

Supplementary Information

**A scalable chemical route to soluble acidified graphitic carbon  
nitride: An ideal precursor for isolated ultrathin g-C<sub>3</sub>N<sub>4</sub> nanosheets**

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**Contents**

**1. Experimental details**

**2. Supporting information for XRD analysis**

**3. High resolution XPS Cl 2p spectra**

**4. FT-IR spectra and UV-vis spectra of the recovered g-C<sub>3</sub>N<sub>4</sub>**

**5. EIS Nyquist plots**

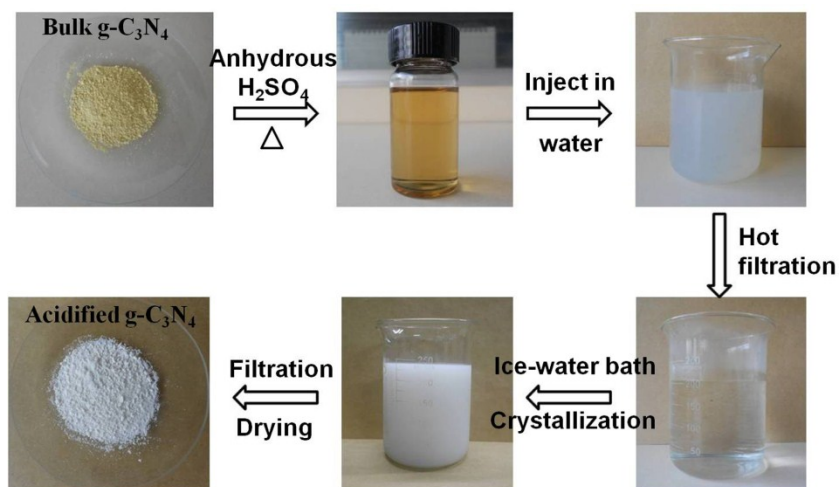
**6. Solubility experiments and results**

**7. TEM and AFM images of dissolved g-C<sub>3</sub>N<sub>4</sub> nanosheets**

**8. Photographs and TEM images of Pt@CNS**

## 1. Experimental details

**Preparation of bulk g-C<sub>3</sub>N<sub>4</sub>:** Bulk g-C<sub>3</sub>N<sub>4</sub> was synthesized according to a previously reported procedure <sup>S1</sup>. In brief, 40 g dicyandiamide was placed into a crucible with a cover and heated to 550 °C for 4 h with a ramp rate of about 2.3 °C /min in a muffle furnace. The obtained yellow product (about 20 g) was subsequently grinded thoroughly for further processing and characterization.



**Figure S1.** Diagrammatic sketch for the exfoliation and acidification procedure of g-C<sub>3</sub>N<sub>4</sub>.

**Preparation of acidified g-C<sub>3</sub>N<sub>4</sub>:** As shown in Figure S1, in a typical synthesis, 4.00 g of yellow bulk g-C<sub>3</sub>N<sub>4</sub> powder, 52 g H<sub>2</sub>SO<sub>4</sub> (98%) <sup>S2</sup>, and 20 g oleum (with free SO<sub>3</sub> 20% ~ 25%) were added into a 100 mL flask successively and stirred at 140 °C for 2 h and 170 °C for 3 h. The obtained transparent yellow sol was natural cooled and then injected into 800 mL of deionized water at 75 °C under stirring (be careful, the injection port need to be below the liquid level). The water gradually turned to be a light white suspension. 85.58 g NH<sub>4</sub>Cl (1.60 mol) was added into the solution afterward, and the solution was maintained stirring at 70 °C for 2 h, allowed to stand for 1h, and then hot filtered to remove residues. The obtained clear and colorless filtrate which was maintained at 70 °C was quickly placed in an ice bath and stirred for 1.5 h. Pure white precipitation generated

and was collected by filter, washed with deionized water and ethanol, and finally dried at 60 °C in vacuo. The obtained pure white fine powder (2.86 g) was acidified g-C<sub>3</sub>N<sub>4</sub>.

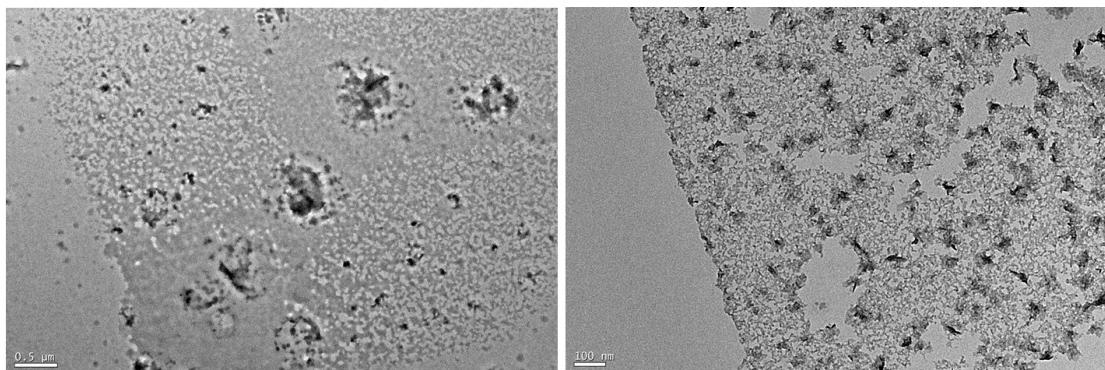
Another sample was prepared as a comparison by similar approach but without adding NH<sub>4</sub>Cl. The sample was denoted as CN-H<sub>2</sub>SO<sub>4</sub>.

The acidified sample was further recrystallized for purification. 1.0 g of acidified g-C<sub>3</sub>N<sub>4</sub> powder was dissolved in 200 mL hydrochloric aqueous solution at 70 °C, and then hot filtered to remove residues. The obtained clear and colorless filtrate which was maintained at 70 °C was quickly placed in an ice bath and stirred for 1.5 h. The product was collected by filter, washed with deionized water and ethanol, and finally dried at 60 °C in vacuo. The recrystallized samples were labeled as R0.5, R1.0, and R2.0 according to the concentration of hydrochloric acid solution (0.5 M, 1.0 M, and 2.0 M respectively).

**Preparation of Pt@CNS:** Pt@CNS was prepared by dissolving H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (7 mg for 5wt.%Pt@CNS, and 24 mg for 15wt.%Pt@CNS) and acidified g-C<sub>3</sub>N<sub>4</sub> (50 mg) in 50 mL of 1.0 M hydrochloric acid aqueous solution, reducing by excess SnCl<sub>2</sub>·2H<sub>2</sub>O (aqueous solution, with a small amount of hydrochloric acid solubilization), precipitating by tuning the pH value of solution to 3 ~ 5, centrifugal washing and drying at 60 °C in air overnight. The product can be dissolved in acidic aqueous solution with pH value of about < 2 (as shown in Figure 5c and Figure S9).

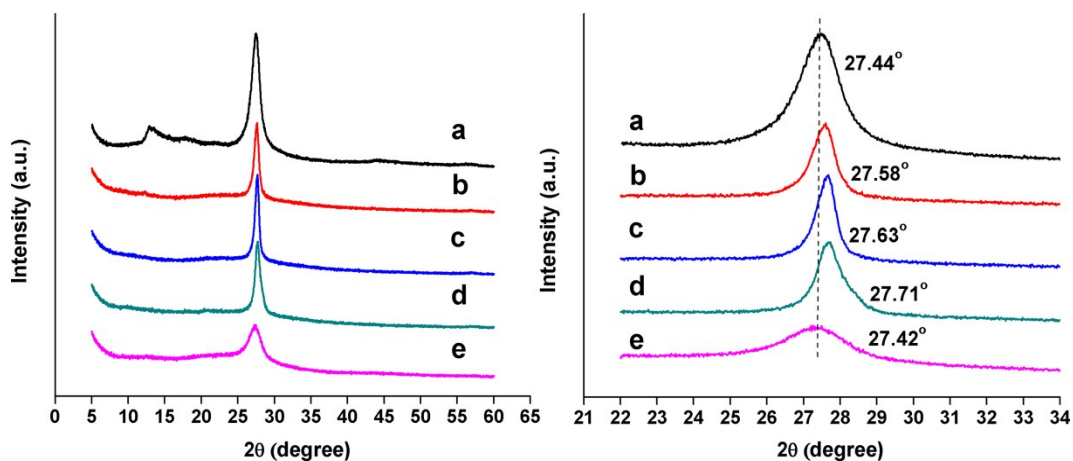
**Material Characterization:** Elemental analysis was performed with a varioEL cube form Elementar Analysensysteme GmbH. For both bulk and acidified g-C<sub>3</sub>N<sub>4</sub>, an average value of the C/N ratio is ca. 0.65, which is consistent with the reported data <sup>S3</sup>. Powder X-ray diffraction (XRD) was performed with a Shimadzu XD-3D X-ray diffractometer with monochromatized Cu-K<sub>α</sub> radiation. X-ray photoelectron spectra (XPS) were taken on a photoelectron spectrometer (VG ESCALAB 210) with a monochromatic X-ray source of Mg K<sub>α</sub> ( $h\nu = 1253.6$  eV), calibrated internally by carbon deposit C (1s) binding energy (BE) at 284.8 eV. The infrared absorption spectra of the samples were recorded by the KBr pellet method on a Fourier transform infrared spectrometer (FTIR; NEXUS 870) in

the range of 500 to 4000  $\text{cm}^{-1}$ . Room-temperature UV-visible diffuse reflectance spectroscopy (DRS) was recorded on a Shimadzu UV-2550 UV-visible spectrophotometer. A white standard of  $\text{BaSO}_4$  was used as a reference. Absorption spectra were calculated from the reflectance data with the Kubelka-Munk function. Transmission electron microscopy (TEM) images were obtained using a TECNAI G<sup>2</sup> F20 field emission transmission electron microscope at an acceleration voltage of 200 kV (the samples were prepared by dropping the dissolved acidified g- $\text{C}_3\text{N}_4$  hydrochloric aqueous solution to carbon film or micro-grid supported by copper mesh.). Atomic force microscopy (AFM) measurements were carried out on a Bruker MultiMode-8 system (The samples were prepared by drop-casting the dissolved acidified g- $\text{C}_3\text{N}_4$  hydrochloric aqueous solution onto fresh silicon surface). The Brunauer-Emmett-Teller (BET) surface area of the catalysts was measured with an ASAP-2010 surface analyzer.



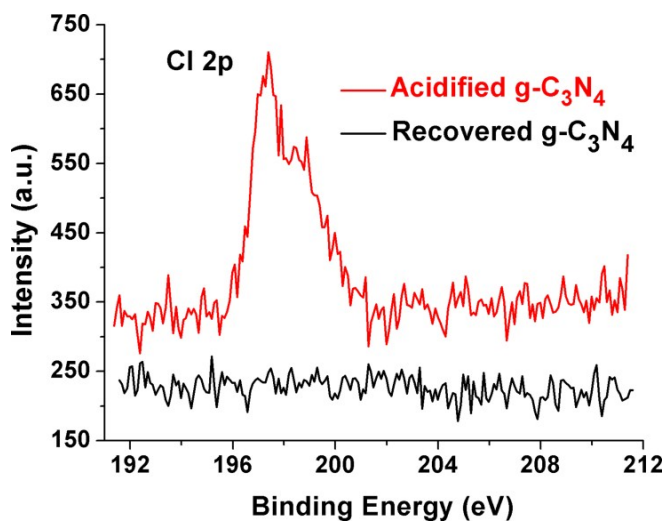
**Figure S2.** TEM images of product that only concentrated  $\text{H}_2\text{SO}_4$  (98 %) was use during the exfoliation-acidification procedure at 140 – 170 °C. It is obvious that g- $\text{C}_3\text{N}_4$  nanosheets were hydrolyzed in the presence of a small amount of water during the process.

## 2. Supporting information for XRD analysis



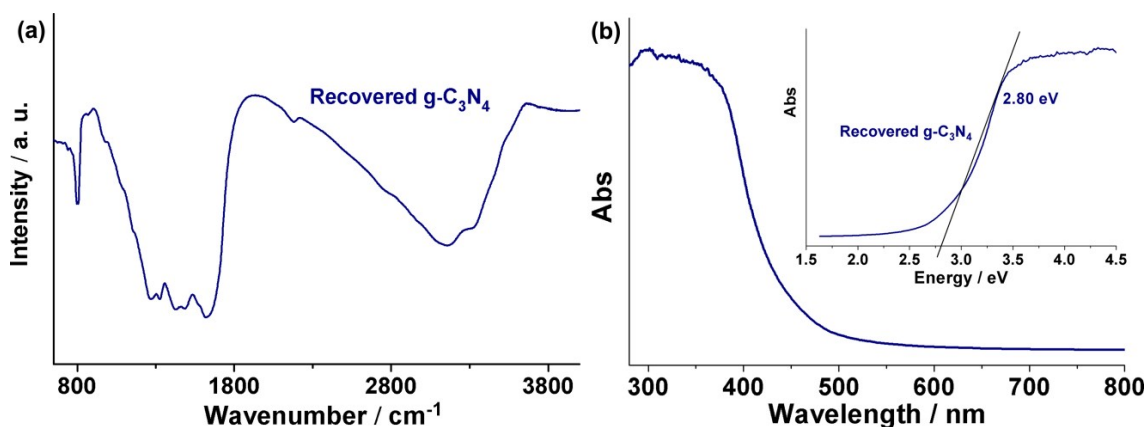
**Figure S3.** XRD patterns (left) and enlarged partial XRD patterns (right) of (a) bulk  $\text{g-C}_3\text{N}_4$ , (b) R0.5, (c) R1.0, (d) R2.0, and (e) recovered  $\text{g-C}_3\text{N}_4$  that obtained by calcinating acidified  $\text{g-C}_3\text{N}_4$  at  $350^\circ\text{C}$  in air for 4 h.

### 3. High resolution XPS Cl 2p spectra



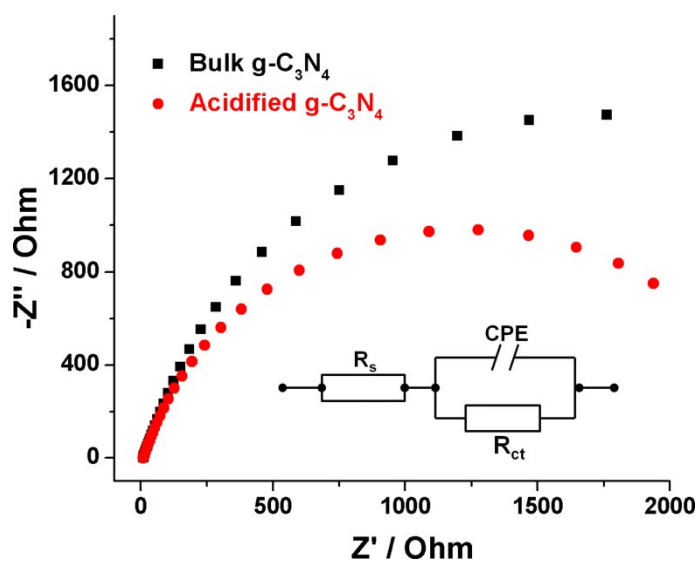
**Figure S4.** The high-resolution XPS Cl 2p spectra of acidified  $\text{g-C}_3\text{N}_4$ , and recovered  $\text{g-C}_3\text{N}_4$  that obtained by calcinating acidified  $\text{g-C}_3\text{N}_4$  at  $350^\circ\text{C}$  in air for 4 h.

### 4. FT-IR spectra and UV-vis spectra of the recovered $\text{g-C}_3\text{N}_4$



**Figure S5.** FT-IR spectra (a) and UV-vis spectra (b) of the recovered  $g\text{-C}_3\text{N}_4$  that obtained by calcinating acidified  $g\text{-C}_3\text{N}_4$  at  $350\text{ }^\circ\text{C}$  in air for 4 h.

## 5. EIS Nyquist plots



**Figure S6.** Nyquist plots of bulk and acidified  $g\text{-C}_3\text{N}_4$  obtained by applying a sine wave with amplitude of  $10.0\text{ mV}$  over the frequency range from  $30\text{ kHz}$  to  $10\text{ mHz}$ . Inset: the equivalent Randle circuit,  $R_s$  is the electrolyte resistance, CPE is the constant phase element for the electrode and electrolyte interface, and  $R_{ct}$  is the interfacial charge transfer resistance across the electrode/electrolyte.

The electrochemical impedance spectroscopy (EIS) measurements were performed on an Autolab PGSTAT302N electrochemical workstation in a three-electrode cell at room temperature. Nickel foam current collectors (1.0 cm × 1.0 cm) deposited with sample (50 mg) film as the working electrode, a saturated calomel electrode as reference electrode, and a Pt wire as counter electrode were used. The aqueous solution of 0.2 M Na<sub>2</sub>SO<sub>4</sub> purged with nitrogen gas was used as the electrolyte.

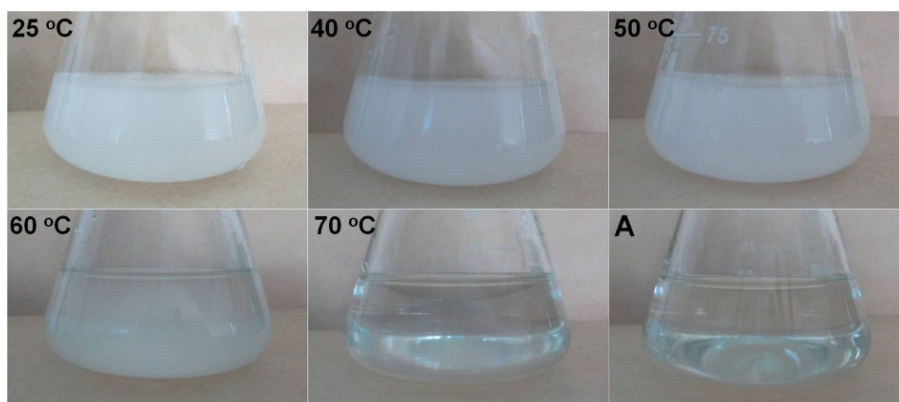
The EIS Nyquist plots will reveal the charge transfer rate of samples. For both the bulk and acidified sample, the expected semicircular plots are presented, while with a smaller diameter for acidified g-C<sub>3</sub>N<sub>4</sub>. The fitted R<sub>ct</sub> values for bulk g-C<sub>3</sub>N<sub>4</sub> and acidified g-C<sub>3</sub>N<sub>4</sub> are 3559 and 2535 Ω, respectively. These results demonstrate more efficient charge transport in acidified g-C<sub>3</sub>N<sub>4</sub>, which is in accordance with the reported results of protonated or exfoliated g-C<sub>3</sub>N<sub>4</sub> nanosheets<sup>S2, S4, S5</sup>.

## 6. Solubility experiments and results

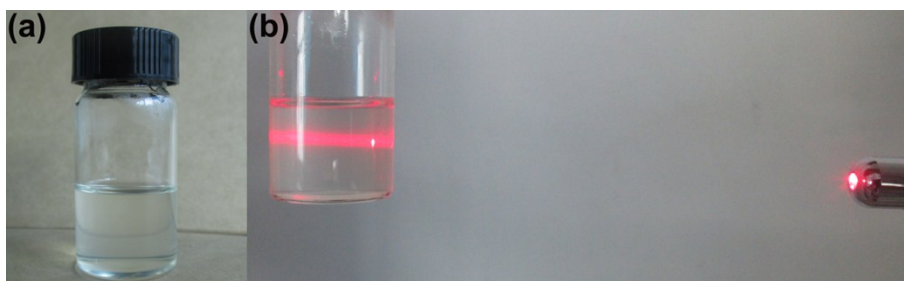
The dissolution of acidified g-C<sub>3</sub>N<sub>4</sub> in acidic aqueous or organic solutions needs auxiliary heating. In a typical dissolution process, 50 mg of acidified g-C<sub>3</sub>N<sub>4</sub> was added into 50 mL of 0.5 M hydrochloric acid solution. The mixture was stirred to form a homogeneous white suspension, and then heated to 65 ~ 75 °C for a while until the solution become clear and transparent. The obtained solution was naturally cooled to desired temperature. Figure S7 shows the status changes of acidified g-C<sub>3</sub>N<sub>4</sub> with different temperature during the dissolution process.

The solubility of acidified g-C<sub>3</sub>N<sub>4</sub> in hydrochloric acid aqueous solution at different acidity and temperature was measured. A certain amount of acidified g-C<sub>3</sub>N<sub>4</sub> was added to 50 g of hydrochloric acid aqueous solution in batches, and heated to 65 ~ 75 °C. After complete dissolution, the solution was preserved at a certain temperature for about 1 h. The operation was continuous loop until white turbidity appeared during the standing. The results are shown in Figure 4c-d.

The corresponding details for Figure 4a, b: In Figure 4a, the photographs show 0.10 g acidified  $g\text{-C}_3\text{N}_4$  dissolved in 100 mL of 0.5 M hydrochloric, nitric, oxalic, citric, and acetic acid aqueous solution, respectively. In Figure 4b, the photographs show 50 mg of acidified  $g\text{-C}_3\text{N}_4$  dissolved in 30 mL of 0.2 M hydrochloric ethylene glycol and DMF solution, and 20 mg of acidified  $g\text{-C}_3\text{N}_4$  dissolved in 30 mL of 0.2 M hydrochloric formamide, THF, ethanol, and acetone solution, respectively.



**Figure S7.** The status of 50 mg acidified  $g\text{-C}_3\text{N}_4$  in 50 mL of 0.5 M hydrochloric aqueous solution at different temperature during the dissolution process; (A) the obtained clear solution allowed to stand at 40 °C.



**Figure S8.** (a) The image of 0.16 g acidified  $g\text{-C}_3\text{N}_4$  dissolved in 10 g of 0.1 M hydrochloric ethylene glycol solution; (b) the Tyndall phenomenon of (a). This solution was allowed to stand at 40 °C for a week, and no turbidity or precipitation appeared during the standing.

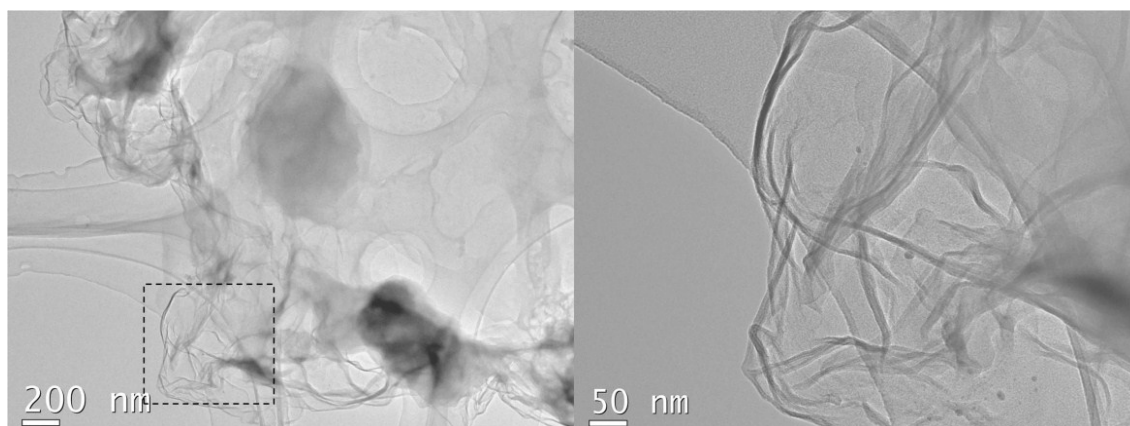




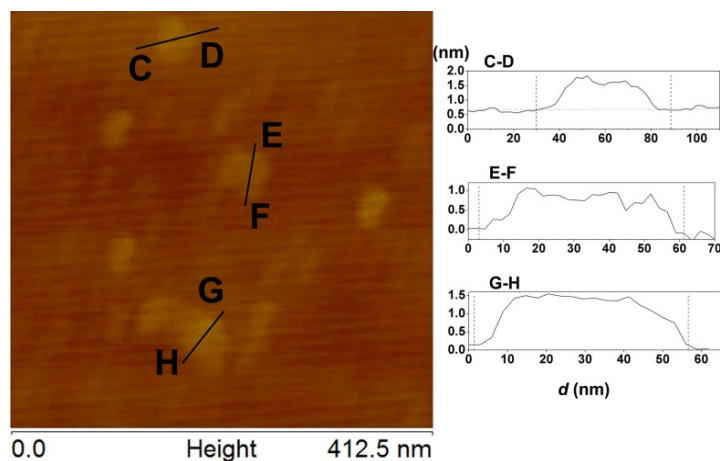
**Figure S9.** The image for solubility contrast between (a) CN-H<sub>2</sub>SO<sub>4</sub> and (b) acidified g-C<sub>3</sub>N<sub>4</sub>: 20 mg samples in 50 g of 0.5 M hydrochloric acid aqueous solution at 60 °C.

### 7. TEM and AFM images of dissolved g-C<sub>3</sub>N<sub>4</sub> nanosheets

After acidified g-C<sub>3</sub>N<sub>4</sub> being dissolved in hydrochloric aqueous solution, the obtained colorless transparent solution was used to observe the morphology of the dissolved substance by TEM and AFM. The results are shown in Figure 5, Figure S10, and Figure S11.



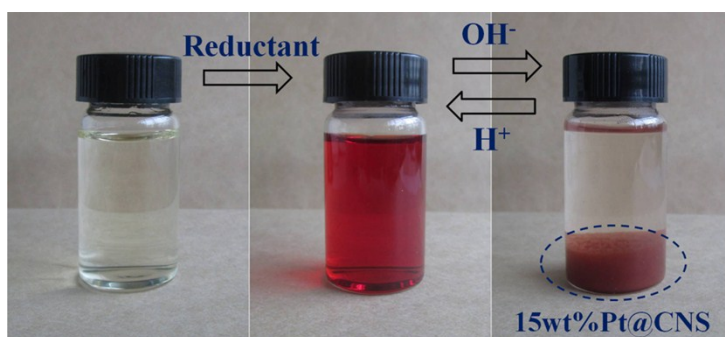
**Figure S10.** The representative TEM images of dissolved g-C<sub>3</sub>N<sub>4</sub> nanosheets.



**Figure S11.** The typical AFM image and thickness analysis results of dissolved  $g\text{-C}_3\text{N}_4$  nanosheets.

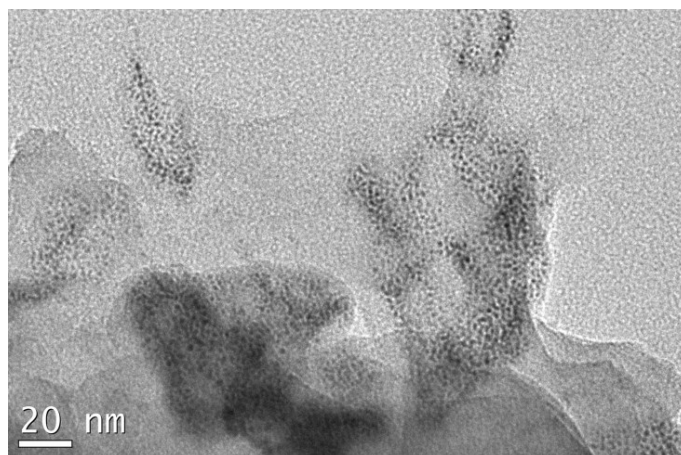
The isolated ultrathin  $g\text{-C}_3\text{N}_4$  nanosheets were formed when acidified  $g\text{-C}_3\text{N}_4$  was dissolved. Since large size flexible  $g\text{-C}_3\text{N}_4$  nanosheets tend to fold, which would interfere with the AFM characterization and thickness analysis, the observed relatively small nanosheets were shown here.

## 8. Photographs and TEM images of Pt@CNS

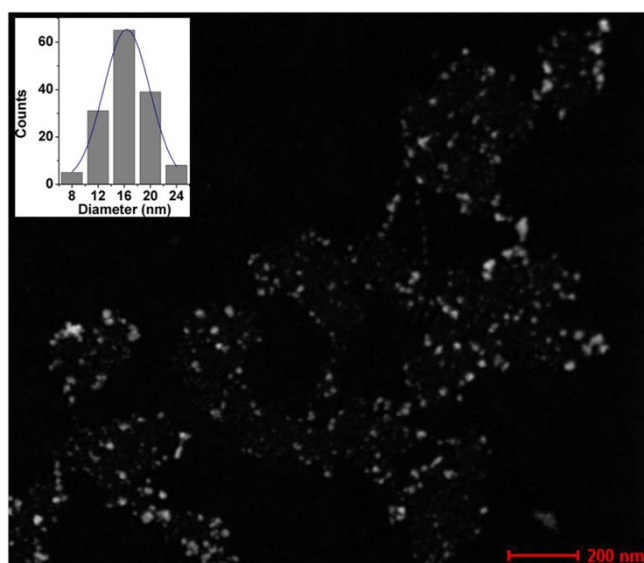


**Figure S12.** Diagrammatic sketch for the reduction procedure and the pH value echoed solubility of 15wt.%Pt@CNS.

5wt.%Pt@CNS was precipitated at pH value of about 5, and 15wt.%Pt@CNS was precipitated at pH value of about 3. Both of them can be dissolved in acidic aqueous solution at pH value of about  $< 2$ .



**Figure S13.** The TEM image of 5wt.%Pt@CNS.



**Figure S14.** The dark field TEM image of 15wt.%Pt@CNS and the corresponding Pt particle size distribution.

The average particle size of Pt in 15wt.%Pt@CNS increases to about 16 nm compared with that in the 5wt.%Pt@CNS sample, indicating that higher Pt / acidified g-C<sub>3</sub>N<sub>4</sub> ratio will result in the particle growth of Pt. However, even so, the Pt nanoparticles are still uniformly dispersed on the g-C<sub>3</sub>N<sub>4</sub> nanosheets. No particles can be observed in the region out of the nanosheets. These demonstrate the good affinity between g-C<sub>3</sub>N<sub>4</sub> nanosheets and Pt nanoparticles.

## References

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