# **Supplementary Information**

# Accurate SERS monitoring of plasmon mediated UV/Visible/NIR photocatalytic and photothermal catalytic process from Ag@carbon dots hybrid

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# **Experimental Section**

### Materials

AgNO<sub>3</sub> were bought from Sinopharm Chemical Reagent Co., Ltd. NaOH and  $H_2O_2$  (30%) were obtained from Beijing Chemical Works, CV was bought from Sigma-Aldrich corporation. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) were obtained from Aladdin. Polymer CDs were prepared with the similar procedure based on the previous report.<sup>1</sup>

### Synthesis of core-shell Ag@CDs nanoparticles (NPs)

2 mg of CDs was dispersed in 10 mL of distilled water to form a transparent solution. Next, 10 mL of AgNO<sub>3</sub> (0.02 mmol/L) aqueous solution was added while vigorous mechanical stirring, followed by the addition of 10 mL of NaOH (4 mmol/L) solution. The above mixed system was kept at a temperature of 120 °C in oil bath for 60 min while keeping mechanical stirring and refluxing. Then, the reaction solution was cooled to room temperature and a brown suspension was obtained. In order to remove the excess CDs, the suspension was washed and centrifuged with distilled water for two times, after that, the obtained nanoparticles were dispersed in 25 mL of deionized water.

### Synthesis of Ag NPs by seed-growth method

In this procedure, the individual Ag NPs with a mean diameter of ca. 40 nm were synthesized by the seed-growth method.<sup>2</sup> The procedure of starter Ag NPs seeds is as followed. 20 mL of 1% (w/v) citrate solution and 75 mL of distilled

water were mixed and kept at a temperature of 70 °C in water bath for 15 min. And then, 1.7 mL of 1% (w/v) AgNO<sub>3</sub> solution and 2 mL of 0.1% (w/v) NaBH<sub>4</sub> solution were quickly introduced to the above mixed system. After that, the mixture was kept at a temperature of 70 °C for 1 h. The obtained suspension was used as starter seeds. Then, the starter seeds were used for two steps growth to obtain the 40 nm uniform Ag NPs. Finally, a certain amount of the Ag NPs was dispersed in distilled water with the same concentration of Ag@CDs NPs.

### Photocatalytic activity measurement

In all the photocatalytic experiments, a 300 W Xe-lamp (CEL-HXUV300) bought from Beijing China Education Au-light, Co., Ltd with a UV reflector ( $\lambda$  < 400 nm), a 420 nm cut-off filter (420 nm <  $\lambda$  < 800 nm) and an 800 nm cut-off filter ( $\lambda$  > 800 nm) was used as the UV, visible and NIR light source, respectively. As shown in Scheme S1, the entire photocatalytic reaction solution system was placed in a quartz glass reactor with recirculating water. Through the tunning of the rated current of the Xe-lamp, the distance between lamp and reaction, and the attenuation rate, the same irradiation energy of UV/visible/NIR light can be controlled. A radiometer (FZ-A) bought from Photoelectric Instrument Factory of Beijing Normal University was used to measure the specific value of light energy, which is fixed as 15 mW/cm<sup>2</sup>. Typically, 0.5 mg of catalysts was dispersed into dye aqueous solution (10<sup>-5</sup> M, 5 mL) by 30 min ultrasonic treatment, respectively. In order to achieve the

adsorption-desorptiion equilibrium, the solution was stirred for 1 h in dark before the photocatalytic reaction. Before the photocatalytic reaction, the newly prepared hydrogen peroxide solution ( $10^{-1}$  M, 50 µL) was added to the reaction system, and the experiment began after oscillation treatment. Every 10 mins of the reaction process, a certain amount of supernatant was taken for UV-vis spectrum or Raman spectrum measurement. The catalytic reaction temperatures were kept through placing the photocatalytic reactor into a sink connected with the reflux water condenser. And the temperature measurement of the reaction system was monitored by a high precision electronic thermometer (HANNA HI98501 ± 0.3 °C) in real-time.

### Characterization

The morphologies of CDs, Ag@CDs and Ag NPs were observed on a JEOL JEM-2100F transmission electron microscope (TEM) operated at 200 kV. UV-vis spectra were obtained from Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. The fluorescence spectra were recorded on Shimadzu 5301PC fluorescence spectrometer. X-Ray photoelectron spectroscopy (XPS) data were obtained from a Thermo ESCALAB 250 photoelectron spectrometer with Al Ka X-ray radiation. Electron paramagnetic resonance (EPR) measurement was carried out on BRUKER E500 EPR spectrometer at room temperature. The Raman spectra for CV molecules and the Raman spectra for monitoring the photocatalytic reactions were measured by Renishaw-1000 spectrometer with a He/Ne laser as excitation line of 532 nm, the laser power at

the sample position was typically 1.1 mW. The spectrometer was calibrated by Raman band at 520.7 cm<sup>-1</sup> of a Si wafer.

### The enhancement factor (EF) calculation details:

$$EF = (I_{SERS}/N_{SERS})/(I_0/N_0)$$

where  $I_{SERS}$  and  $I_0$  denote the integrated intensity of the quivalent bands ascribed to PATP in SERS and normal Raman spectra, respectively,  $N_{SERS}$  and  $N_0$  represent the average number of adsorbed molecules in the detection region for the SERS experiments and normal Raman experiments respectively.

$$N_{SERS} = AC_{surf}VN_A/A_0$$
$$N_0 = C_0AhN_A$$

where *A* is the area of the laser spot (1  $\mu$ m),  $C_{surf}$  is the concentration of the determined CV molecules,  $C_0$  is the concentration of CV for the normal Raman measurement,  $N_A$  is the Avogadro constant, *V* is the volume of the adsorbed molecules,  $A_0$  is the area of the modified substrate, *h* is the effective focused depth which can be calculated based on the confocal feature of the microscope. We suppose that all molecules within the effective focused depth contribute to the whole Raman signal, and neglect the Raman signal from outside of the effective focused depth. The effective focused depth can be calculated to be 200  $\mu$ m. The SERS spectra and normal Raman were measured under the same laser power, excitation wavenumber, and same acquisition time.

Calculation of the contribution of photo-excited and photothermal catalytic process:

The photodegradation reaction of CV with Ag@CDs NPs as catalysts in the presence of  $H_2O_2$  followed a first-order kinetic process. According to the definition of pseudo -first-order reaction:

$$-kt = \frac{C_t}{C_0} \#(1)$$

Simply, expression (1) could be converted into the following form:

$$e^{-kt} = \frac{C_t}{C_0} \#(2)$$

where *e* was natural logarithm, *k* was the reaction rate, *t* was the reaction time,  $C_t$  was the remaining concentration of the reactant at time *t*, and  $C_0$  was the initial concentration of the reactant.

And  $C_t$  could be expressed in terms of the amount of reactant consumed ( $C_{con}$ ) at time t:

$$C_t = C_0 - C_{con} \#(3)$$

For the reaction system irradiated by UV/vis/NIR light at 25 °C, the photothermal effect was ignored due to the additional circulating water keeping the constancy of temperature. Therefore, it could be assumed that only photo-excited effect drives the catalytic reaction in this case:

$$e^{-k(total25)t} = e^{-k(photo25)t} = \frac{C_0 - C_{con}}{C_0} = \frac{C_0 - C_{photo25}}{C_0} = 1 - \frac{C_{photo25}}{C_0} \#(4)$$

where k(total25) and k(photo25) both stand for the apparent total reaction rate of the reaction system irradiated by UV/vis/NIR light at 25 °C,  $C_{photo25}$  were the amount of reactant consumed by the photo-excited catalytic process based on the hot carriers transfer.

For the reaction system irradiated by visible light without additional circulating

water, photo-excited and photothermal effect collectively drive the catalytic reaction in this case:

$$e^{-k(vis50)t} = \frac{C_0 - C_{visphoto50} - C_{photother50}}{C_0} = 1 - \frac{C_{visphoto50}}{C_0} - \frac{C_{photother50}}{C_0} \#(5)$$

where  $C_{visphoto50}$  and  $C_{photother50}$  were the amount of reactant consumed by the above two processes.

If these two separate processes still satisfy the pseudo-first-order dynamics formula:

$$e^{-k(visphoto50)t} = 1 - \frac{C_{visphoto50}}{C_0} \#(6)$$
$$e^{-k(photother50)t} = 1 - \frac{C_{photother50}}{C_0} \#(7)$$

Therefore, the expression (5) can be further written:

$$e^{-k(vis50)t} = 1 - \frac{C_{photo50}}{C_0} - \frac{C_{photother50}}{C_0}$$
$$= e^{-k(photo50)t} + e^{-k(photother50)t} - 1\#(8)$$

What's more, if we assume that the photothermal effect is equivalent to the dark catalytic reaction at the same temperature, then the reaction rate of the photo-excited catalytic process can be calculated:

$$e^{-k(visphoto50)t} = e^{-k(vis50)t} - e^{-k(dark50)t} + 1\#(9)$$

Similarly, for the photocatalytic system under UV light irradiation:

$$e^{-k(UVphoto30)t} = e^{-k(UV30)t} - e^{-k(dark30)t} + 1\#(10)$$

And for the photocatalytic system under NIR light irradiation:

$$e^{-k(NIRphoto50)t} = e^{-k(NIR50)t} - e^{-k(dark50)t} + 1\#(11)$$

where k(vis50), k(UV30) and k(NIR50) were the apparent total reaction rate of the reaction system irradiated by UV/vis/NIR light without additional circulating water, k(dark30) and k(dark50) were the reaction rate of dark catalytic processes at 30 and 50 °C, k(visphoto50), k(UVphoto30), and k(NIRphoto50) were the reaction rate of photo-excited catalytic process by UV/vis/NIR light, respectively.

# Ke Lamp Filter Filter External cooling water

# **Supporting Scheme**

Scheme S1. Schematic diagram of experimental set-up for the photodegradation of CV illuminated by Xe lamp.

# **Supporting Figures**



Figure S1. TEM image of Ag@CDs NPs, the inset shows the corresponding size distribution.



Figure S2. (a) UV–vis-NIR absorption spectra of individual Ag NPs and Ag@CDs NPs. Inset: photographs of 1) Ag NPs and 2) Ag@CDs in aqueous solution under visible light. (b) TEM image of individual Ag NPs with a mean diameter of *ca.* 40 nm.



Figure S3. Selected area electron diffraction (SAED) pattern of the prepared Ag@CDs.



Figure S4. (a) Excitation-dependent PL behavior of CDs aqueous solution and (b) schematic illustration of possible energy structures and PL emission processes of CDs.



Figure S5. UPS spectra of CDs.

From the UV-vis spectra, the band gaps of CDs are calculated to be 1.99 eV (Figure 2a). Then according to the UPS spectra, the work function is 4.09 eV, the highest

occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of CDs are calculated to be 5.35eV and 3.32 eV, respectively.



Figure S6. FTIR spectrum of Ag@CDs NPs.



Figure S7. The absorbance versus wavelength plots at various times for the photodegradation of CV by Ag NPs under (a) UV light, (b) visible light, (c) NIR light irradiation, respectively, and (d-f) comparison plot of degradation processes using Ag NPs and Ag@CDs NPs under different light irradiation.



Figure S8. SERS spectra of  $1.0 \times 10^{-5}$  M CV using individual Ag NPs and the Ag@CDs NPs as SERS substrates in aqueous suspension before and after the storage of 48 h, respectively.



Figure S9. (a) SERS spectra of CV molecules with different concentrations using Ag@CDs NPs as SERS substrates in aqueous suspension, and (b) and their corresponding calibration curve of peak intensity versus CV concentration at 1620 cm<sup>-1</sup>.



Figure S10. (a) SERS spectra collected from 10 random spots for CV  $(10^{-5} \text{ M})$  on Ag@CDs NPs substrate, (b) the corresponding RSD results of SERS peak intensity at 1620 cm<sup>-1</sup>.



Figure S11 Temperature of  $Ag@CDs+H_2O_2+CV$  system due to photothermal effect under UV, visible and NIR light irradiation.



Figure S12. The SERS spectra under different reaction time for the photodegradation of CV under (a) UV-light irradiation (30 °C), (b) dark environment (30 °C), (d) visible light irradiation (50 °C), (e) dark environment (50 °C), (g) NIR-light irradiation (50 °C), (h) dark environment (50 °C) respectively, and (c)(f)(i) kinetic fitting plot of these degradation processes.



Figure S13. Arrhenius plots of apparent activation barriers for dark reaction and visible light irradiation reaction.



Figure S14. EPR spectra of DMPO-•OH adducts of Ag@CDs+H<sub>2</sub>O<sub>2</sub> system under different light irradiation.

# **Supporting Tables**

Raman shift (cm <sup>-1</sup> )	Irreducible representation	Assignment			
420	Е	$\delta$ (CNC) / $\delta$ (CC <sub>center</sub> C)			
441	A <sub>1</sub>	δ (CNC)			
525	Е	δ (CNC)			
565	Е	$\gamma$ (CCC) / $\delta$ (CNC) / $\delta$ (CC <sub>center</sub> C)			
606	A <sub>1</sub>	$\delta$ (CCC) / $\delta$ (CNC) / $v_s$ (CC <sub>center</sub> C)			
725	Е	ν (CN)			
763	A <sub>1</sub>	$v_{s} (CC_{center}C) / v (CN)$			
805	Е	δ (CH) <sub>ring</sub>			
912	Е	$\delta (CC_{center}C)$			
1175	Е	$v_{as}$ (CC <sub>center</sub> C)			
1299	Е	$v_{as} (CC_{center}C) / \delta (CCC)_{ring} / \delta (CH)$			
1374	Е	$v_{as} \left( CC_{center}C \right) / \delta \left( CCC \right)_{ring} / \delta \left( CH \right)$			
1445	Е	$\delta_{as}$ (CH <sub>3</sub> )			
1476	E	δ <sub>as</sub> (CH <sub>3</sub> )			
1535	E	$\nu \left( C_{ring} N \right) / \delta_s \left( C H_3 \right)$			
1588	Е	v (CC) <sub>ring</sub>			
1620	A <sub>1</sub>	v (CC) <sub>ring</sub>			

Table S1. Detailed information of Raman shifts of crystal violet<sup>3,4</sup>.

v, stretching (s, symmetric; as, asymmetric);  $\delta$ , bending;  $\gamma$ , out-of-plane deformation (respect to the benzene ring).

In the previous work, the catalytic performance and mechanism of the carbon dot-based catalysts under NIR light irradiation have been rarely studied, and the band gap transition effect of semiconductors is always the main process of photoelectron generation. In this work, we directly used plasmon effect of Ag to promote the catalytic reaction and introduced the carbon dot with red light emission to extend the absorption of the catalyst to NIR light region, and distinguished the contribution of the photo-excited and photothermal catalytic effects of the reaction represents differences under UV/visible/NIR light irradiation conditions.

Catalyst	Loading	Dye and the	Time	Irradiation	Photocatalytic	Reference
		concentration	(min)		Processes	
Ag <sup>+</sup> -CDs-Bi <sub>2</sub> WO <sub>6</sub>	0.01 g	Tetracycline	60	Solar light	Bandgap	Li et al.
		(20 mg/L)			excitation	2016 <sup>5</sup>
Photoactive-CD	0.2 mg/mL	Crystal violet	90	Solar light	Bandgap	Aggarwal
		(20 ppm)			excitation	et al. 2020 <sup>6</sup>
Ag@CDs-TiO <sub>2</sub>	-	Methylene	60	Visible light	Bandgap	Jin et al.
		blue			excitation +	2020 <sup>7</sup>
		(10 <sup>-5</sup> M)			plasmon	
BiOBr/CDs/g-C <sub>3</sub> N <sub>4</sub>	65 mg	Ciprofloxacin	100	Visible light	Bandgap	Zhang et al.
		(10 mg/L)			excitation	2019 <sup>8</sup>
	20 mg	Tetracycline	180	NIR light		
		(20mg/L)				
Fe/Ag@CQDs	100mg	Fast Green	240	Sodium light	Adsorption +	Sharma et
		dye			plasmon	al. 2018 <sup>9</sup>
		(10 <sup>-5</sup> M)				
Ag-GQDs-ZnO	-	Rhodamine B	480	Visible light	Bandgap	Wang et al.
					excitation +	2015 <sup>10</sup>
					plasmon	
AgNPs/CDs/CNNs	50 mg	Methyl	100	Sunlight	Bandgap	Dadigala et
		orange			excitation +	al. 2017 <sup>11</sup>
		(10 mg/L)			plasmon	
	50 mg	P-nitrophenol	100	Sunlight		
		(10 mg/L)				
Ag@CDs	1 mg/mL	Crystal violet	90	UV light	Plasmon	This work
		(10 <sup>-5</sup> M)	90	Visible light	-mediated	
			90	NIR light	photocatalytic	
					and photothermal	
					catalytic	

Table S2. Comparative analysis of photocatalysis of dye based on different types of CDs-based catalysts.

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