiago, N. Andrade Neto, E. Longo, C. Paskocimas, F. Motta and M. Bomio,
13		Journal of Materials Science: Materials in Electronics, 2019, 30, 11508-11519.
14	7.	W. Cai, Y. Shi, Y. Zhao, M. Chen, Q. Zhong and Y. Bu, RSC advances, 2018, 8,
15		40731-40739.
16	8.	M. Zhao, H. Li, X. Shen, Z. Ji and K. Xu, Dalton Transactions, 2015, 44, 19935-
17		19941.
18	10.	Y. Shi, X. Zhang, Y. Zhu, H. Tan, X. Chen and ZH. Lu, RSC advances, 2016, 6,
19		47966-47973.
20	11.	G. Murugadoss, D. D. Kumar, M. R. Kumar, N. Venkatesh and P. Sakthivel,
21		Scientific Reports, 2021, 11, 1-13.
22	12.	S. Selvi, R. Rajendran and N. Jayamani, Applied Water Science, 2021, 11, 1-14.
23	13.	S. Singh and SL. Lo, Environmental Science and Pollution Research, 2018, 25,
24		6532-6544.

1	14.	H. H. Hernández, A. M. R. Reynoso, J. C. T. González, C. O. G. Morán, J. G. M.
2		Hernández, A. M. Ruiz, J. M. Hernández and R. O. Cruz, Electrochemical Impedance
3		Spectroscopy, 2020, 137-144.
4	15.	C. Lefrou, P. Fabry and JC. Poignet, <i>Electrochemistry: the basics, with examples</i> ,
5		Springer Science & Business Media, 2012.
6	16.	L. Huang, Y. Li, H. Xu, Y. Xu, J. Xia, K. Wang, H. Li and X. Cheng, RSC Advances,
7		2013, 3 , 22269-22279.
8	17.	(a) Y. Mordekovitz, S. Sagi, S. Barzilai and S. Hayun, J. Mater. Chem. A, 2020, 8,
9		21842-21851. (b) L. Gerward, J. Staun Olsen, L. Petit, G. Vaitheeswaran, V.
10		Kanchana and A. Svane, Journal of Alloys and Compounds, 2005, 400, 56-61.
11	18.	C. Nwosu, Journal of Technical Science and Technologies, 2012, 25-28.
12		

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