Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Electronic Supplementary Information for Directional electrons delivery *via* vertical channel between g-C_3N_4 layers promoting the photocatalysis efficiency

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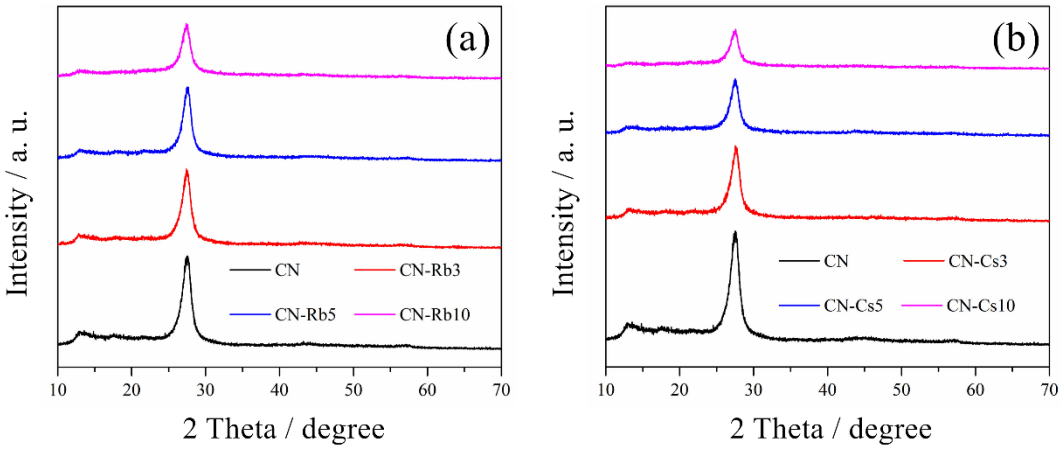

Figure S1. XRD patterns of CN-Rb (a) and CN-Cs (b) with different doping content.

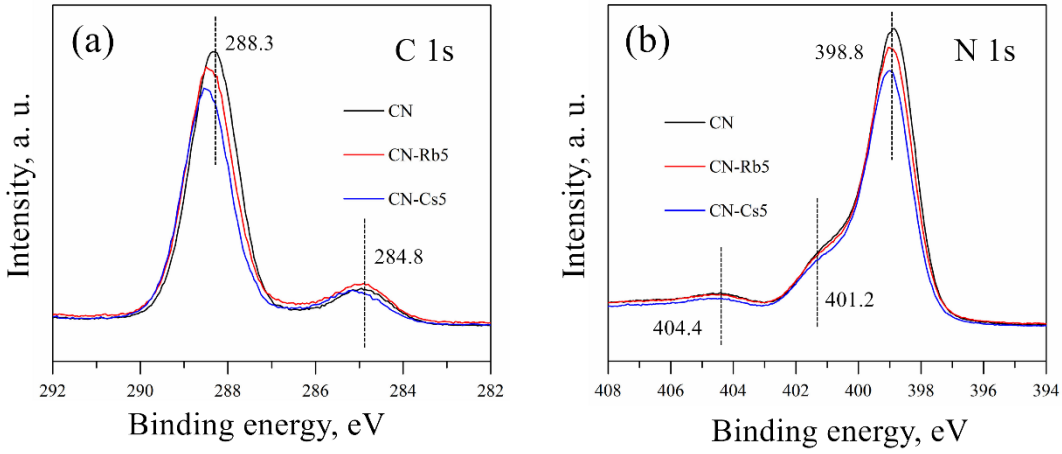

Figure S2. XPS spectra of C 1s (a) and N 1s (b) in CN, CN-Rb5 and CN-Cs5, respectively.

In Figure S2a, the two bonding states of carbon species are observed with the C 1s binding energy of *ca.* 284.8 and 288.3 eV, which are assigned as the surface C-C bonds in plane and the sp^2 hybridized C-N bonds.[1] Moreover, the predominant peaks at a binding energy of 398.8 eV (Figure S2b) can be ascribed to the sp^2 nitrogen involved in the triazine rings (C−N=C). Whereas the other two peaks with binding energies of 401.2 and 404.4 eV are assigned to the N−H groups and the charging effects about the π-excitations, separately.[2] The slight shift of the binding energy of

C1s and N1s in CN-Rb5 and CN-Cs5 can be ascribed to the interaction of Rb and Cs into the interlayer of g-C_3N_4.

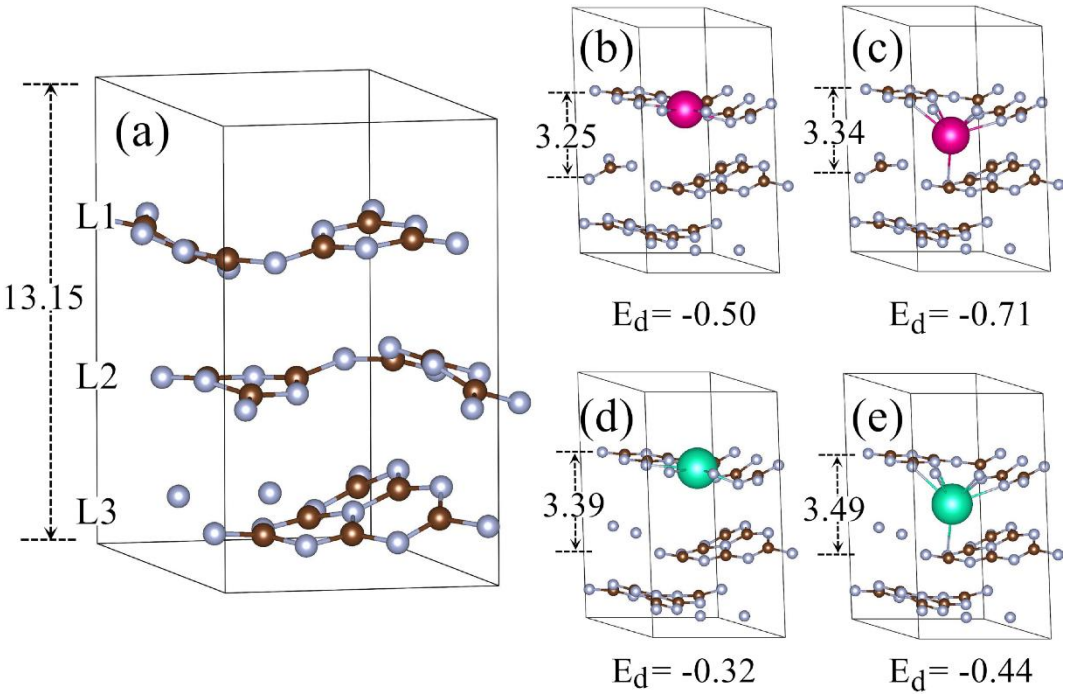

Figure S3. Optimized local calculation model of CN (a), optimized local structures of Rb (b, c) and Cs (d, e) doped CN at in-plane and intercalated sites, correspondingly. The order of CN layers is stipulated as L1-L3 from up to bottom. All the lengths and energies are given in Å and eV, brown, blue, purple, red and green spheres depict C, N, K, Rb and Cs atoms, respectively. E_d stands for the doping energy, negative means heat release.

It is found that Rb and Cs atoms are preferably doped between the CN layers, for the E_d of the intercalated structures (Figure S3c and S3e) are obviously lower than that of the in-plane ones (Figure S3b and S3d). Besides, the crystal structure of CN is not changed *via* Rb/Cs interaction.

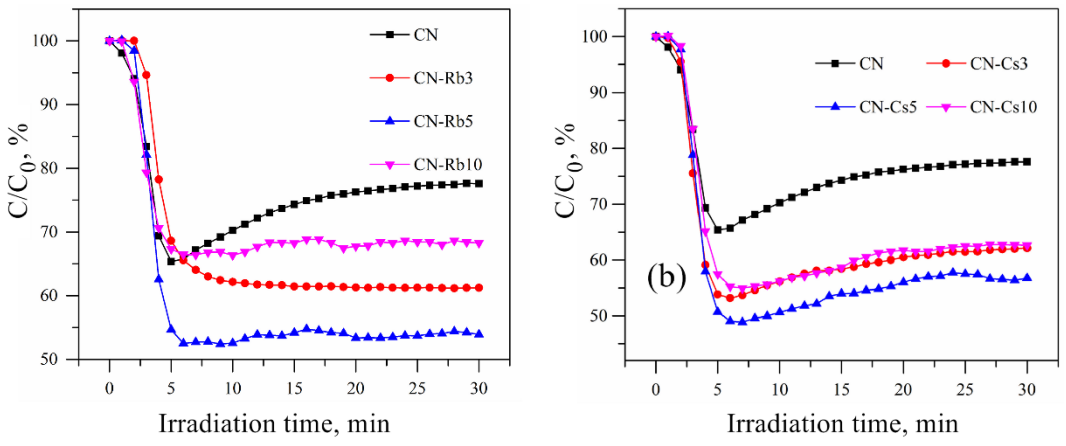

Figure S4. Comparison of visible photocatalytic activity of CN-Rb (a) and CN-Cs (b) over the individual CN, respectively at different doping content.

The reaction mechanism of photocatalytic removal of NO by g-C_3N_4 (eqs S1-S7):

$$g\text{-}C_3N_4 + h\nu \rightarrow e^- + h^+ \quad (S1)$$

$$e^- + O_2 \rightarrow {}^{\bullet}O_2^- \quad (S2)$$

$${}^{\bullet}O_2^- + 2H^+ + e^- \rightarrow H_2O_2 \quad (S3)$$

$$H_2O_2 + e^- \rightarrow {}^{\bullet}OH + OH^- \quad (S4)$$

$$NO + {}^{\bullet}O_2^- \rightarrow NO_3^- \quad (S5)$$

$$2{}^{\bullet}OH + NO \rightarrow NO_2 + H_2O \quad (S6)$$

$$NO_2 + {}^{\bullet}OH \rightarrow NO_3^- + H^+ \quad (S7)$$

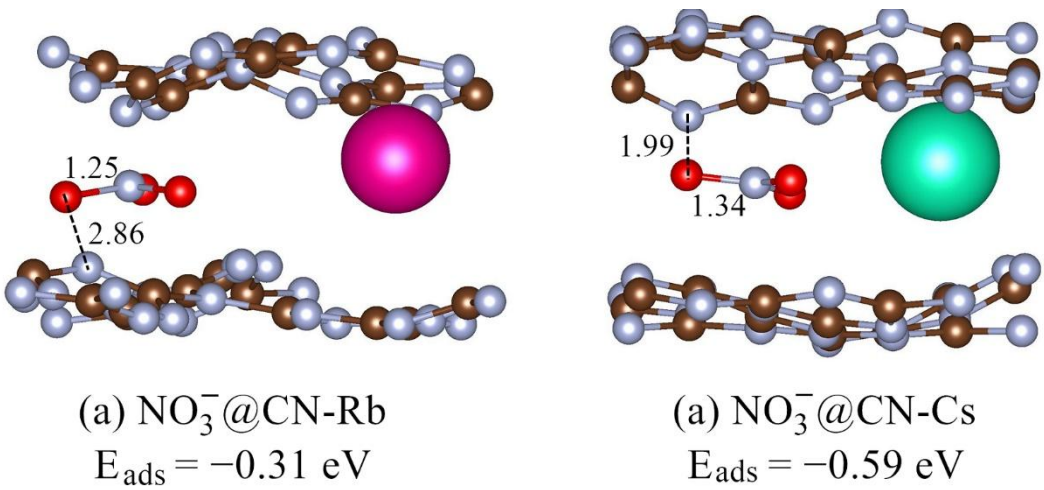

Figure S5. NO_3^- adsorption at the interlayer at CN-Rb (a) and CN-Cs (b). E_{ads}

refers to the absorption energy (equ S2) and negative means heat release. All the lengths and energies are given in Å and eV, brown, blue, red, purple, red and green spheres depict C, N, O, K, Rb and Cs atoms, respectively.

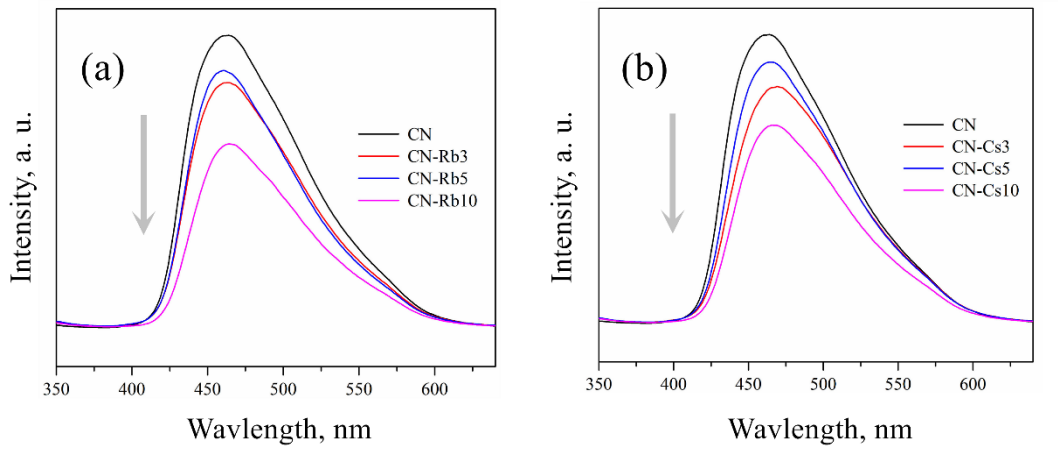

Figure S6. PL spectra of CN-Rb (a) and CN-Cs (b) at different doping content, compared with the individual CN.

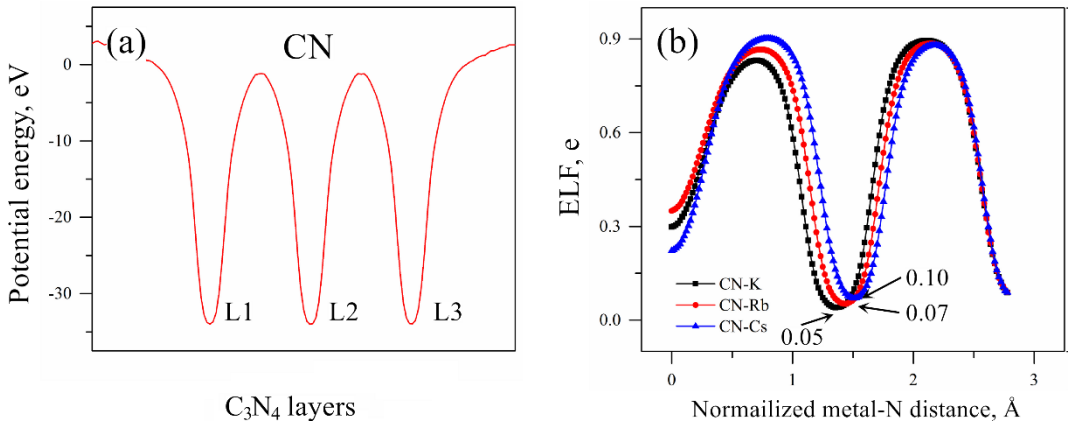

Figure S7. Electrostatic potential for individual CN (a) and ELF difference among CN-K, CN-Rb and CN-Cs.

It is observed in Fig. S8a that there is no obvious potential difference between the layers the individual CN, manifesting no preferable tendency for interlayer electrons transfer. Fig. S8b quantitatively demonstrates that the minimal covalence is increased in the order of CN-K (0.05 e) < CN-Rb (0.07 e) < CN-Cs (0.10 e).

Table S1. Calculated results corresponding to Figure 3c-f

Configuration	ΔE_{L1-L2} [a], eV	ΔE_{L2-L3} [a], eV	ELF [b]	Δq [c], e
CN	0.02	0.01	–	–
CN-K	0.03	3.63	0.05	1.14
CN-Rb	0.85	4.25	0.07	3.83
CN-Cs	0.95	5.01	0.10	5.96

a: Electrostatic potential energy difference between neighboring CN layers.

b: ELF difference between metal atoms and N atoms (Figure S7b).

c: Δq stands for the total charge of metal atoms and is calculated with Bader method.[3]

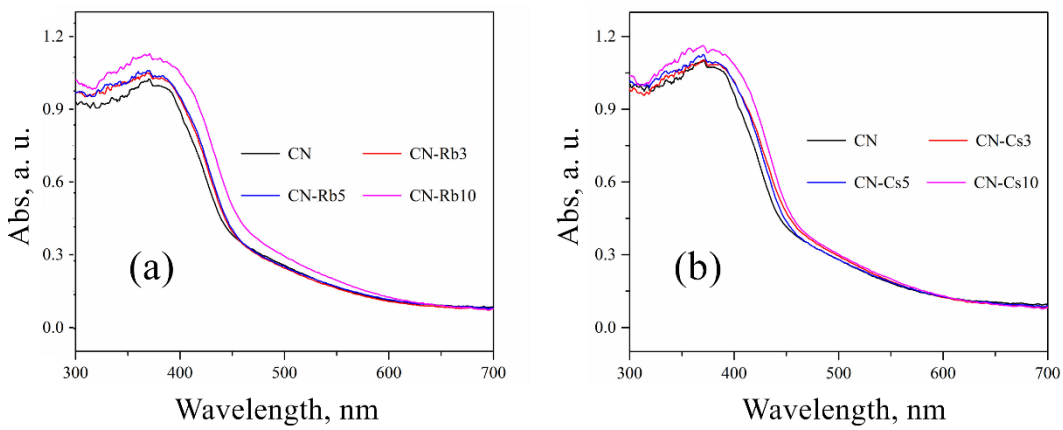

Figure S8. UV-vis spectra of CN-Rb (a) and CN-Cs (b) at different doping content over the individual CN.

References:

[1] S. Cao, J. Low, J. Yu, M. Jaroniec, *Adv. Mater.* **2015**, *27*, 2150-2176.

[2] G. Zhang, J. Zhang, M. Zhang, X. J. Wang, *J. Mater. Chem.* **2012**, *22*, 8083-8091.

[3] R. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford Unverisity Press, **1994**.