

## Photochemical Method for Laser Absorption

### 2.2. Characterization

The crystal phase was determined by Bruker D8 CEVANCE using Cu-K $\alpha$  radiation. Transmission electron microscopy (TEM, including mapping) images were obtained at room temperature on a Tecnai G2 F20 field-emission transmitting electron microscope (Philips) operating at 30kV. The BET surface area was determined by a physical adsorption instrument (Quantachrome Instruments, Autosorb-IQ).



Picture. S1 Constant Temperature Water-bathing (EYELA PSL-1810).

Constant Temperature Water-bathing can easily be controlled the temperature at 25 °C, and -40 °C with stirring for 1- 4 h. It adopts double compressors and strong refrigeration to achieve the required temperature faster. The temperature range is -80 °C -0 °C. And we can easily control the temperature at -40 °C by stirring for 4 h.

### 2.3. Electrochemical measurements and Computational details

Electrochemical measurements were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua, China) using a standard three-electrode cell with a working electrode, a standard Ag/AgCl electrode as a reference electrode, and a Pt electrode as the counter electrode. The preparation of working electrode: samples were dispersed in water to form a 5 mg · mL<sup>-1</sup> solution and ultrasonicated for 20 min; 0.1 mL of solution was dropped on the FTO glass and dry at room temperature. Spin-polarization calculations were performed using VASP (Vienna ab initio simulation package) code on DFT (density functional theory). The PBE (Perdew-Burke Ernzerhoff) was adopted to treat the electron transfer effects by GGA (generalized gradient approximation). The DFT-D3 methodology, cutoff energy of 450 eV, and a 3 × 3 × 1 Monkhorst-Pack grid were simulated by PBE. The optimized structures were obtained with the criteria of < 0.03 eV/Å in force and 10<sup>-5</sup> eV in energy. Valence electrons: C 2s<sup>2</sup>2p<sup>2</sup>, N 2s<sup>2</sup>2p<sup>3</sup>, and Ag 4d<sup>10</sup>5s<sup>1</sup>.

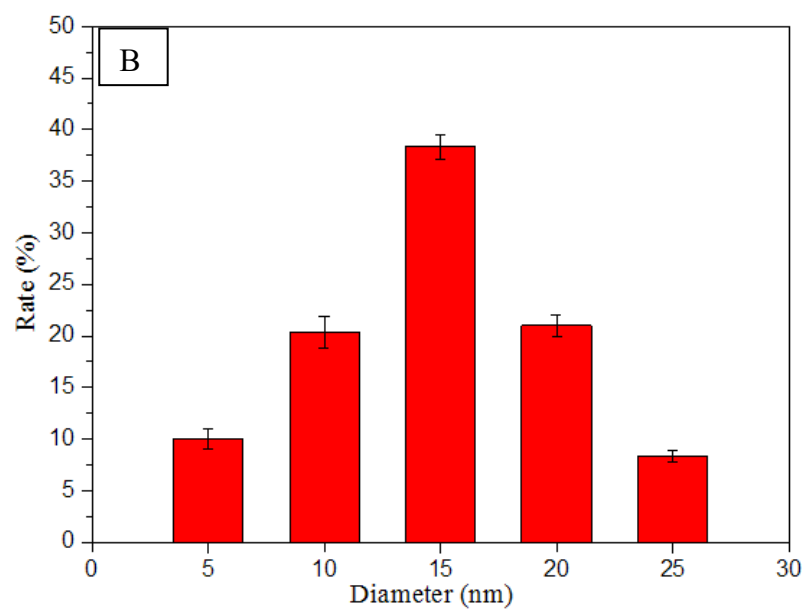
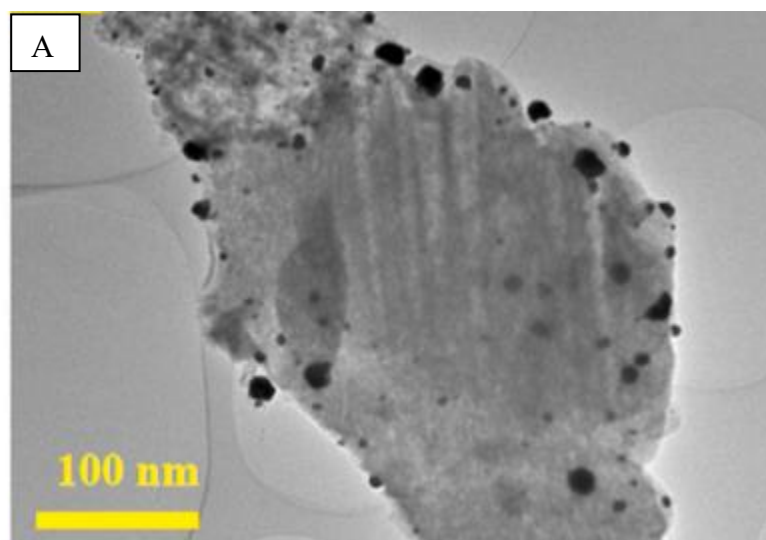


Figure. S1. TEM image (A) and its corresponding particle size distribution (B) for Ag/C<sub>3</sub>N<sub>4</sub>(- 40)

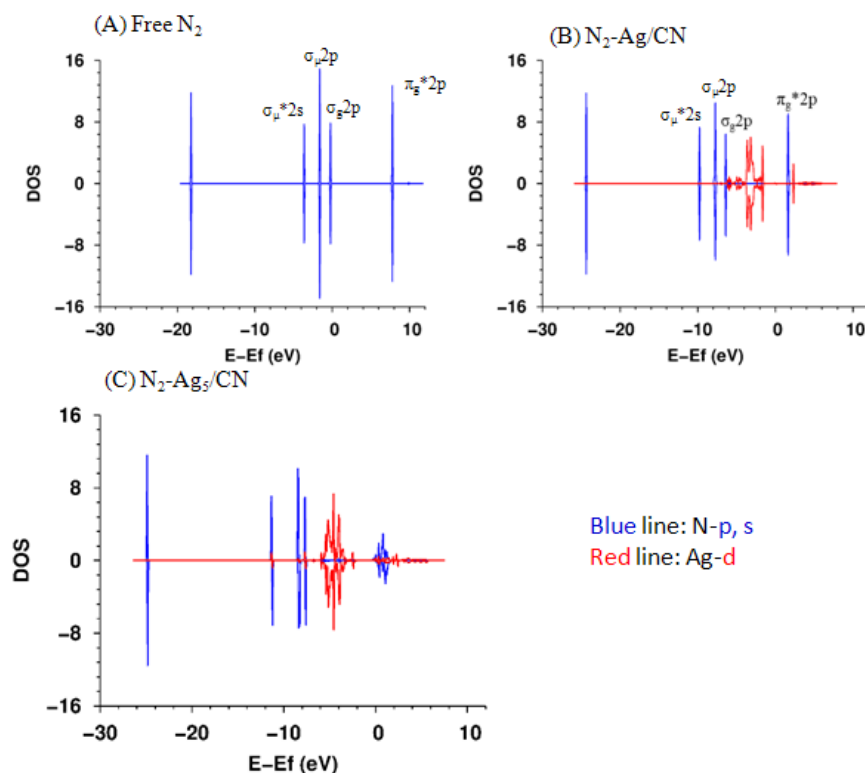


Figure. S2. DOS of (A) free  $N_2$  (B)  $N_2$ -Ag/CN and (C)  $N_2$ -Ag<sub>5</sub>/CN.

The density of states (DOS) of free  $N_2$ , adsorbed on two kinds of  $Ag_5$ -CN, improves the electron transfer between the Ag and  $N_2$ . There are four peaks near the Fermi level in the control blank sample in Fig.S2(A). In Fig.S2(B) and (C), the  $\pi_g^*2p$  orbit moves towards the Fermi level, and the  $\sigma_g^*2p$  orbit moves away from the Fermi level, indicating an increase in the number of electrons in the  $\pi_g^*2p$  orbit over all of the two samples. Additionally, the  $\sigma_g^*2p$  orbit is hybridized with the d orbit of Ag, and there is an obvious overlap of state density peaks near -6.3 eV and 1.1 eV, indicating that Ag atoms transfer electrons to the  $\pi_u^*2p$  orbit of N through the  $\sigma_g^*2p$  orbit. The  $\pi_g^*2p$  orbit of N and d orbit of Ag also undergo strong hybridization, indicating the electron transfer between Ag and  $N_2$ .

## Calculated band gap energy

The valence band ( $E_{VB}$ ) and conduction band ( $E_{CB}$ ) position of the samples were calculated on the follow equation:

$$E_{VB} = X - E^e + 0.5 E_g$$

$$E_{CB} = E_{VB} - E_g$$

Where  $X$  is the electronegativity of CN (4.73 eV vs. NHE),  $E^e$  is the free electron energy on the hydrgoen scale ( $\sim 4.5$  eV vs. NHE). The corresponding estimated band gap energy  $E_g$  are calculated and given in Fig 3.

**Table. S1** The effect of Ag nanoparticle size for electronic properties.

Sample	Ag particle size (nm) <sup>a</sup>	Work function ( $\phi$ , eV) <sup>b</sup>	SBH (eV) <sup>c</sup>	lifetime ( $\tau$ , ms)
C <sub>3</sub> N <sub>4</sub>	-	4.62		0.17
Ag/C <sub>3</sub> N <sub>4</sub> (-40)	$\sim 13.2$	4.82	0.20	0.29
Ag/C <sub>3</sub> N <sub>4</sub> (-60)	$\sim 9.2$	4.86	0.24	0.24

<sup>a</sup>From TEM.

<sup>b</sup> $\phi = \phi_b + 1.08/d_p$ ,  $\phi_b$  is the work function of bulk Ag (4.74 eV),  $d_p$  is the Ag particle size; the work function of C<sub>3</sub>N<sub>4</sub> is 4.62 eV (obtained from DFT calculation).

<sup>c</sup>Schottky barrier height (SBH),  $SBH = \phi - x$ , where  $x$  is the work function of C<sub>3</sub>N<sub>4</sub> (4.62 eV).

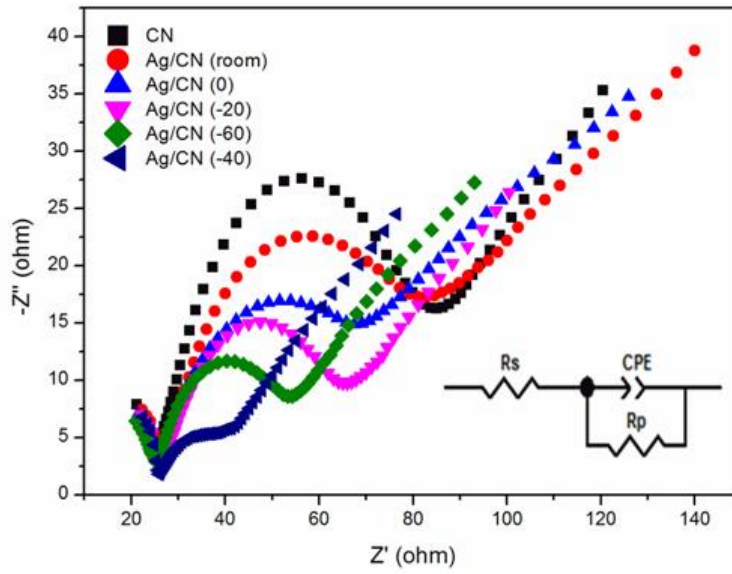


Figure. S3. EIS changes for the samples.

$$\eta = \left( \frac{B}{A} \right) \times 100\%$$

$$A = A_0 \cdot S_A$$

$$B = \frac{n \cdot h}{S_0}$$

$$h = 5 \cdot h_0$$

$$n = \frac{S}{S_{Ag_5}}$$

$$S = \alpha \cdot S_{BET} \cdot \omega$$

$$S_{Ag_5} = \pi \left( \frac{d}{2} \right)^2$$

Scheme S1 calculation method

$\eta$  : Energy absorption rate, %

$A$  : Energy of laser, mJ

$A_0$  : Laser incident energy per unit area, 5mJ/cm<sup>2</sup> [14]

$S_A$  : The area of the laser-energy window, 0.01cm×0.01cm

$B$  : Energy absorbed by N<sub>2</sub> photofixation, mJ

$h$  : Energy transferred by Ag<sub>5</sub> of Ag/C<sub>3</sub>N<sub>4</sub>(-40), mJ

$h_0$  : Energy transferred by per Ag atom of Ag/C<sub>3</sub>N<sub>4</sub>(-40), mJ (1eV=1.6 × 10<sup>-16</sup>mJ )

$n$  : The number of Ag<sub>5</sub>

$S$  : The total surface area of Ag<sub>5</sub>, mJ/cm<sup>2</sup>

$\alpha$  : The area ratio of Ag<sub>5</sub> to the BET surface area of Ag/C<sub>3</sub>N<sub>4</sub>(-40), 0.1(calculated by TEM mapping)

$S_{BET}$  : The BET surface area of Ag/C<sub>3</sub>N<sub>4</sub>(-40), 1.2· 10<sup>5</sup>cm<sup>2</sup>/g(12m<sup>2</sup>/g)

$\omega$  : The average unit mass of catalyst for TEM mapping, 0.001g

$S_{Ag_5}$  : The surface area of each Ag<sub>5</sub>, cm<sup>2</sup>

$d$  : The diameter of Ag NPs, cm