<u>**Supplementary Information**</u>

One-Pot Synthesized Plasmonic Black Gold Nanoparticles for Efficient Photocatalytic CO Oxidation

Rishi Verma[#], Sushma Kundu[#], and Vivek Polshettiwar*

Department of Chemical Sciences, Tata Institute of Fundamental Research (TIFR), Mumbai, 400005, India
Email: vivekpol@tifr.res.in

[#]Shared 1st authors

Experimental

Catalysts Characterizations

Scanning transmission electron microscopy (STEM) analysis was carried out using FEI-Tecnai operated at an accelerating voltage of 300 kV. Elemental mapping was carried out using energy-dispersive X-ray spectroscopy (EDS). Samples were prepared by dispersing a small amount of solid powder in ethanol by sonicating for 10 sec and the dispersion was drop-casted onto a holey carbon-coated 200 mesh copper TEM grid. SEM imaging was performed on a ZEISS ULTRA field emission scanning electron microscope. The SEM was operated with an accelerating voltage of 3 to 10 kV. SEM samples were prepared by drop-casting diluted ethanolic suspension of the powder onto the aluminum stub. PXRD patterns were obtained using a Panalytical X'Pert Pro powder X-ray diffractometer with Cu-Kα radiation. The Fourier transform infrared (FTIR) spectra were recorded using a JASCO FT/IR-4700. N_2 sorption measurements were performed using a Micromeritics 3-Flex surface analyzer (samples were degassed at 150 °C for 12 h under vacuum before analysis). UV-Vis absorption measurements were conducted using a JASCO UV/Vis/NIR spectrophotometer. To prepare the samples, 1.5 mg of DFNS-APTS or DPC-N, or 3 mg of DPC-30, DPC-60, DPC-120, or DPC-C4 were dispersed in 1 mL of ethanol and sonicated for 20 seconds to create a stock solution. Then, 300 μL of this stock solution was diluted with 1 mL of ethanol. The absorption spectrum was recorded using the diluted solution, and the baseline was recorded with the diluted DFNS-APTS solution.

Photocatalytic CO Oxidation using Plasmonic Black Gold

Photocatalytic CO oxidation was carried out in a PIKE technologies flow reaction chamber with a quartz window, equipped with a heater, and a thermocouple to precisely measure the temperature of the catalyst bed, and connected to a temperature controller. The inlet of the flow reactor chamber was connected to mass flow controllers (MFCs), and the outlet was connected to an Agilent 490 MicroGC equipped with a 10 m Molesieve 5A, and 10 m CP-PoraPLOT U columns and a thermal conductivity detector (TCD).

The catalyst (8 mg) was taken in a ceramic porous base crucible, which was placed inside the reactor chamber. Argon (Ar) gas (50 mL min^{-1}) flowed through the reactor for 10 minutes, and then the reactor was heated up to

110 °C (20 °C min^{-1}) for 30 minutes to remove any moisture adsorbed on the catalyst surface. The reactor was then cooled to 25 °C under Ar flow (10 mL min^{-1}). The reactant gases were then introduced into the reactor chamber through Alicat mass flow controllers; CO (10 % in He), O_2 (100 %), and Ar (100 %) at 1 bar pressure. The catalyst was then irradiated with light (300 W Xenon Lamp ~ 0.29 - 4 W cm^{-2}, 260-1100 nm), and the progress of the reaction was monitored by using online MicroGC every 3 minutes.

Higher temperature studies (45-140 °C) in the dark were performed by providing external heating to the catalyst bed by the heater inside the reaction chamber. For tests under different light intensities, the light power was tuned by changing the light intensity of the Xenon lamp. For quantification, the GC was calibrated by injecting known concentrations of standard gases like CO_2, CO, O_2, alkanes, etc. The slope of peak area versus ppm plot gives the calibration constant (area/ppm), which was used to calculate the product formation rate and selectivity of the products formed.

$$CO\ Conversion\ (\%) = \frac{(CO\ in - \ CO\ out)(in\ ppm) \ \times \ 100}{(CO\ in)(in\ ppm)}$$

$$CO_2\ Productivity\ (mmol\ g^{-1}h^{-1}) = \frac{CO_2(in\ ppm) \ \times\ Total\ flow\left(\frac{mL}{min}\right) \ \times\ 60}{Wt.\ of\ catalyst\ (in\ g)\ \times\ 22400\ \times\ 1000}$$

**Mechanism of CO Oxidation using *In-situ* DRIFTS Studies**

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed on a JASCO FT/IR-4700 instrument with a DiffusIR™-PIKE technologies high-temperature reaction chamber with KBr windows. The catalyst (15% DPC diluted in KBr, 8 mg) was taken in a ceramic porous base crucible, which was placed inside the reactor chamber. Reactant gases were introduced in the DRIFTS cell with a total flow of 44 mL min^{-1} with zero air (2 mL min^{-1}), CO (100 %, 2 mL min^{-1}), and argon (100 %, 40 mL min^{-1}). The dark spectra were recorded at 25 °C and the spectra in light were recorded using a Xenon lamp as a light source (240-1100 nm, 2.6 W cm^{-2}) (Supplementary Fig. 4). The spectra were recorded and averaged out using 400 scans and with a resolution of 4 cm^{-1}. The spectra were recorded against the baseline of the argon-filled reactor (40 mL min^{-1}) in the dark.
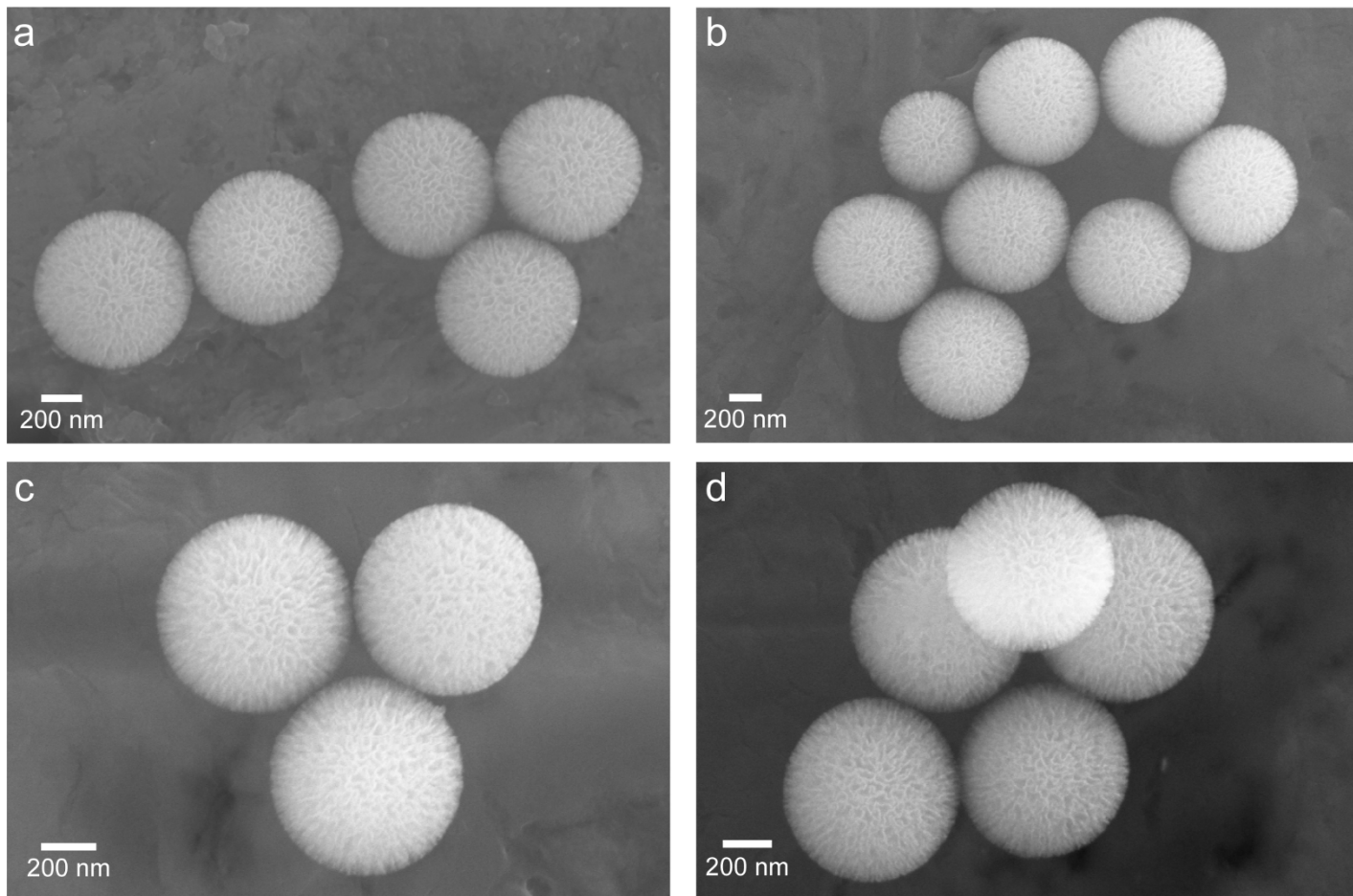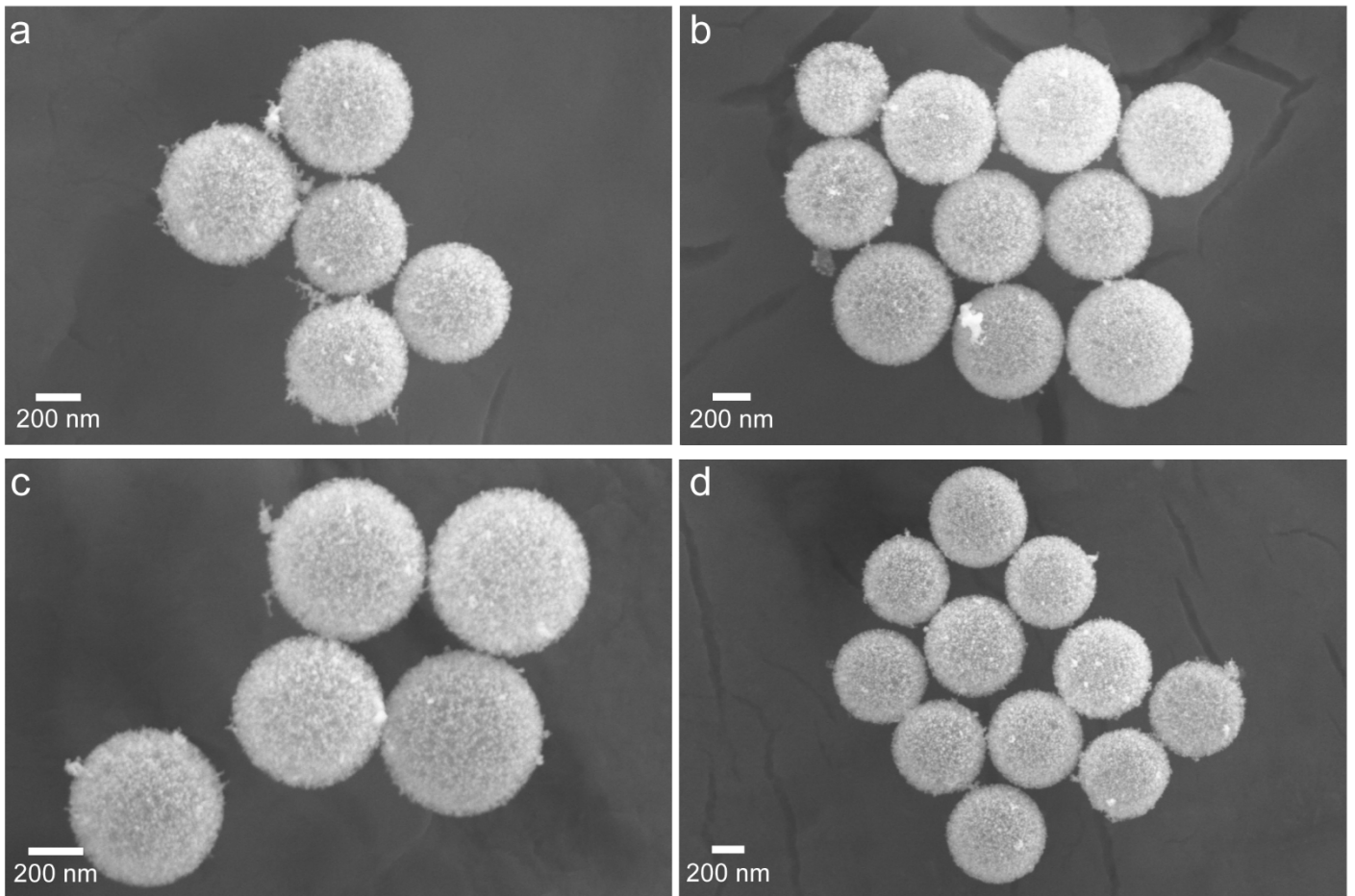
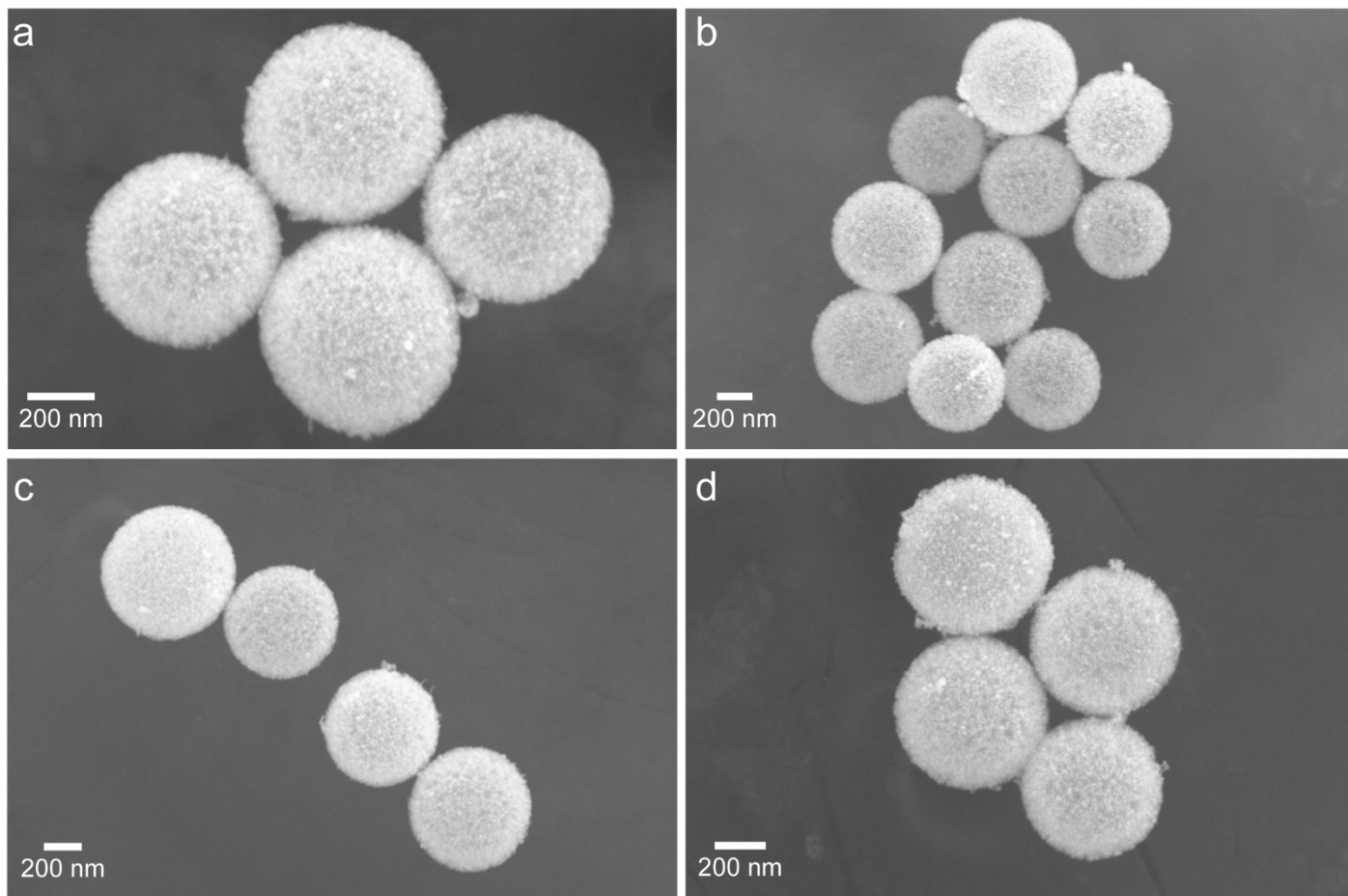**Figure S1. Morphological Characterization of DPC-N.** (a-d) SEM images of DPC-N.
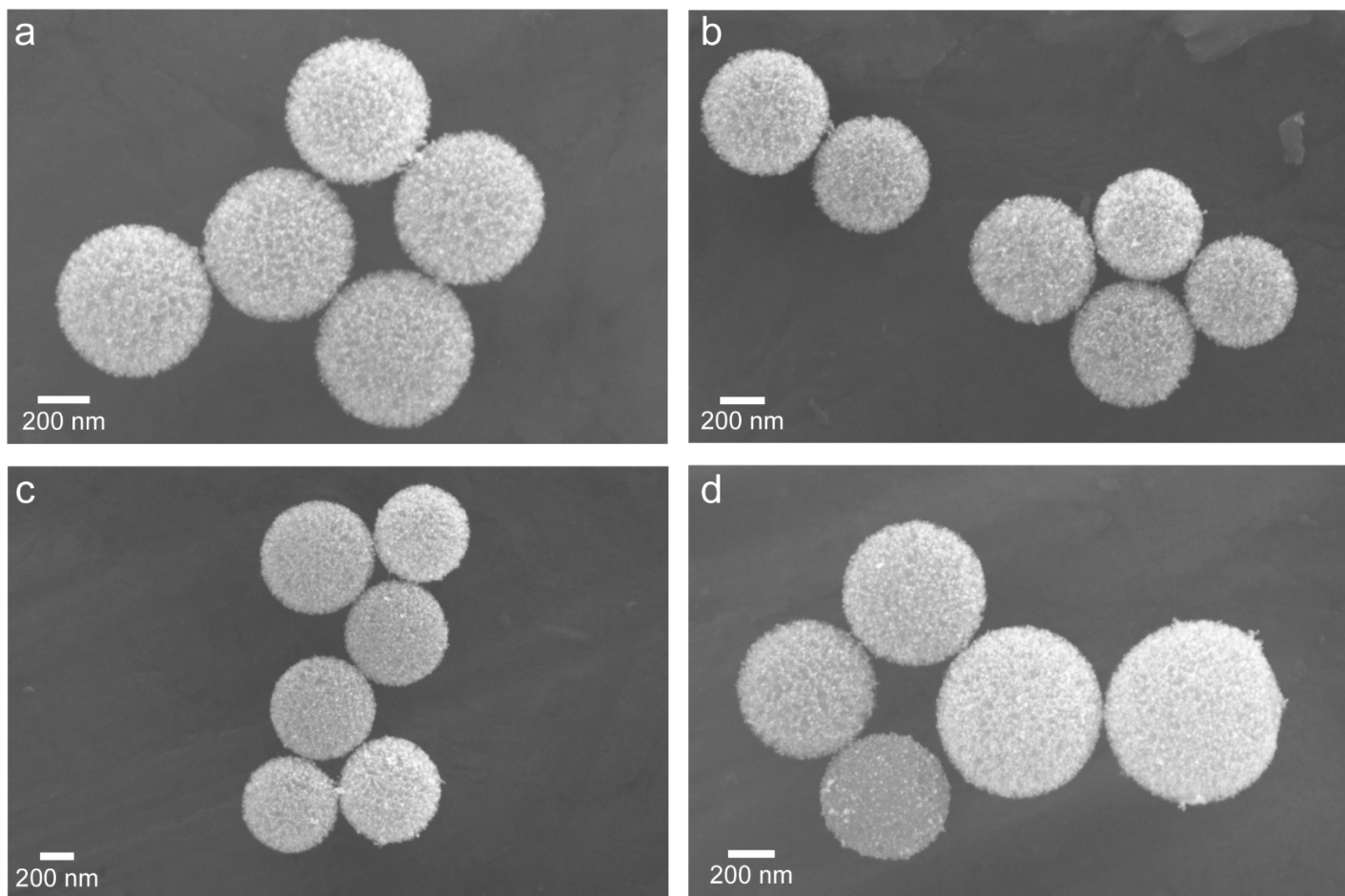
Figure S2. Morphological Characterization of DPC-30. (a-d) SEM images of DPC-30.
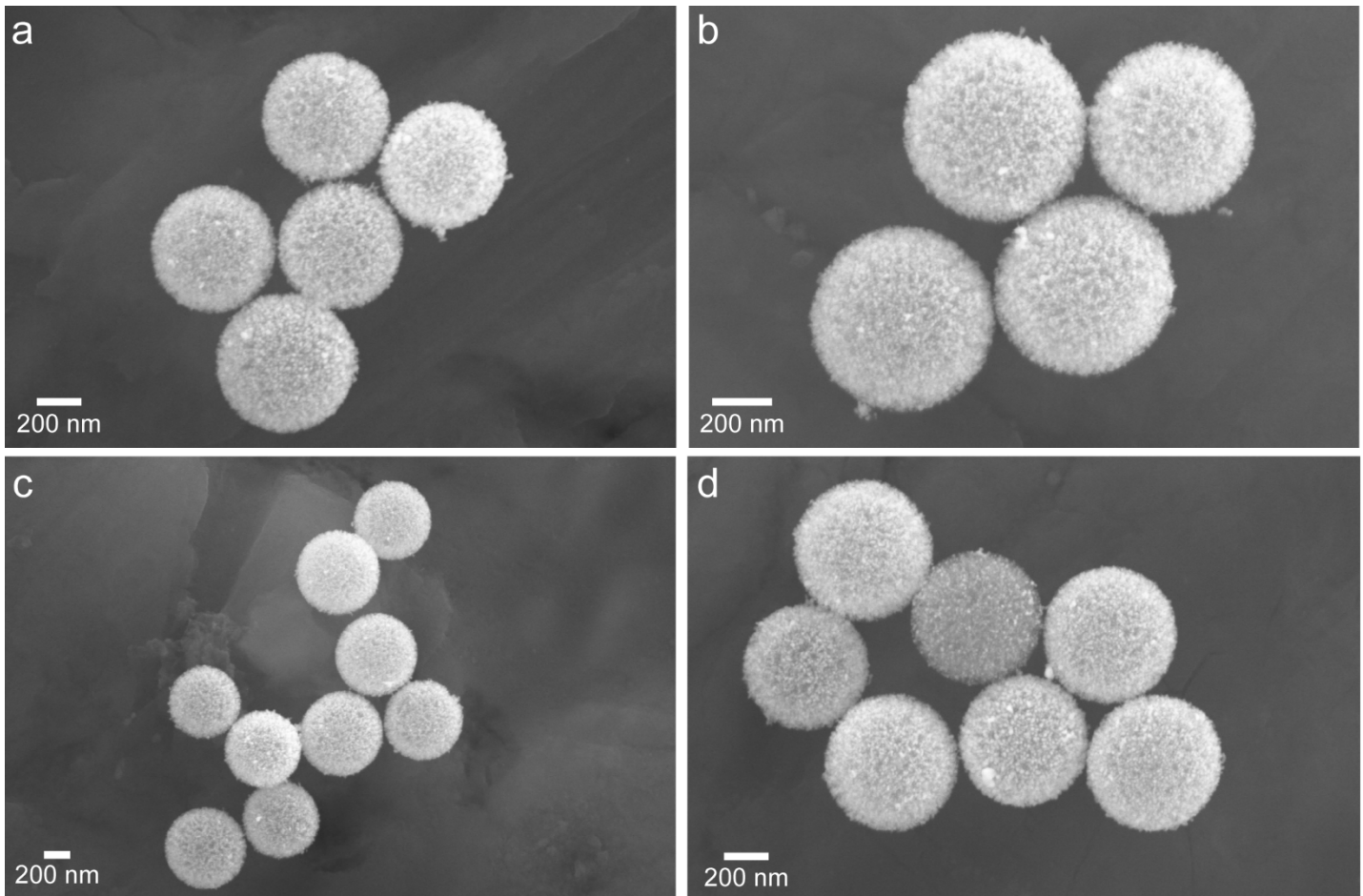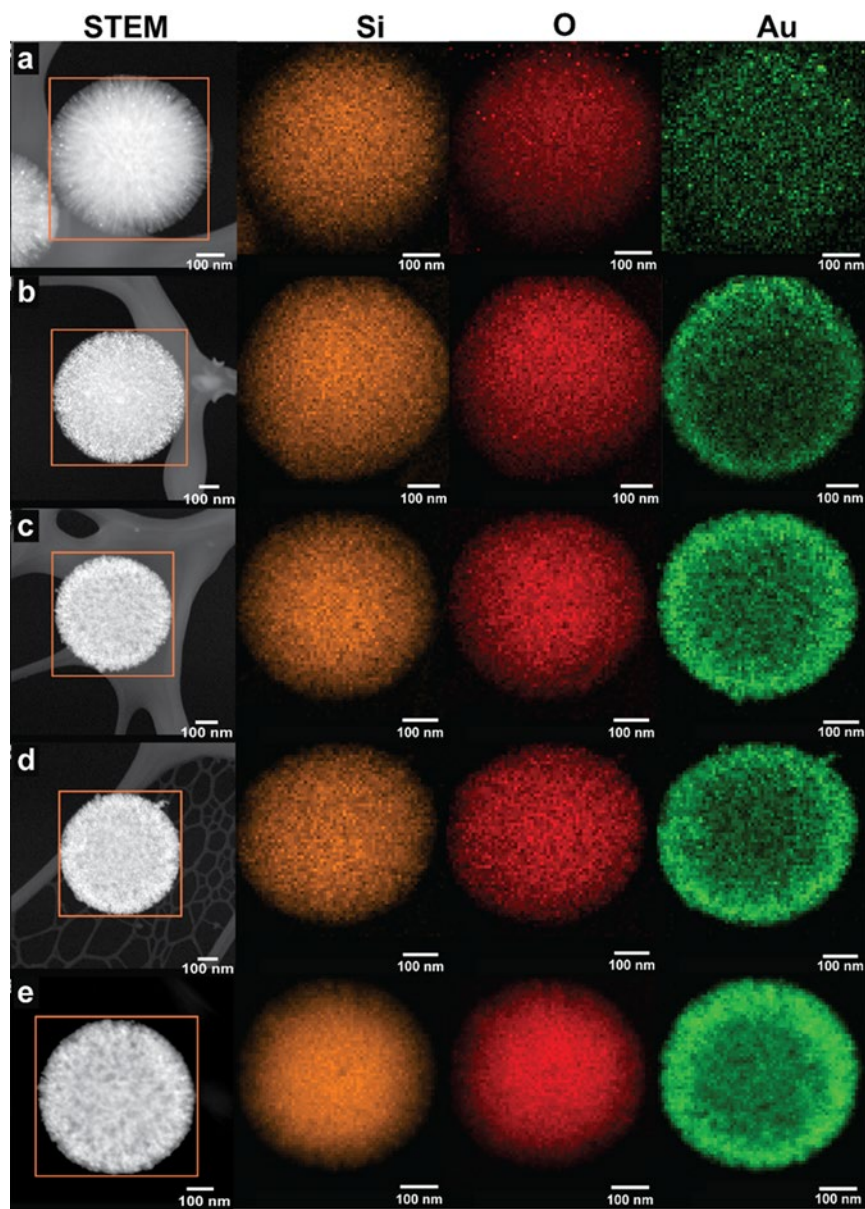
Figure S3. Morphological Characterization of DPC-60. (a-d) SEM images of DPC-60.

Figure S4. Morphological Characterization of DPC-120. (a-d) SEM images of DPC-120.
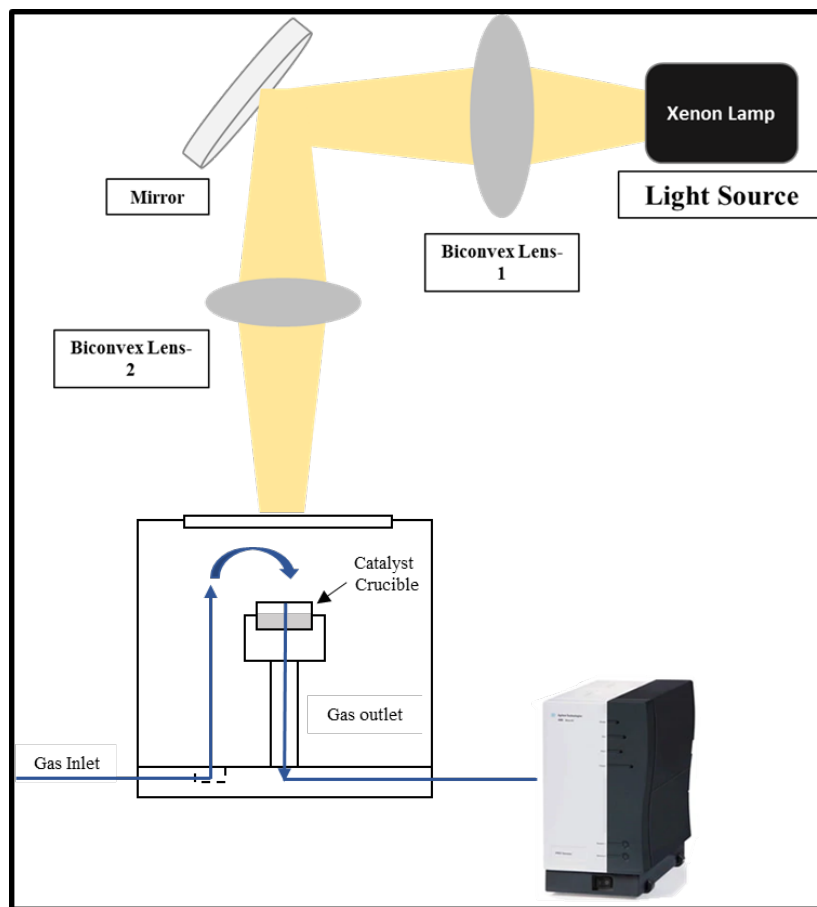
Figure S5. Morphological Characterization of DPC-C4. (a-d) SEM images of DPC-C4.
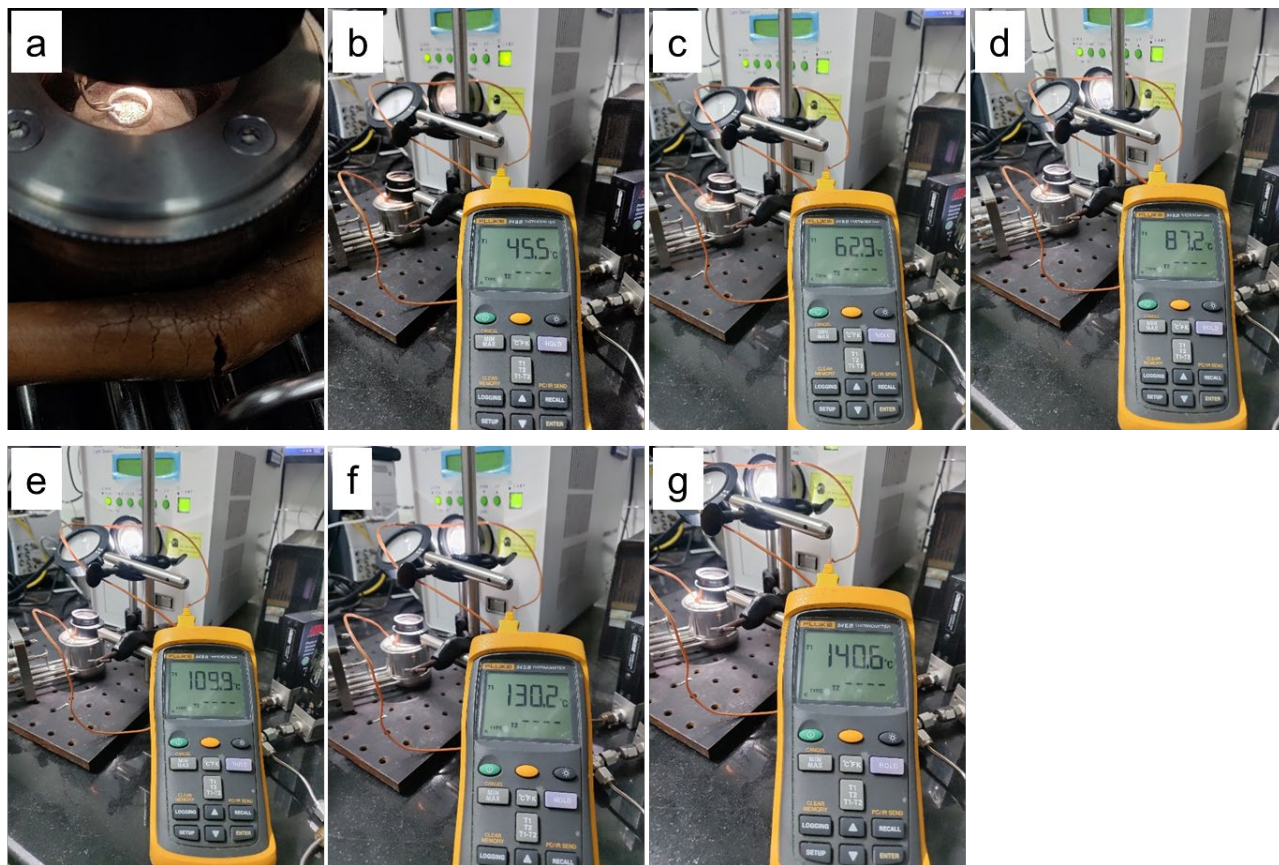
Figure S6. Compositional Characterization of Black Gold (DPC). STEM-EDS elemental mapping of (a) DPC-N, (b) DPC-30, (c) DPC-60, (d) DPC-120, and (e) DPC-C4.
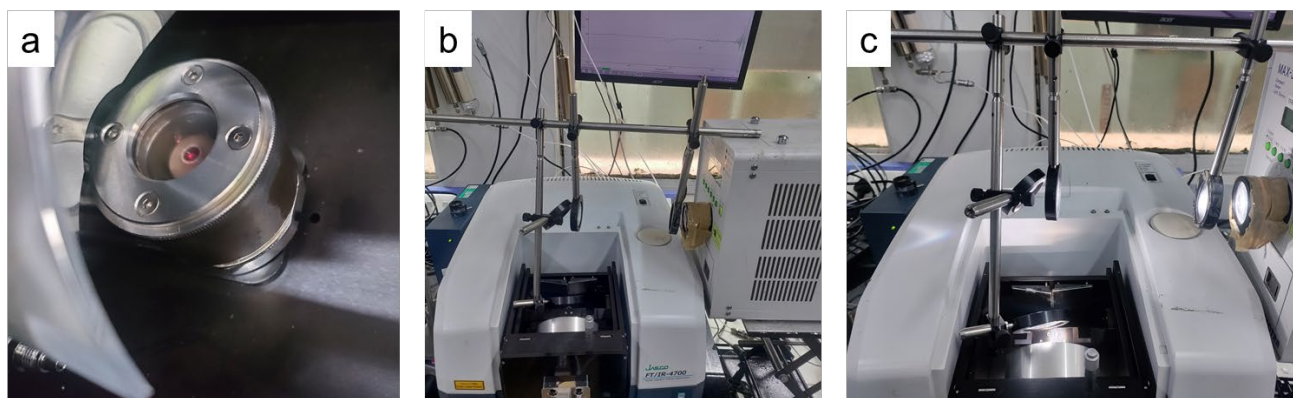
Figure S7. CO oxidation in light and dark experimental set-up. Diagrammatic sketch of a pike reactor, illustrating the interaction of gas flow with the catalyst powder in the crucible and the light pathway from the light source.

Figure S8. Catalyst bed temperature measurement in light. (a) Thermocouple positioning on the catalyst bed. The surface temperature under different light intensities (W cm^{-2}) (b) 0.29,(c) 0.77, (d) 1.6, (e) 2.4, (f) 3.3, and (g) 4.0.
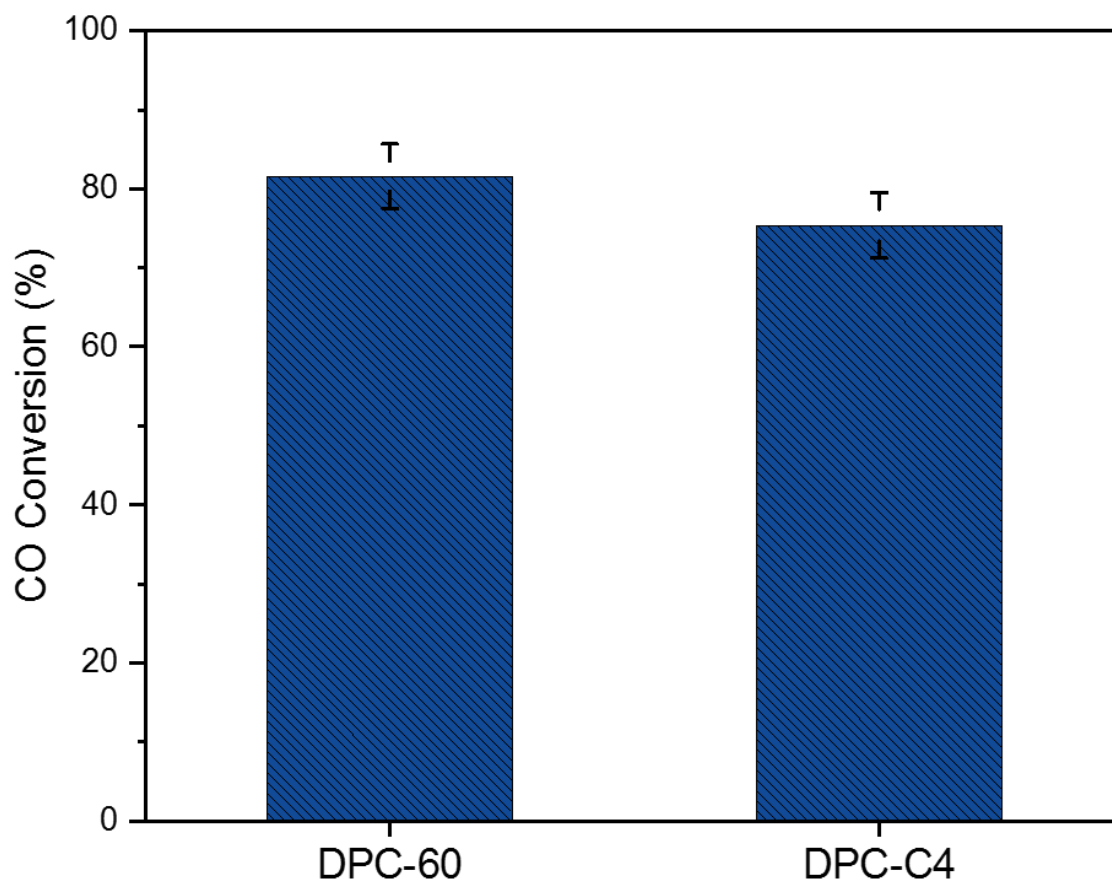
Figure S9. Photocatalytic CO conversion comparison between DPC-C4 and DPC-60. Photocatalytic CO conversion by DPC-C4 and DPC-60 at a total flow of 6 mL min^{-1} with an O$_2$:CO:Ar ratio of 1:2:0 at light intensity of 3.3 W cm^{-2}.

Figure S10. In-situ DRIFTS of CO oxidation in light and dark experimental set-up. (a) Photograph of the catalyst powder in the DRIFTS pike flow cell. Photograph of the light set-up for in-situ DRIFTS setup (b) light off, and (c) light On.
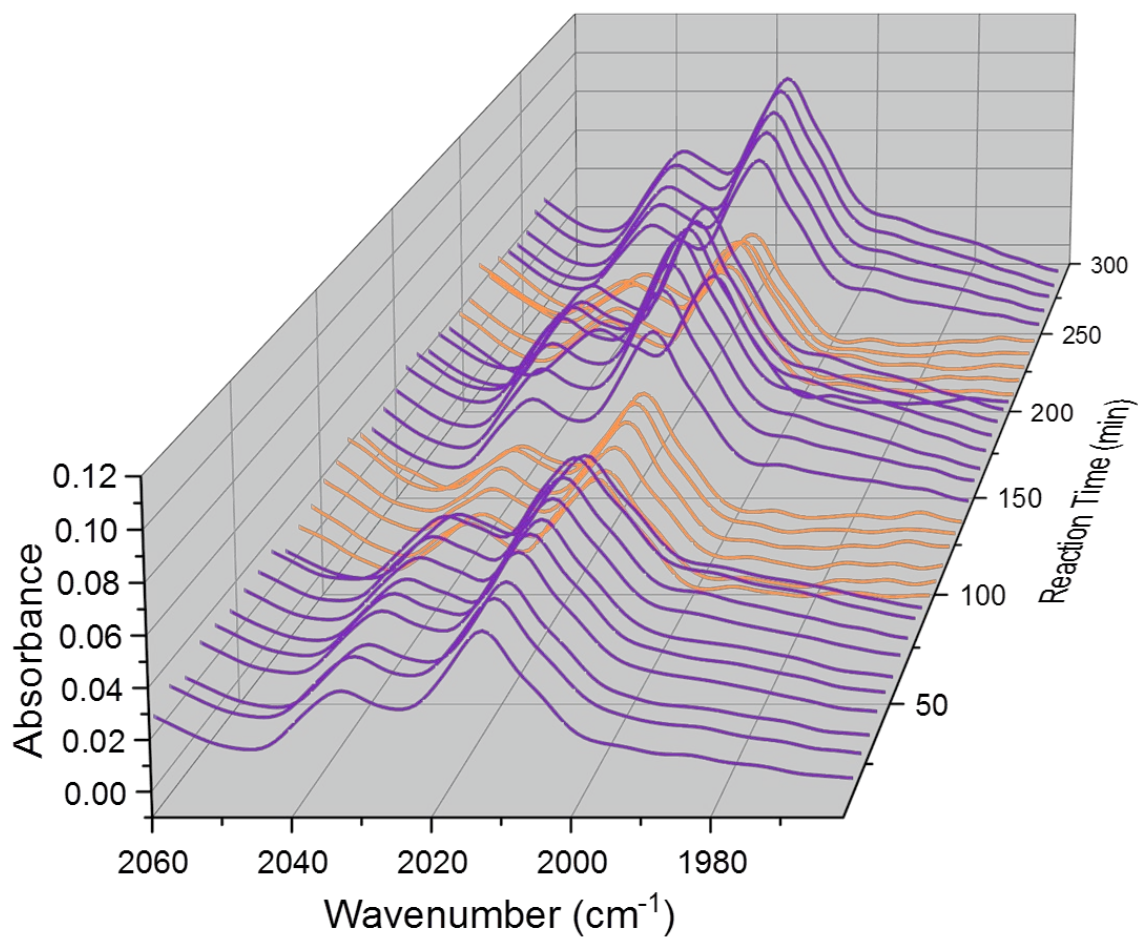
Figure S11. In-situ DRIFTS of CO oxidation in light and dark. (a) In-situ time-dependent DRIFTS spectra of CO oxidation by DPC-60 in light and dark cycles. Blue spectra represent the DARK condition, while orange spectra represent the LIGHT condition.

Table S1. Calculation of ratio of intensities of peak at 2033 and 2013 cm^{-1} in various light on-off cycles.

Reaction Condition	Intensity		Ratio
	2033 cm^{-1}	2013 cm^{-1}	(I$_{2033}$/I$_{2013}$)
DARK-1	0.231	0.371	0.622
	0.240	0.379	0.632
	0.245	0.393	0.623
	0.251	0.401	0.626
	0.255	0.406	0.628
	0.259	0.413	0.626
	0.259	0.411	0.631
	0.259	0.412	0.630
	0.254	0.407	0.624
	0.262	0.412	0.637
LIGHT-1	0.235	0.384	0.612
	0.199	0.333	0.598
	0.202	0.346	0.584
	0.222	0.361	0.616
	0.212	0.356	0.596
	0.207	0.364	0.567
DARK-2	0.300	0.475	0.633
	0.323	0.525	0.615
	0.336	0.537	0.626
	0.337	0.539	0.625
	0.336	0.539	0.624
	0.338	0.542	0.623
	0.329	0.524	0.627
LIGHT-2	0.197	0.335	0.588
	0.189	0.317	0.599
	0.192	0.308	0.625
	0.185	0.306	0.605
	0.192	0.314	0.612
	0.195	0.314	0.619
DARK-3	0.290	0.467	0.621
	0.302	0.484	0.624
	0.306	0.489	0.624
	0.313	0.501	0.625