Electronic supplementary information for

Charge Carrier Kinetics of Carbon Nitride Colloid: Femtosecond Transient Absorption Spectroscopy Study

Huiyu Zhang, Yaping Chen, Rong Lu, Ruiyu Li and Anchi Yu*

Department of Chemistry, Renmin University of China, Beijing 100872, People's Republic of China

*To whom correspondence should be addressed: E-mail: a.yu@chem.ruc.edu.cn

Sample preparation

Carbon nitride (CN) was synthesized according to the procedure described by Thomas et al.[S1] Briefly, 10 g dicyandiamide (DCDA) was put into a close crucible and was heated to a designed temperature of 550 ^{o}C with a 2.3 ^{o}C·min^{-1} ramp rate, where it was held for 4 h. After cooling to room temperature, the respective product was milled into a fine powder in an agate mortar for further characterization and measurement.

CN Colloid was produced according to the reported method by Panasiuk et al.,[S2] where bulk CN was dispersed in 1.36 M $N(CH_2CH_3)_4OH$ aqueous solution at about 100 ^{o}C. In our typical procedure, 0.25 g bulk CN was mixed with 5.00 ml 1.36 M $N(CH_2CH_3)_4OH$ aqueous solution and kept for 4 h at boiling temperature (about 100 ^{o}C) with magnetic stirring and using a reflux condenser to avoid water evaporation. The bulk CN was completely dissolved and gives a stable and optically transparent solution.

Experimetal methods

Characterizations UV-vis diffuse reflectance spectrum was recorded on a Shimadzu UV-3600 spectrophotometer equipped with a diffuse reflectance accessory, where its absorption spectrum was referenced to $BaSO_4$. Steady-state fluorescence emission and excitation spectra were recorded on an Edinburgh FLS 980 spectrometer equipped with an integration sphere accessory. FTIR spectrum was recorded on a Brucker Tensor 27 Spectrometer. AFM image was recorded on a Bruker Dimension Icon microscope.

Femtosecond transient absorption spectroscopy measuremeat Our femtosecond transient absorption spectroscopy setup has been described elsewhere.[S3] Briefly, the outputs of a Spectra Physics 1 kHz amplified Ti:sapphire laser were used to pump an optical parametric amplifier (OPA) and to generate the white light continuum. The outputs of the OPA or the second harmonic of the outputs of the Spectra Physics 1 kHz amplified Ti:sapphire laser were used as the pump pulses, and the white light continuum generated by a spinning fused silica disk were used as the probe pulses. The timing between the pump and probe pulses was controlled using a Newport M-ILS250CC motorized translation stage. The polarization of the pump pulses was set at 54.7° with respect to the polarization of the probe pulses to get rid of the molecular reorientation effect. The time resolution of this apparatus was about 150 fs. To record the transient spectrum at a certain delay time, we used a Spec-10:400B CCD, which was coupled to the axial output port of a Princeton Instruments SP2358 monochromator, as the detector. A shutter was used to sequentially block and unblock the pump beam for an equal amount of time (~0.5 s). During the open and closed cycles, the spectra of the probe light were collected and averaged, and the net spectrum with the pump opened was divided by the net spectrum with the pump blocked. The logarithm of the ratio yielded the absolute magnitude of the pump-induced transient absorption difference spectrum.

Picosecond time-resolved fluorescence spectroscopy measurement The time-resolved fluorescence was measured using a home-made time correlated single photon counting apparatus.[S4] Briefly, the second harmonic (395) of the output of a Spectra Physics 1 kHz amplified Ti:sapphire laser or the output (440-560 nm) of an OPA pumped by a Spectra Physics 1 kHz amplified Ti:sapphire laser was used as the excitation source. The emission was collected and sent into a Princeton Instruments SP2358 monochromator and detected with a Hamamatsu R3809U-50 MCP-PMT. Next the signal from the R3809U-50 MCP-PMT was amplified by a Becher & Hickl GmbH HFAC-26 preamplifier. Then the output of the HFAC-26 preamplifier and the output of a fast PicoQuant TDA 200 photodiode were respectively connected to a Becher & Hickl GmbH SPC-130 module as the start and stop pulses. Magic angle detection was used to get rid of the molecular reorientation effect. The instrumental response function (IRF) of this setup was about 70 ps.

Additional Figures

The UV-Vis diffuse reflectance spectrum of the prepared bulk CN solids used in this study is shown in Figure S1, which is well in agreement with the previous reports.[S1,S5,S6] From the Tauc plot shown in inset of Figure S1, it is determined that the band gap of our prepared bulk CN is about 2.76 eV.

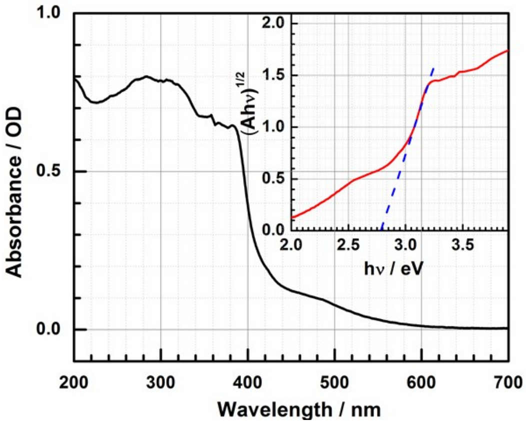

Figure S1 UV-Vis diffuse reflectance spectrum of bulk CN synthesized at 550 $^{\mathrm{o}}$C. Inset is its Tauc plot.

The fluorescence excitation spectrum of CN colloid at different fluorescence emission wavelengths is shown in Figure S2. The fluorescence excitation spectrum shown in Figure S2 clearly reveals at least three absorption bands, which one located in the wavelength range of 200-280 nm, one located in the wavelength range of 290-360 nm, and one located in the wavelength range of 370-510 nm. When comparing the obtained fluorescence excitation spectrum at emission wavelength of 460 nm with that at emission wavelength of 515 nm (Figure S3), it is further found that the absorption band of CN colloid in the wavelength range of 370-510 nm also include two absorption bands.

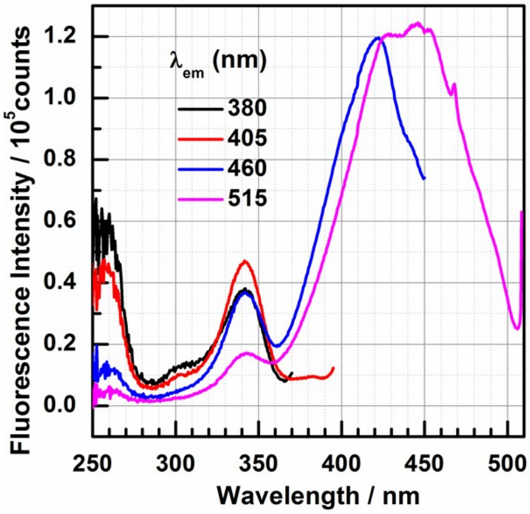

Figure S2 Fluorescence excitation spectrum of CN colloid at different fluorescence emission wavelengths.

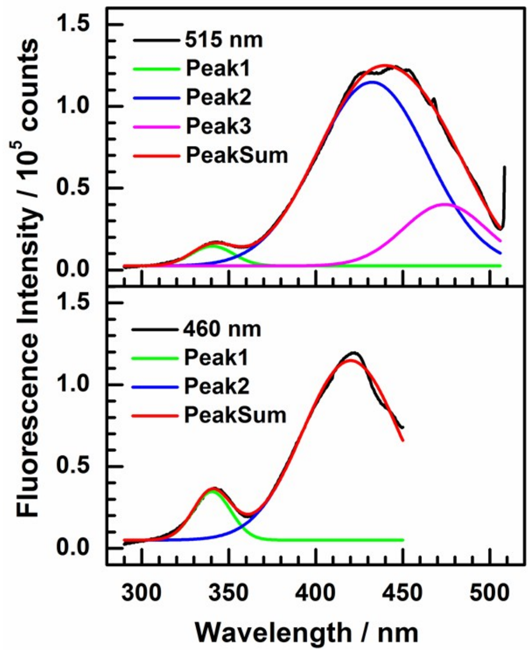

Figure S3 Gaussian peak fits for the fluorescence excitation spectrum of CN colloid at different fluorescence emission wavelengths.

Figure S4 shows the electrochemical absorption spectrum of CN colloid under different anodic electrical biases. The obtained electrochemical absorption spectrum of CN colloid under 2V anodic electrical bias is very similar as the reported transient absorption spectrum of the photogenerated hole of CN by Ye et al.[S7]

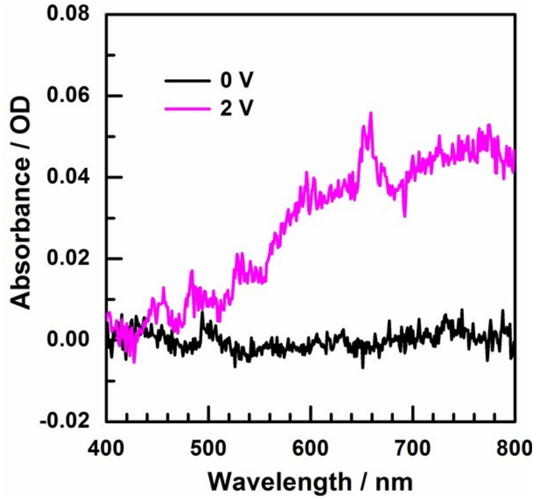

Figure S4 Electrochemical absorption spectrum of CN colloid in aqueous solution under different anodic electrical biases

References

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