Electronic Supplementary Information (ESI)

Non-Covalent Doping of Graphitic Carbon Nitride Polymer with Graphene: Controlled Electronic Structure and Enhanced Optoelectronic Conversion

Yuanjian Zhang,[a] Toshiyuki Mori,[a] Li Niu,*[b] and Jinhua Ye[a]*

[a]International Center for Young Scientists (ICYS), International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044 Japan, Email: ZHANG.Yuanjian@nims.go.jp

[b]Engineering Laboratory for Modern Analytical Techniques, c/o State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Renming street 5625, Changchun 130022, P. R. China, E-mail: lniu@ciac.jl.cn

Experimental

Preparation of graphene oxide (GO) by a modified Hummer's method[1]: Typically, natural graphite flake (1 g, Alfa) was mixed with H_2SO_4 (98%, 34 mL, Wako) and $NaNO_3$ (0.74 g, Wako, JIS special grade) and vigorously stirred in an ice-water bath. $KMnO_4$ (99%, 5 g, Nacalai) was later slowly added, and the temperature was kept at less than 20 ^oC. Then, it was stirred for 3 hrs at 35 ^oC. After that, 250 mL of water and 4 mL of H_2O_2 (30 wt.%, Wako) was further added slowly. The obtained bright yellow suspension was washed 5 times with HCl (1:10 v/v, Wako) and water. The solid (GO) was finally dried in vacuum at 60 ^oC overnight. The GO suspension was prepared by ultrasonic dispersion of GO solid in water (1 mg/mL) for 2 hrs. The trace aggregate was removed by centrifugation at 10,000 rpm for 15 min. The concentration of the final GO solution was a little lower than 1 mg/mL, but was supposed to be 1 mg/mL in the graphene-doped carbon nitride preparation. Ultra-pure water (18.2 MΩ) was used in all experiments.

Preparation of rGO-doped g-C_3N_4: GO aqueous solution (1 mg/mL) was mixed with dicyandiamide (DCDA, 99%, Nacalai) with different weight ratios, and then was concentrated into a paste at 150 ^oC on a hot plate. After that the obtained paste was put into a crucible and heated to 550 ^oC in 4 hrs and kept at this temperature for another 4 hrs in air or Ar atmosphere. Pristine g-C_3N_4 was prepared by heating only DCDA under the same heating program according to our previous report.[2] Before characterization, all bulk samples were hand-grinded with an agate mortar.

Characterization: XRD patterns were recorded on a RINT-ultra3 diffractometer (Cu Kα radiation, Rigaku, Japan). The IR spectra were collected with a Nicolet 4700 FTIR spectrometer (Thermo, USA), equipped

with an attenuated total reflection (ATR) setup. SEM images were measured on a Hatachi S-4800 (15 kV, Japan), equipped with an EDAX 7593-H (Horiba, England). AFM measurements were performed on a SPI4000 (Seiko, Japan) in dynamic force microscopy (DFM) mode at optimal force. A rectangular shaped silicon cantilever (SI-DF20, f=129 kHz, c=14N/m, Seiko) was used for imaging. For AFM observation, the sample was prepared by soaking a Si substrate (pretreated with a 4 mM 3-aminopropyltriethoxysilane aqueous solution for 20 min) in the GO suspension for 5 min, rising with water and then blow-drying with nitrogen flow. TEM and high resolution TEM images were obtained on a JEM2100F (200 kV, Japan) equipped with an EELS spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-2500PC UV-vis spectrometer with a diffuse reflectance accessory, and $BaSO_4$ was used as the reference sample (100% reflectance). X-ray Photoelectron Spectroscopy (XPS) experiments were performed in a Theta probe (Thermo Fisher) using monochromated Al Kα X-rays at hυ = 1486.6 eV. Peak positions were internally referenced to the C_{1s} peak at 284.6 eV. TGA measurements were performed on Shimadzu DTG-60H in air or SII Exstar 6000 (TG-DTA 6200) in N_2. In the control TAG experiments, the reduced graphene oxide (rGO) was prepared by stirring a GO solution (20 mL, 1 mg/mL) with a strong reduction reagent, hydrazine monohydrate (98+%, 10 mL, Wako), at 80 ^{o}C overnight, washing with water, and drying in vacuum at 60 ^{o}C overnight. The Brunauer-Emmett-Teller (BET) surface area was obtained by nitrogen sorption experiments conducting at 77 K using a Micromeritics TriStar II 3020 automated gas adsorption analyzer.

Photoelectrochemical experiments were performed in a conventional three-electrode cell with a platinum wire as the auxiliary electrode and an Ag/AgCl (saturated KCl) as the reference electrode on a CHI 650A workstation (USA). A solar simulator (AM 1.5G, Peccell, Japan) was used as the light source. The light energy density in the vicinity of the photoelectrodes was measured by a USHIO energy meter (USR-40D-B, Japan) to be ca. 84 mW/cm^2 (200-800 nm). The photoelectrode (working electrode, 0.49 cm^2) was inserted in a 0.1 M KCl aqueous solution with the glass side facing the incident light. The photoelectrode was prepared by spreading aqueous slurries of various rGO-doped or pristine g-C_3N_4 on ITO glass (10 ohm/cm^2) with a glass rod, using adhesive tapes as spaces. It was dried in air and then annealed at 150 ^{o}C for 10 min. The suspension was prepared by grinding 5 mg of doped or pristine C_3N_4, 10 μL of PEDOT-PSS (Sigma-Aldrich, 1.3-1.7%) aqueous solution and 50 μL of water.

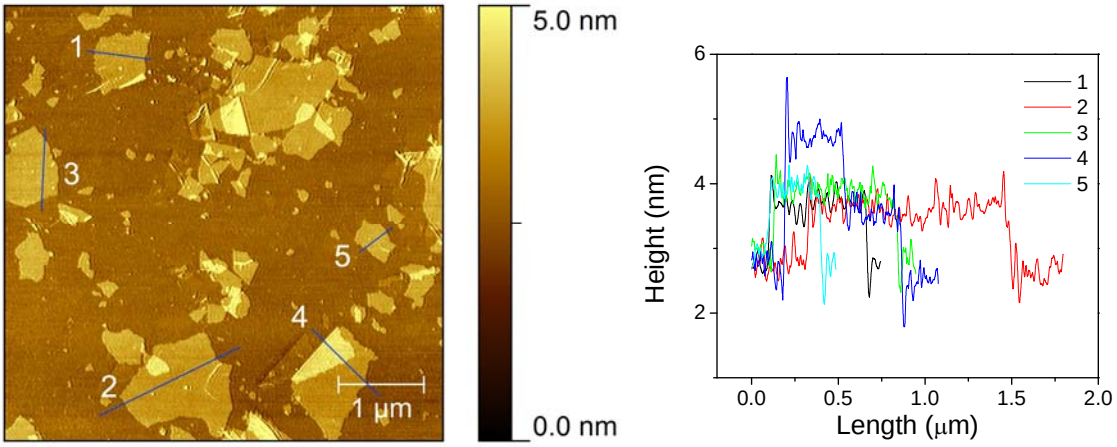

Figure S1. AFM image of the GO sheets and the height profiles (1-5). Most sheets were blow 1 nm, indicating they were of single layer.

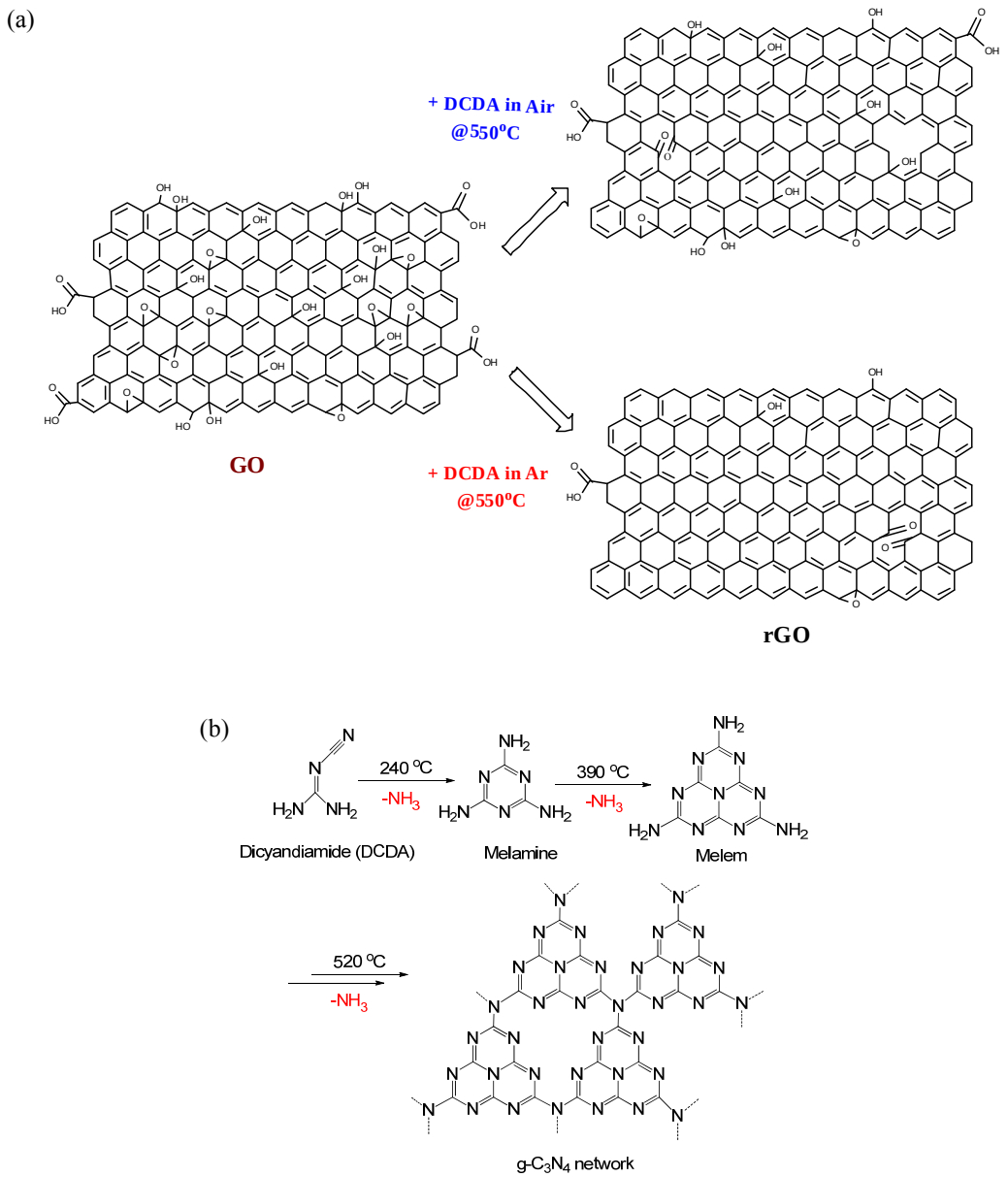

Figure S2. (a) Scheme of GO and that after the reduction in air or Ar atmospheres, respectively. The amount of oxygen defects in rGO prepared in Ar was less than that prepared in air (see elemental analysis in Table S1). (b) Proposed reaction pathway of condensation of dicyandiamide (DCDA) into g-C_3N_4. The byproduct, NH_3, promoted the reduction of GO.

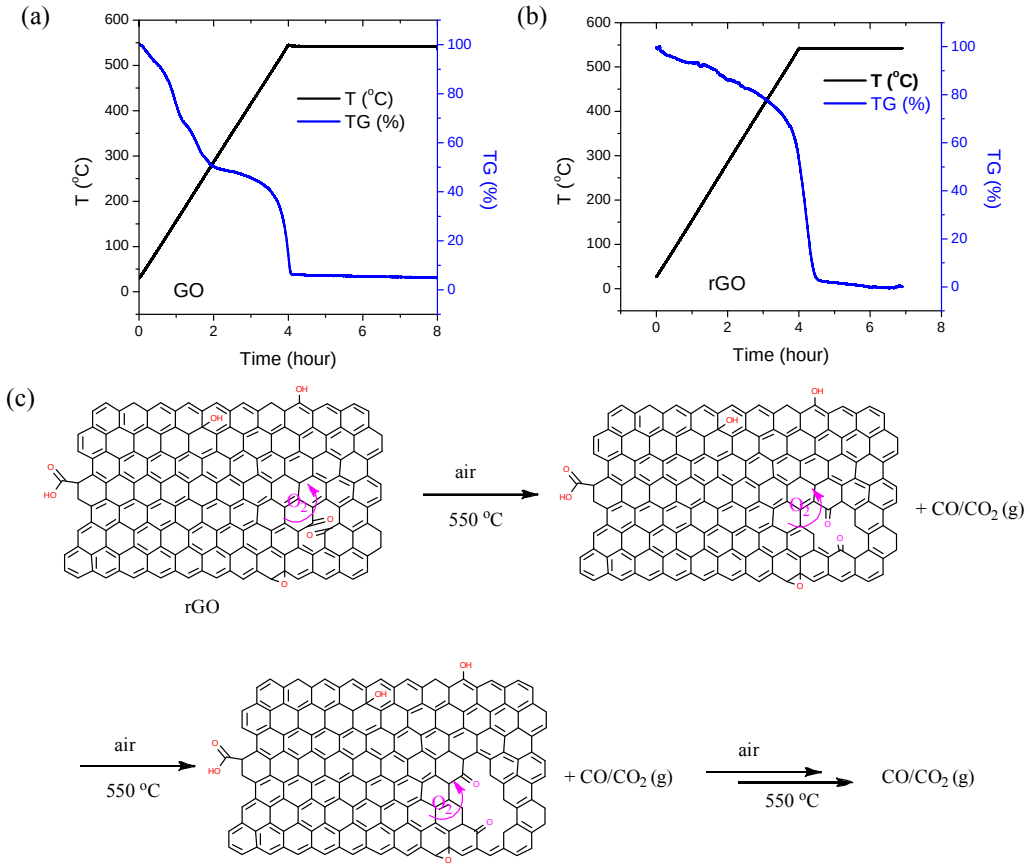

Figure S3. TGA curves of GO (a) and rGO (b) in air. The air flow was 20 mL/min. The heat program was the same as that for the preparation of rGO-doped g-C_3N_4 in air (heating from room temperature to 550 °C in 4 hrs and keeping at 550 °C for another 4 hrs). Proposed domino-like self-decomposition of rGO initiated by the oxygen-defects at 550 °C in air (c).

The TGA curves (Figure S3a, b) showed that both GO and rGO decomposed into gases in the absence of DCDA under the thermal treatment in air. This was because some oxygen residuals in GO, such as some carbonyl groups, were hardly removed even when annealed in H_2 at higher temperature such as 1500 °C.[3] In this case, if GO or rGO was heated in air at high temperature, these oxygen defects would initiate a domino-like self-decomposition (Figure S3c).[4] In contrast, rGO could survive if it was intercalated into g-C_3N_4 during the co-thermal condensation of DCDA at the same temperature in air. Therefore, it implicated g-C_3N_4 might have a strong interaction with rGO, presumably via a stacked structure, which protected rGO against oxidation in air at 550 °C.

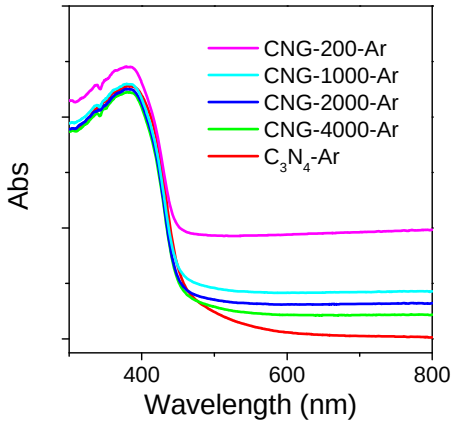

Figure S4. UV-vis absorption spectra of rGO-doped (CNG-n-Ar) and pristine g-C_3N_4 prepared in Ar.

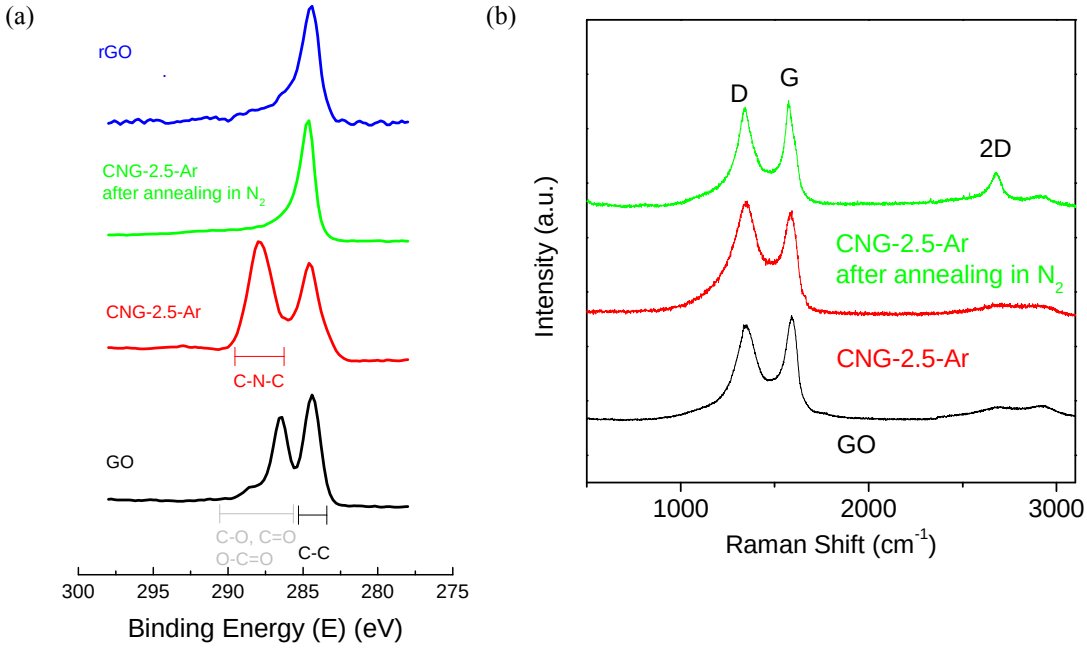

Figure S5. XPS (a) and Raman (b) spectra of GO, CNG-2.5-Ar, CNG-2.5-Ar after annealing in N_2, and rGO

The characteristic sp^2 C-C structure in GO before and after the reduction was investigated by Raman spectra (Fig. S5b). In all cases, it displayed two prominent peaks around 1340 and 1590 cm^{-1} that were contributed to the D and G bands, respectively. Similar to previous studies,[5] the small increase of the ratio of the D/G intensity after the reduction, indicated the deoxygenation of GO and the increase of smaller graphene domains during the reaction.

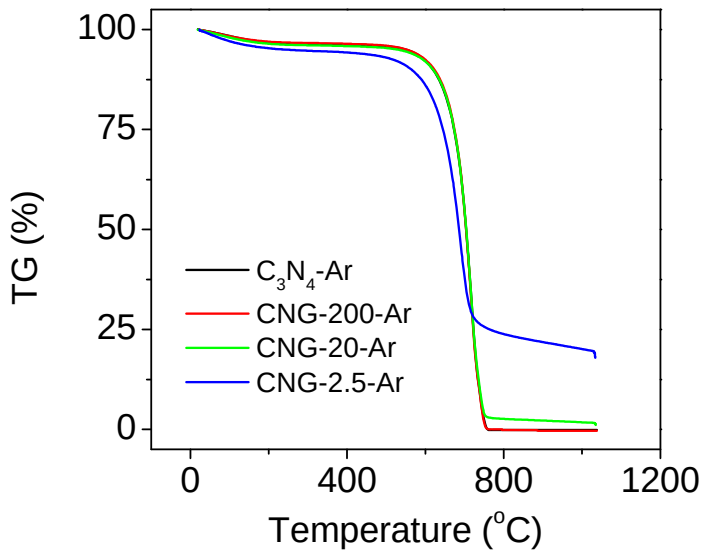

Figure S6. TGA curves of rGO-doped and pristine g-C_3N_4 prepared in Ar (N_2 flow: 30 mL/min, heating rate: 10 °C/min).

It seemed strange that the decomposition temperature of rGO-doped g-C_3N_4 was lower than that pristine g-C_3N_4 in N_2, especially when the concentration of rGO increased. Ideally, graphene should "protect" g-C_3N_4 from decomposition at such a high temperature. However, oxygen-defects in the rGO were not completely removed by the co-thermal treatment with DCDA at 550 °C. Therefore, some residual oxygen-defects would initial a self-decomposition at high temperature, resulting in a lower stability. Moreover, the TGA curve of CNG-2.5-Ar shows that the residual carbon is around 20wt.% after heating to 1000 °C. This was compatible with the result of the EELS quantification (Fig. 3a inset, rGO wt.% ~40%).

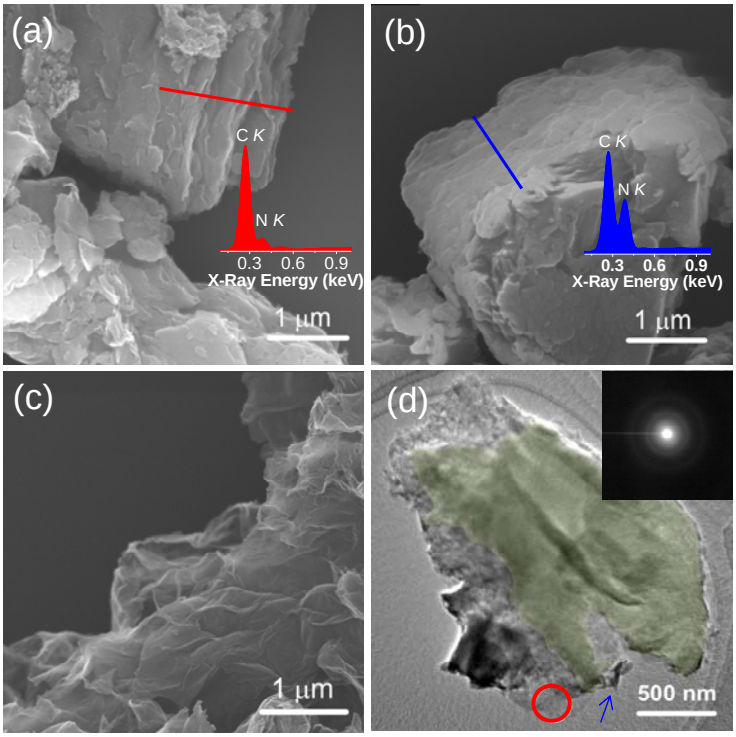

Figure S7 SEM images of (a) rGO-doped g-C_3N_4 (CNG-2.5-Ar), and (b) g-C_3N_4-Ar, inset: quantitative EDX line scans of the edges, which indicated the C/N ratio of CNG-2.5-Ar was higher than that of pristine g-C_3N_4 due to the presence of rGO. (c) SEM image of wrinkled rGO sheets exposing from CNG-2.5-Ar by heating in N_2 at 1000 ^{o}C. (d) Low resolution TEM image of CNG-2.5-Ar. The top layer is indicated by pale yellow. The blue arrow suggests the layered edge profile. And the inset depicts the selected-area (marked by red circle) election diffraction (SAED) pattern of a graphitic structure (see more complementary evidences for the layered structure in XRD and high resolution TEM image in Figure 3)

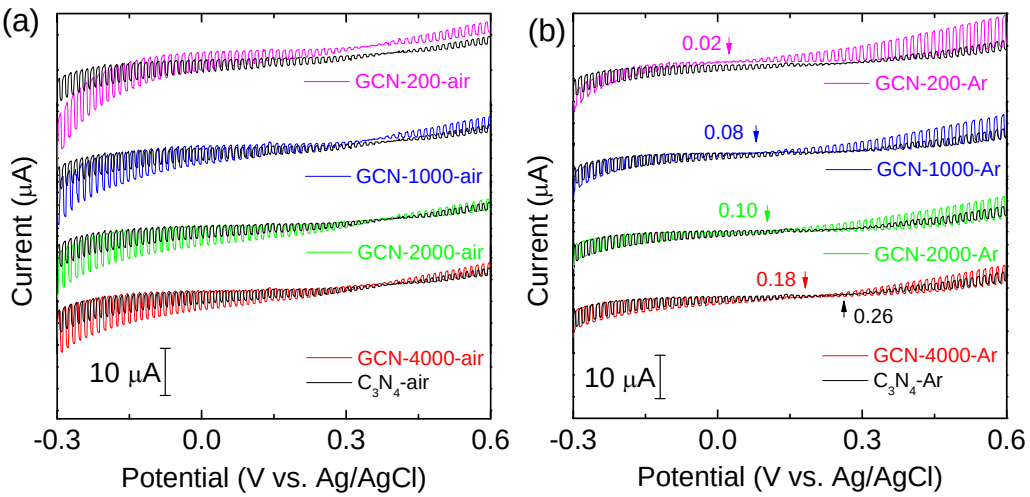

Figure S8 Photovoltammograms of rGO-doped g-C_3N_4 (rGO wt% ≤1 %) under chopped light (AM 1.5 G) in 0.1 M KCl aqueous solution, scan rate: 10 mV/s. The arrows in (b) indicated the E_{fb}.

It was worthy to note that rGO would also promote charge recombination. Thus, if the concentration of rGO was too much, the large dark current became very high. In this case, heavily doped g-C_3N_4 (n< 200) was not a good candidate for photocurrent conversion (data not shown).

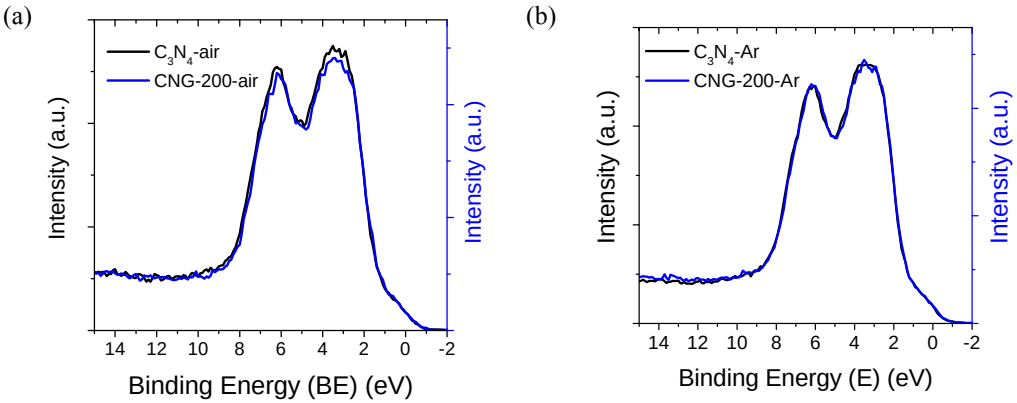

Figure S9. Valence band XPS spectra of rGO-doped and pristine g-C_3N_4 prepared in air (a) and Ar (b).

Table S1 Elemental analysis of oxygen for rGO-doped g-C_3N_4 synthesized in air and Ar

Entry	Product mass (g)[a]	O At. % (XPS)[b]	O At. % (EDX)[b]
CNG-200-air	0.872	12.83	1.12
CNG-200-Ar	0.886	6.22	0.71

[a] 2 g of initial DCDA, [b] Only C, N, and O were considered in calculation.

Table S2 BET surface area of g-C_3N_4 and rGO-doped g-C_3N_4 prepared in air and Ar.

Entry	**BET surface area (m^2/g)**
C_3N_4-air	9.99
CNG-200-air	11.26
CNG-20-air	24.44
C_3N_4-Ar	5.95
CNG-200-Ar	6.11
CNG-20-Ar	6.28

Supporting references

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