Supporting Information

**Construction of K+ ions gradient in crystalline carbon nitride to accelerate charge separation for efficient** **visible light H2 production**

Guoqiang Zhang,a Yangsen Xu,c Chuanxin He,a,b Yongliang Li,a,b Xiangzhong Ren,a,b Peixin Zhang,\*,a,b Hongwei Mi\*,a,b

a College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, Guangdong, 518060, PR China

b Guangdong Flexible Wearable Energy and Tools Engineering Technology Research Centre Shenzhen University, Shenzhen, Guangdong, 518060, PR China

c Institute of Microscale Optoelectronics, Shenzhen University, Shenzhen 518060, PR China

\* Correspondence E-mail: pxzhang@szu.edu.cn, milia807@szu.edu.cn

**1. Experimental Section**

* 1. *Chemicals and Materials*

Melamine (99.0%), KCl (AR, 99.5%), H2PtCl6**.**6H2O (AR, Pt≥37.5%) and triethanolamine (TEOA, AR, 98.0%) were purchased from Aladdin Reagent Company. All chemicals were used without further purification.

* 1. *Preparation of* *CN*

Typically, the 50 g of melamine powder is put into a 50 ml of crucible with a cover and then heat to 550℃ at a rate of 2 ℃/min in a muffle furnace and maintain at this temperature for 3 h. CN is obtained after cooling down to room temperature. The mass of CN product is about 23 g. By further grinding CN into powder to facilitate the use of the next step.

* 1. *Preparation of KCN x*

The 1.5 g of CN powder and 10 g of KCl were ground and mixed evenly, and then heat to 600℃ at a rate of 10 ℃/min in a muffle furnace and maintain at this temperature for several hours. The bright yellow products were obtained after cooled to room temperature, washed with plenty of water and dried at 60℃ under vacuum. According to the different maintain time at 600℃, we denote the samples as KCN *x* (*x* = 0.5-4), where *x* is the maintain time.

* 1. *Preparation of CN-U, CN-C, CN-D,* *KCN-U, KCN-C and KCN-D*

Typically, the 30 g of urea/cyanamide/dicyandiamide is put into a 50 ml of crucible with a cover and then heat to 550℃ at a rate of 2 ℃/min in a muffle furnace and maintain at this temperature for 3 h. According to different precursors (urea, cyanamide, dicyandiamide), the products are named CN-U, CN-C and CN-D in turn. Subsequently, the 1.5 g of CN-U/CN-C/CN-D powder and 10 g of KCl were ground and mixed evenly, and then heat to 600℃ at a rate of 10 ℃/min in a muffle furnace and maintain at this temperature for 2 h. The bright yellow products were obtained after cooled to room temperature, washed with plenty of water and dried at 60℃ under vacuum. According to the different precursors, we denote the samples as KCN-U, KCN-C and KCN-D.

* 1. *Characterizations*

The crystalline structure was recorded by using an X-ray diffractometer (XRD) (Empyrean), using Cu K radiation (λ = 1.54056 A). Scanning electron microscope (SEM) images are measured on Hitachi SU8010. Transmission electron microscope (TEM) images were taken using a JEOL JEM-2010 operated at 200 kV. The UV-Vis absorption spectra were recorded on a UV-3600 scanning spectrophotometer (Shimadzu). The Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iz10 spectrometer. Fluorescence emission spectra were recorded on a LabRAM HR Evolution spectrograph. X-ray photoelectron spectrum (XPS) analyses were performed on an ESCALAB 250Xi spectrometer with an Al-Kα (1486.6 eV) achromatic X-ray source. Transient state fluorescence spectra were recorded on an Edinburgh instruments FS5 fluorescence spectrometer. Inductively coupled plasma spectrometry (ICP-OES) was performed on Ultima 2, Horiba. Brunauer-Emmett-Teller (BET) specific surface area was measured using a Micrometrics ASAP 2020 HD88 Surface Area and Pore Size Analyzer. The solid-state 13C NMR spectra were recorded on a Bruker Avance II instrument in cross-polarization magic-angle spinning sequence mode.

* 1. *Photocatalytic H2 production Measurements*

The 50 mg of samples added with H2PtCl6 (3 wt% Pt) is placed into a 50 mL of TEOA solution (20 vol%) in a closed gas circulation system (Beijing Perfectlight, Labsolar-6A). The visible-light irradiations were obtained from a 300 W Xe lamp (Beijing Perfectlight, PLS-SXE300) with a UVCUT-420 nm filter. All tests are controlled at 15℃ by circulating condensate. The evolved gases are detected *in situ* by using an online gas chromatograph (GC9790II, Fuli) equipped with a thermal conductivity detector (TCD).

* 1. *AQE calculations of H2 production*

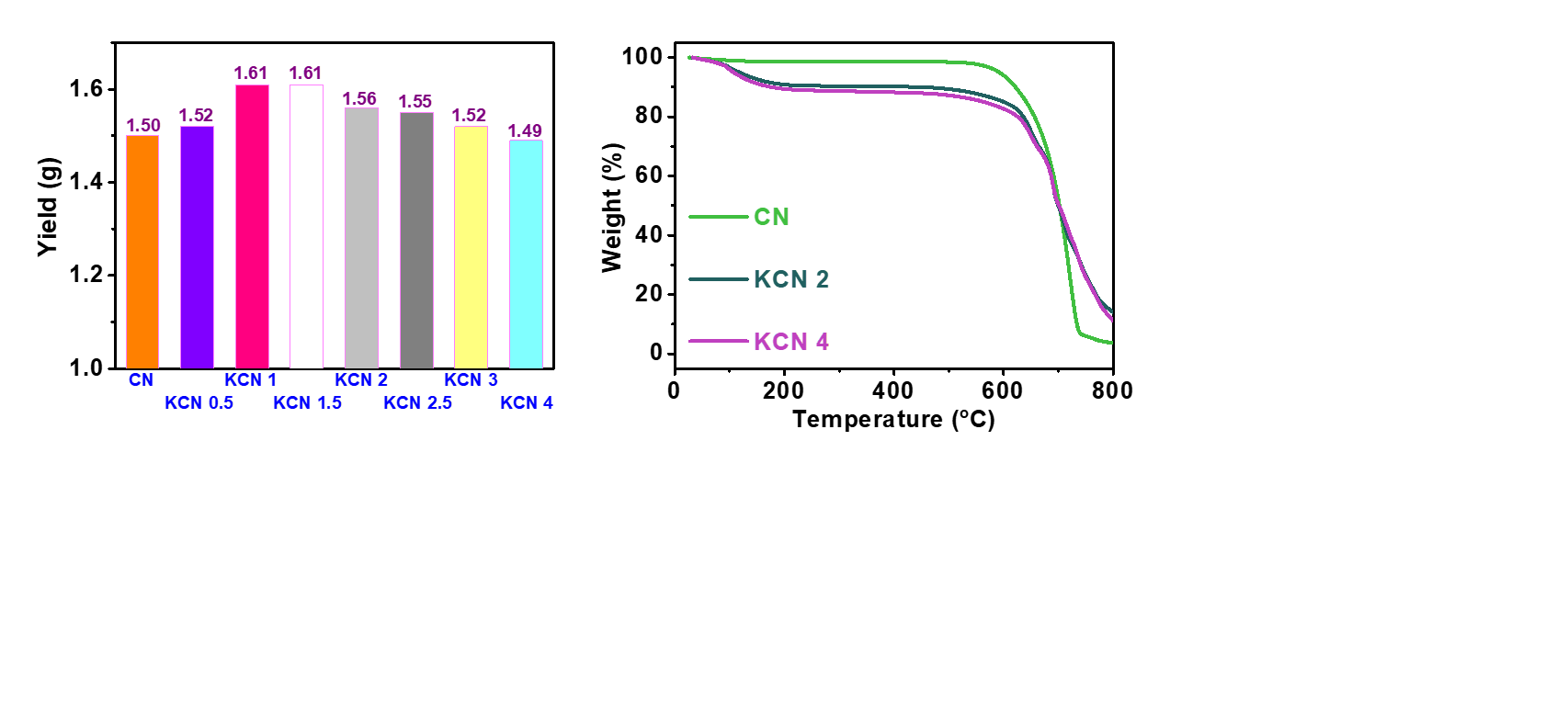
The 100 mg of samples added with H2PtCl6 (3 wt% Pt) is placed into a 50 mL of TEOA solution (20 vol%) in a closed gas circulation system. The catalyst solution was irradiated by a 300W Xe lamp applying bandpass filters (center at 400, 420, 475 and 500 nm) for 2 h. All tests are controlled at 25℃ by circulating condensate. The average intensity of irradiation is determined by an FZ-A spectroradiometer (Photoelectric Instrument Factory of Beijing Normal University). The apparent quantum efficiency (AQE) was calculated from equation:

* 1. *Photo-deposition of* *Pt Nanoparticles*

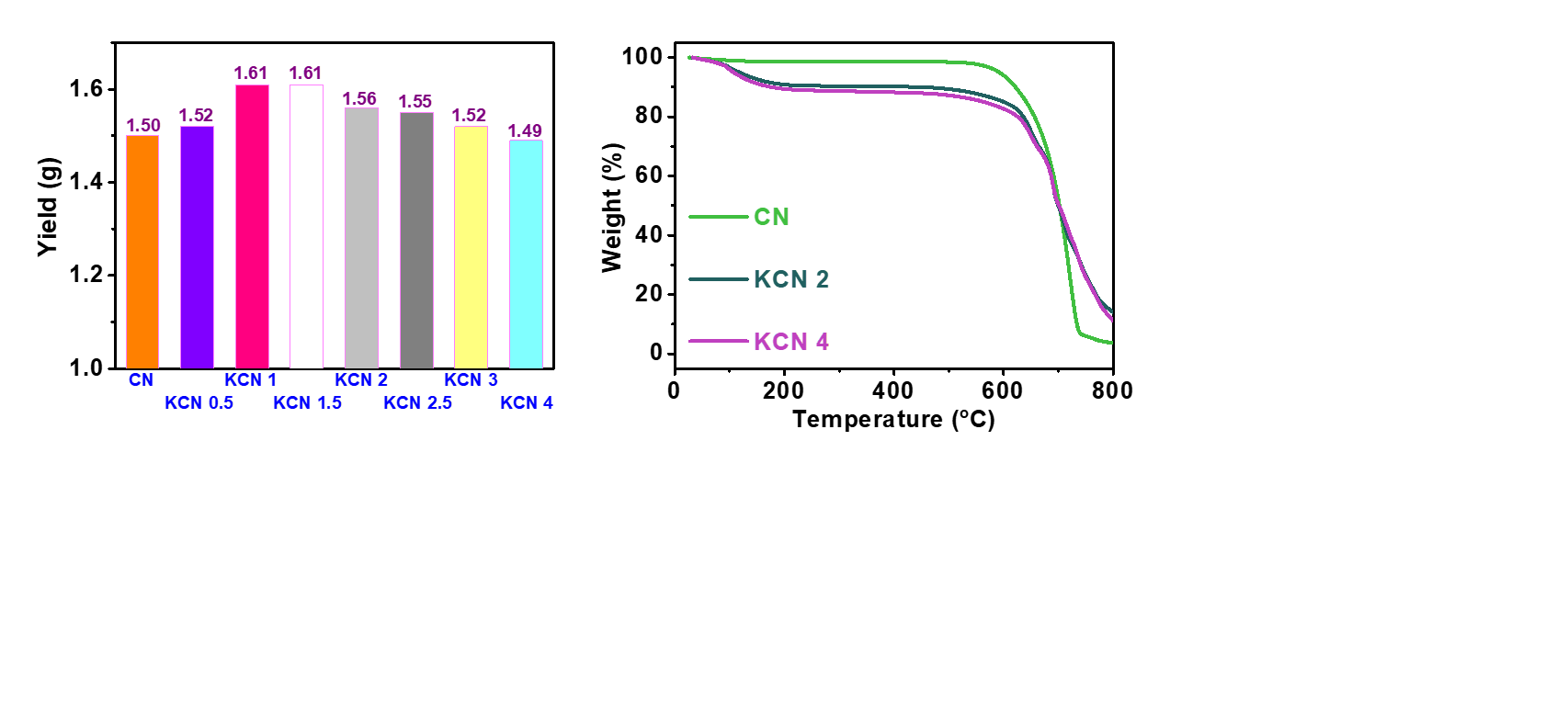
The 50 mg of samples added with H2PtCl6 (3 wt% Pt) is placed into a 50 mL of TEOA solution (20 vol%) in a closed gas circulation system. The catalyst solution was irradiated by a 300W Xe lamp with a UVCUT-420 nm filter for 1 h. All tests are controlled at 15℃ by circulating condensate. The catalyst solution was then tested by TEM to describe the distribution of Pt nanoparticles on the catalyst surface.

* 1. *Surface photovoltage measurements*

Surface photovoltage (SPV) measurement system consisted of a source of monochromatic light, a lock-in ampliﬁer (SR 830-DSP) with a light chopper (SR 540) and a sample chamber. Monochromatic light is provided by a 300 W Xe lamp (PLS-SXE 300, Beijing Trusttech Co. Ltd, China) and a monochromator (SBP500, Zolix). All measurements are operated at room temperature and under ambient pressure and samples are not pretreated prior to the SPV measurement.



**Figure S1.** The mass of obtained samples of CN and KCN *x* (*x* = 0.5-4).



**Figure S2.** The thermogravimetry of CN, KCN 2 and KCN 4.

**Table S1.** The element content in CN, KCN 0.5, KCN 2 and KCN 4 estimated by elemental analysis.

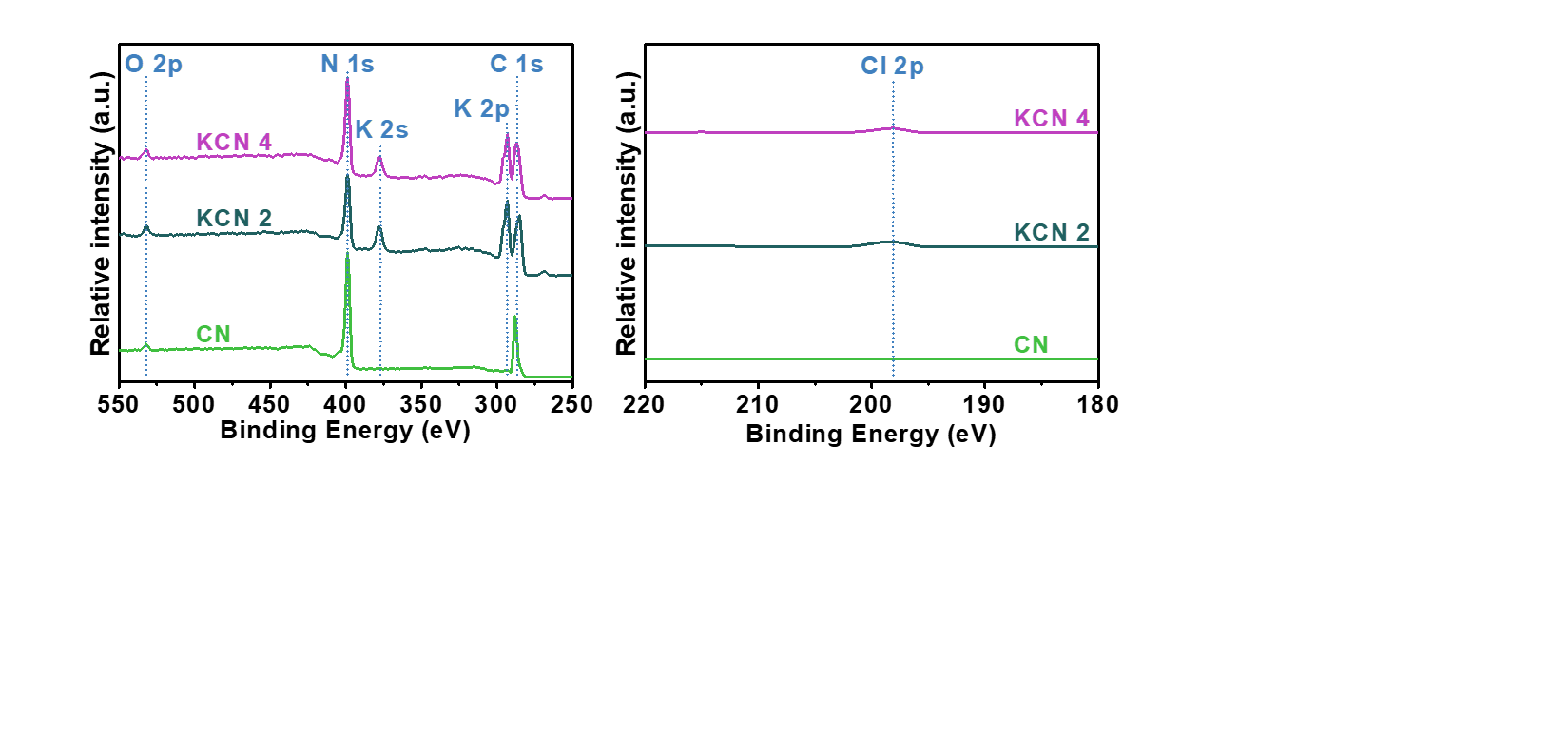
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Elemental analysis | CN | KCN 0.5 | KCN 2 | KCN 4 |
| C (wt%) | 34.31 | 31.43 | 28.71 | 27.02 |
| N (wt%) | 61.28 | 54.88 | 48.65 | 44.18 |
| H (wt%) | 2.19 | 2.05 | 1.70 | 1.53 |
| C/N (mol ratio) | 0.653 | 0.668 | 0.688 | 0.714 |

**Table S2.** The K element content in CN, KCN 0.5, KCN 2 and KCN 4 estimated by ICP-OES.

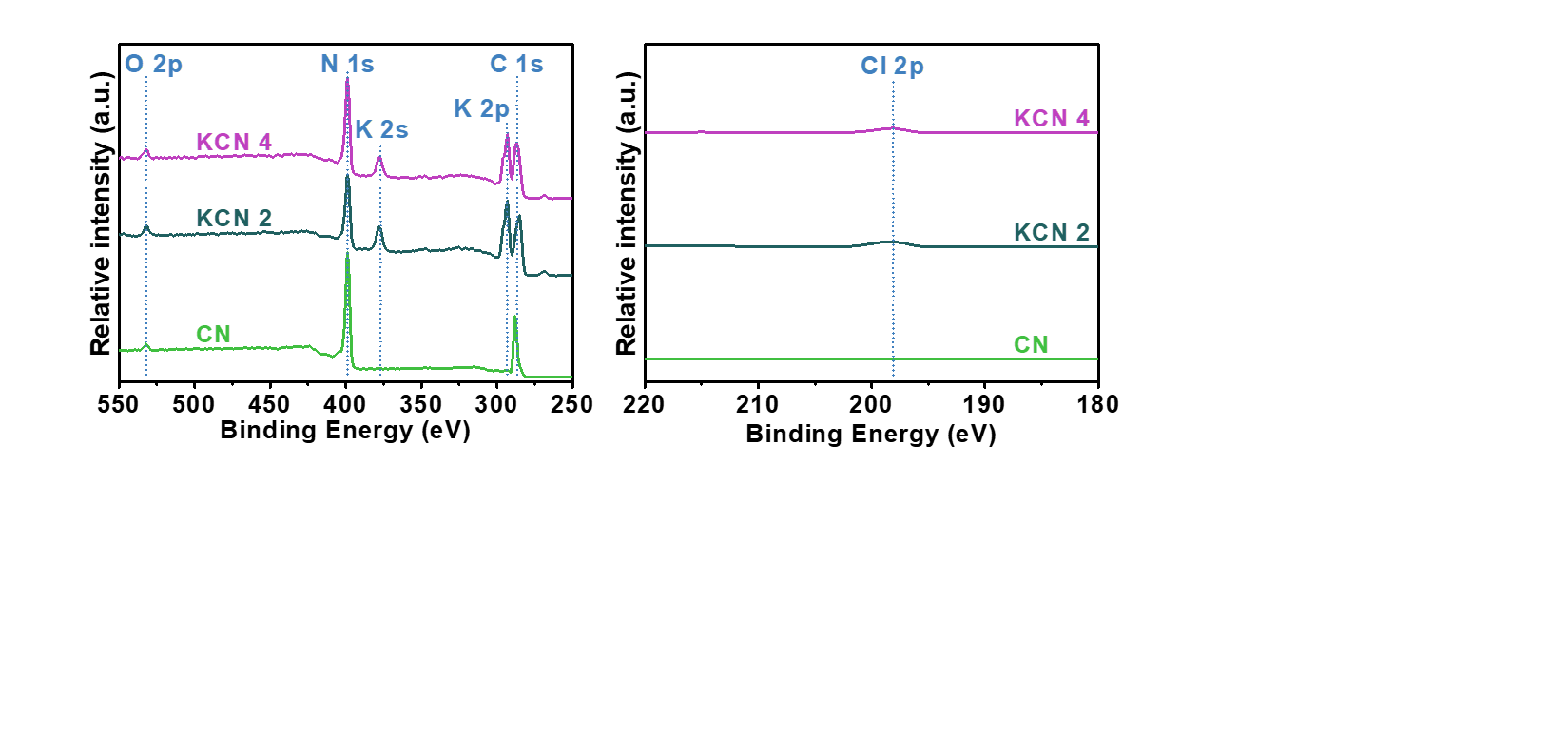
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| ICP | CN | KCN 0.5 | KCN 2 | KCN 4 |
| K (wt%) | Trace | 3.13 | 10.80 | 15.19 |

**Table S3.** The full width at half maxima (FWHM) values of the (0 0 2) diffraction peak of CN and KCN *x* (*x* = 0.5-4) estimated by XRD results in Figure 2a.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| XRD | CN | KCN 0.5 | KCN 1 | KCN 1.5 | KCN 2 | KCN 2.5 | KCN 3 | KCN 4 |
| FWHM (°) | 1.01 | 0.92 | 0.61 | 0.53 | 0.51 | 0.50 | 0.48 | 0.47 |

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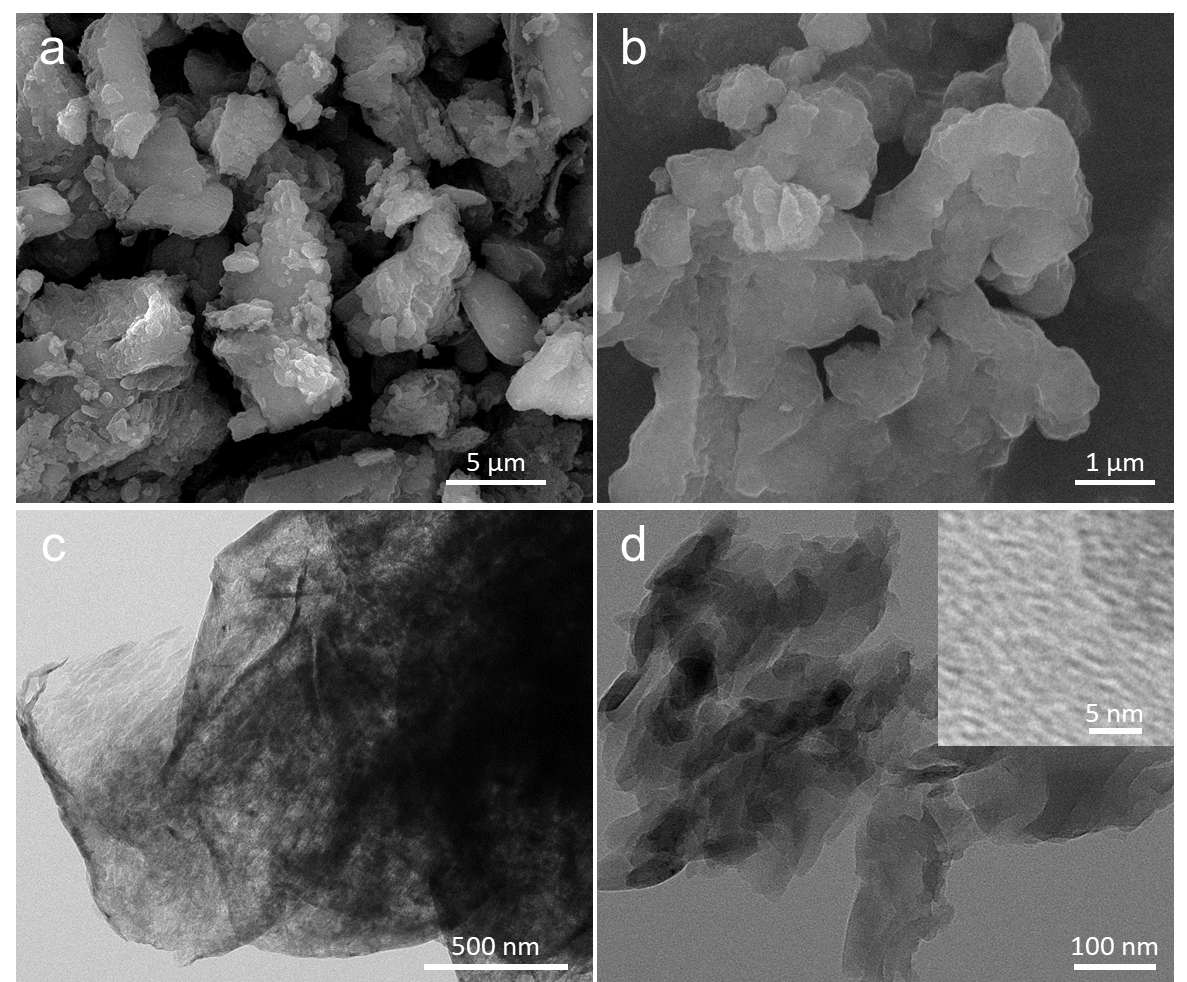
**Figure S3.** The XPS survey spectra of CN, KCN 2 and KCN 4.

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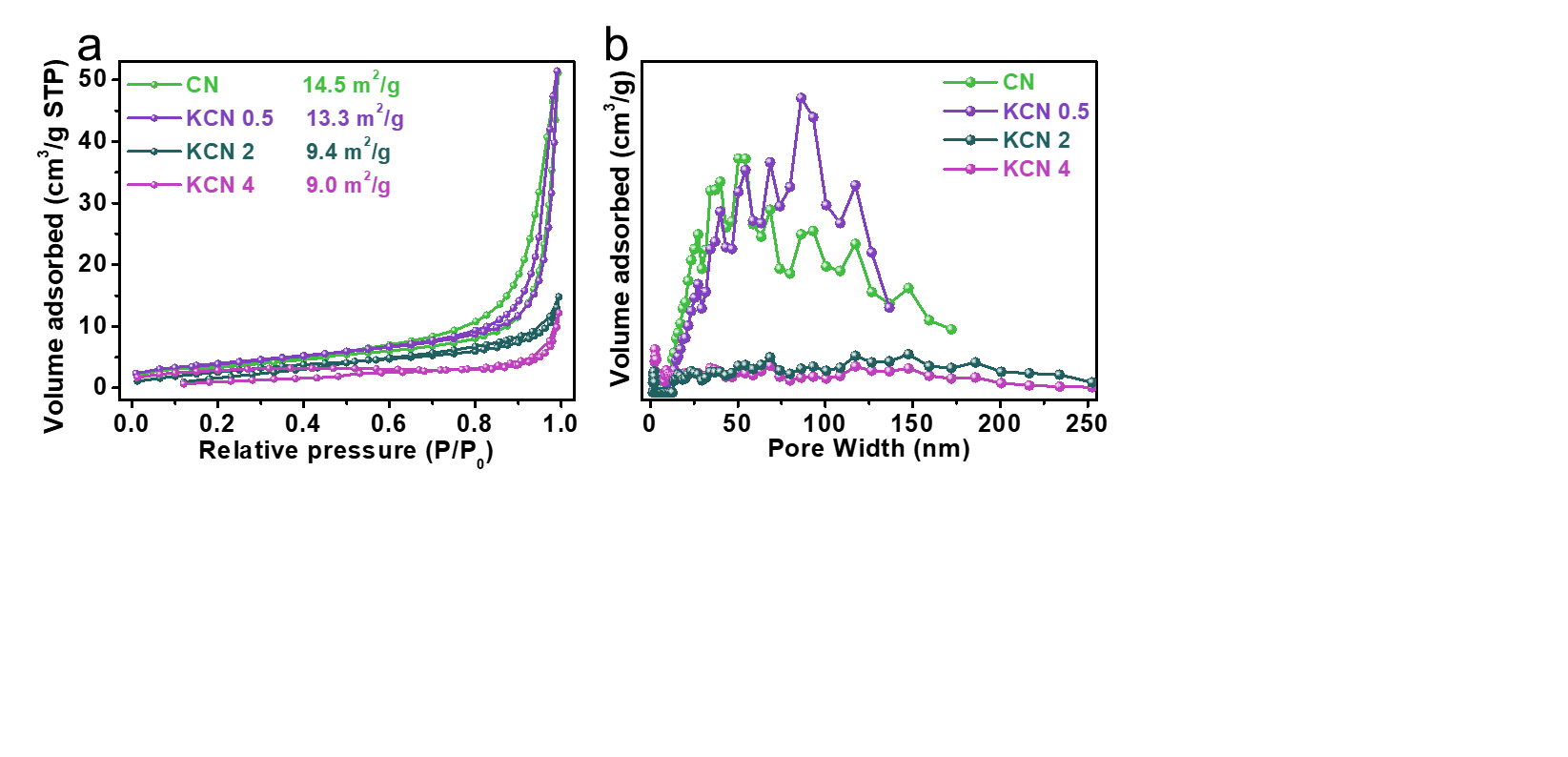
**Figure S4.** The high-resolution Cl 2p XPS spectra of CN, KCN 2 and KCN 4.

**Table S4.** The peak area of N-C=N, C≡N and C-C species, and the ratio of C≡N and graphite carbon in C 1s XPS spectra (Figure 3b) of CN, KCN 2 and KCN 4.

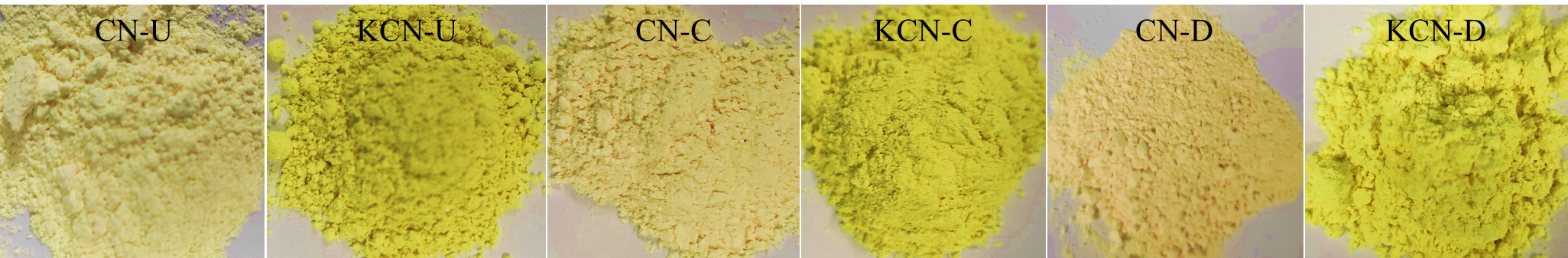
|  |  |  |  |
| --- | --- | --- | --- |
|  | CN | KCN 2 | KCN 4 |
| N-C=N | 43377.82 | 31721.53 | 29599.23 |
| C≡N | - | 2691.34 | 4509.89 |
| C-C | 5082.95 | 5046.77 | 13406.81 |
| Proportion of C≡N | - | 0.07 | 0.09 |
| Proportion of C-C | 0.10 | 0.15 | 0.28 |



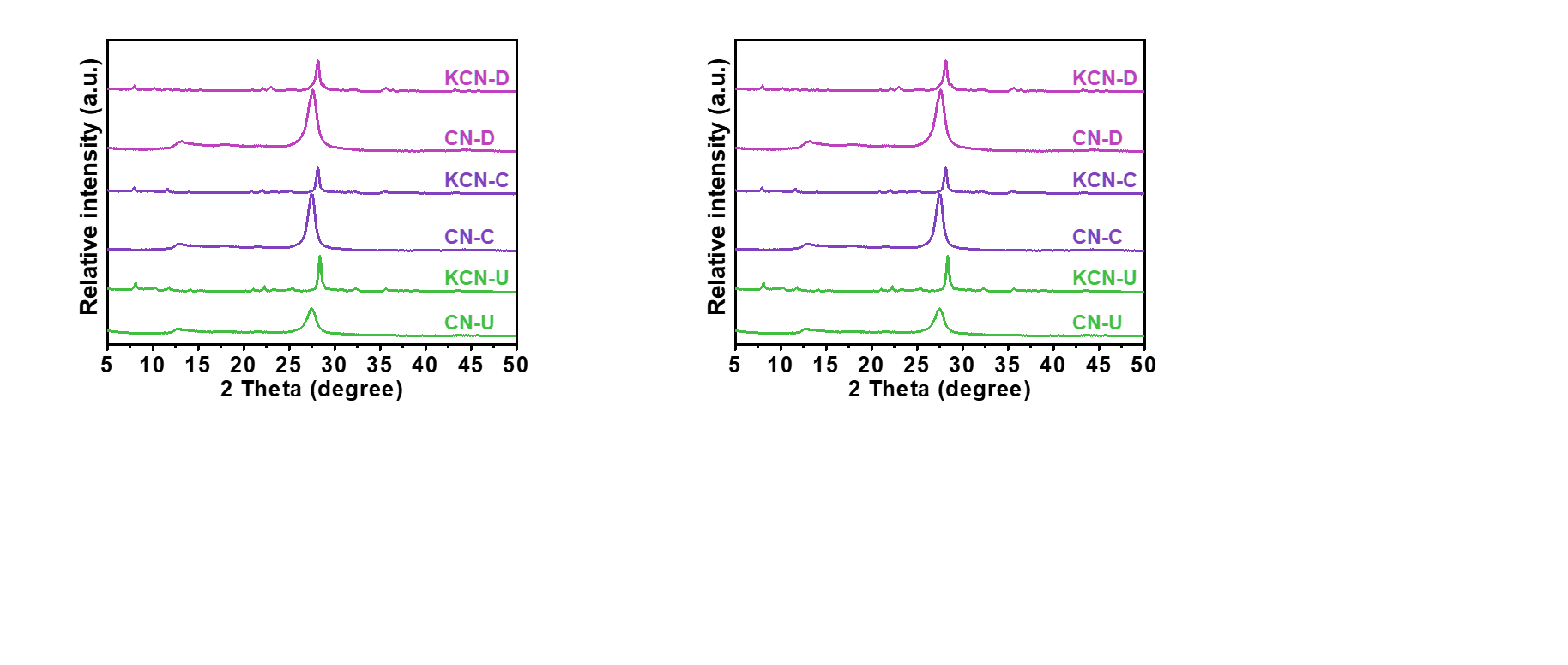
**Figure S5.** The SEM (a-b) and TEM (c-d) images of CN. Inset in (d) is the high-resolution TEM image.



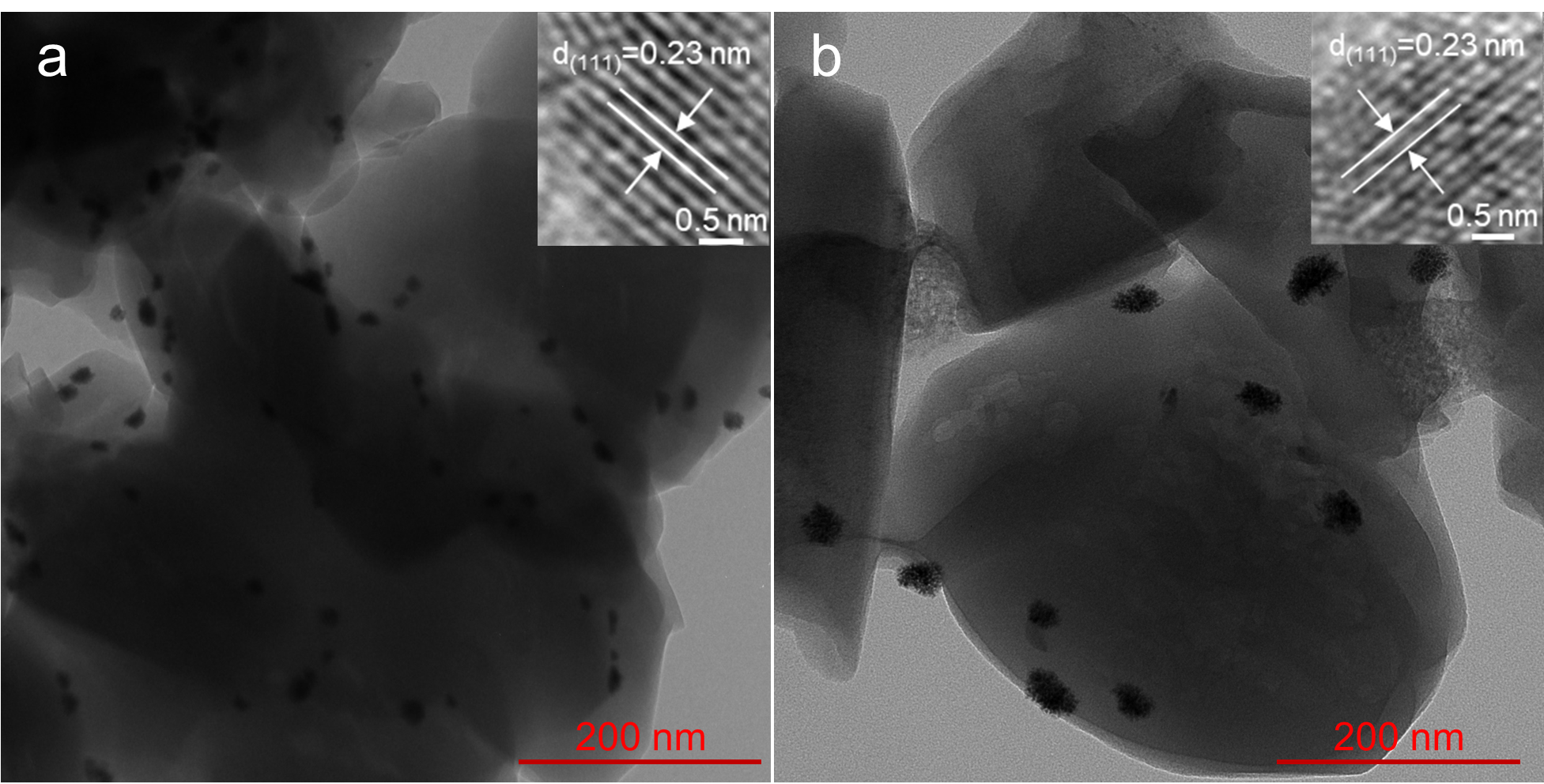
**Figure S6.** The N2 adsorption-desorption isotherms (a) and pore size distribution curves (b) of CN, KCN 0.5, KCN 2 and KCN 4.

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**Figure S7.** The optical images of CN and KCN obtained from different precursors (urea, cyanamide and dicyandiamide).

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**Figure S8.** The XRD patterns of CN and KCN obtained from different precursors (urea, cyanamide and dicyandiamide).



**Figure S9.** TEM images of the photo-deposited Pt nanoparticles on KCN 2 and KCN 4.