# Electronic Supporting Information

# Nickel as a co-catalyst for photocatalytic hydrogen evolution on graphitic-carbon nitride (*sg*-CN): what is the nature of the active species?

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# **Experimental Section**

# Chemicals

All the chemicals are purchased from either Sigma Aldrich or Alfa-Aesar and used without further purification. Carbon nitride, *sg*-CN has been synthesized according the literature reported procedure.<sup>[S1]</sup>

# Instruments

Powder XRD was measured in Bruker AXS D8 advanced diffractometer equipped with a position sensitive detector (PSD) and a curved germanium (111) primary monochromator and the radiation used was Cu-*Ka* ( $\lambda = 1.5418$  Å). The solid-state <sup>13</sup>C{<sup>1</sup>H} cross-polarization magic angle spinning (CP/MAS) measurements were carried out by using a Bruker Advance 400 spectrometer. UV-vis spectroscopy was measured in Lambda 35 UV/Vis spectrometer from Perkin Elmer (USA). BET surface areas were measured with a micromeritics Nova 4200e surface-area analyzer using nitrogen adsorption at 77 K. TEM studies were performed on a FEI Tecnai G2 20 S-TWIN with an energy-dispersive X-ray spectrometer (EDAX, r-TEM SUTW) located at the ZELMI, TU Berlin. The IR spectra were collected with a BIORAD FTS 6000 FTIR spectrometer, equipped with an attenuated total reflection (ATR) setup. In situ EPR measurements in X-band (microwave frequency  $\approx$  9.8 GHz) were performed at 300 K with a Bruker EMX CW-micro spectrometer equipped with an ER 4119HS-WI high-sensitivity optical resonator with a grid in the front side.

# Syntheses of the catalysts

### *Synthesis of Cat-1:*

500 mg of NiCl<sub>2</sub>.6H<sub>2</sub>O, 250 mg *sg*-CN and 50 mL TEOA/H<sub>2</sub>O (1:9) were mixed together in a water jacket fitted reactor and degassed by purging Ar. In a closed system, the reactor was irradiated with 300 W Xe lamp with a cut off filter of 420 nm for 48 h maintaining the temperature at  $20\pm1$  °C. The solid material formed was then centrifuged out, washed several times with H<sub>2</sub>O/EtOH and dried at 50 °C in the oven for 24 h to obtain Cat-1.

# Synthesis of Cat-2:

500 mg of NiCl<sub>2</sub>.6H<sub>2</sub>O, 250 mg *sg*-CN and 50 mL TEOA/H<sub>2</sub>O (1:9) were mixed together in a water jacket fitted reactor and degassed by purging Ar. The mixture was constantly stirred for 48 h in dark by maintaining the temperature at  $20\pm1$  °C. The solid material formed was centrifuged out, washed several times with H<sub>2</sub>O/EtOH and dried at 50 °C in the oven for 24 h to obtain Cat-2.

# Synthesis of Cat-3:

500 mg of NiCl<sub>2</sub>.6H<sub>2</sub>O, 250 mg *sg*-CN and 50 mL H<sub>2</sub>O were mixed together in a water jacket fitted reactor and degassed by purging Ar. In a closed system, the reactor was irradiated with 300 W Xe lamp for 48 h with a cut off filter of 420 nm and maintained the temperature at  $20\pm1$  °C. The obtained solid material was then centrifuged out, washed several times with H<sub>2</sub>O/EtOH and dried at 50 °C in the oven for 24 h in order to acquire Cat-3.

Catalyst	Description	Amount of total [Ni]	Amount of [Ni] in
		by ICP (%)	surface by XPS (%)
Cat-1	<i>sg</i> -CN + Ni <sup>2+</sup> +	0.73	0.12
	TEOA + light		
	irradiation for 48 h		
Cat-1R	Cat-1 after recycling	0.62	0.06
Cat-2	<i>sg</i> -CN + Ni <sup>2+</sup> +	0.53	0.03
	TEOA + 48 h stirring		
	in dark		
Cat-3	sg-CN + Ni <sup>2+</sup> + light	0.10	0.03
	irradiation for 48 h		

Table	<b>S1</b> .	Descri	ption	of the	catalysts
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## **EPR studies**:

In situ EPR measurements in X-band (microwave frequency  $\approx 9.8$  GHz) were performed at 300 K with a Bruker EMX CW-micro spectrometer equipped with an ER 4119HS-WI highsensitivity optical resonator with a grid in the front side. The samples were irradiated with a 300 W Xe lamp (LOT Oriel). All CN and CN-Ni samples were measured with microwave power 7.15 mW, receiver gain 1\*10<sup>4</sup>, modulation frequency 100 kHz, modulation amplitude 5 G, sweep width 6900 G, sweep time 122.8 s, 2048 points for Ni(0) and modulation amplitude 1 G, sweep width 100 G, sweep time 122.8 s, 2048 points for CB-e<sup>-</sup>. *g* values have been calculated from the resonance field  $B_0$  and the resonance frequency  $\nu$  using the resonance condition  $h\nu = g\beta B_0$ . The calibration of the *g* values was performed using DPPH (2,2-diphenyl-1-picrylhydrazyl;  $g = 2.0036\pm0.00004$ ). For the analysis of the charge separation and recombination, the spectra under irradiation with light and after light switch-off were double integrated and the corresponding background signals before starting the experiment were subtracted.

Two temperature areas are determined: 1. > 320K

Due to strong anisotropy below 320 K, the Langvin equation<sup>[S2,S3]</sup> can only be applied for the temperatures above 320 K. However, the intensity obtained from the measurement did not exactly match to a specific particle diameter. This deviation could be due to (i) Non-spherical particles, (ii) distribution for different particle sizes or (iii) interference with the CB-e<sup>-</sup> signal.

$$M(t) = M_s(T) \cdot L(x)$$
(S1)

$$L(x) = \operatorname{coth}(x) \cdot x^{-1} \tag{S2}$$

$$\mathbf{x} = \mathbf{M}_{\mathbf{s}}(\mathbf{T}) \bullet \mathbf{V} \bullet \mathbf{H} \bullet \mathbf{k}^{-1} \bullet \mathbf{T}^{-1}$$
(S3)

with  $M_s(298 \text{ K}) = 0.6149 \text{ T}$  (saturation magnetization per unit volume), T - temperature /K, V - the volume of the Ni particle (assuming spherical NP), H - the applied external field /T, k - the Boltzman constant.

# Hydrogen evolution studies:

Hydrogen gas evolution was measured in a 60 mL home-made teflon reactor fitted with quartz glass window and temperature controller. 50 mg of catalyst, 6 mL sacrificial agent and 54 mL water were filled inside the reactor, degassed and then irradiated with a 300 W Xe lamp with a cut off filter of 420 nm. Irradiation area of the light was 19.63 m<sup>2</sup> and time vs pressure profile was recorded. At the end of the reaction, the gas obtained from the head space was injected into GC and the volume % was determined.



## Figures

**Figure S1.** PXRD patterns of the synthesized catalysts showing the reflectance from *sg*-CN without any additional peak for the deposited nickel species.



**Figure S2**. EDX spectra of the (a) Cat-1, (b) Cat-2, (c) Cat-1R and (d) Cat-3 showing the presence of Ni. The signal for Cu is from the TEM grid.



Figure S3. Solid state <sup>13</sup>C CP/MAS NMR spectra of Cat-1 and *sg*-CN.



Figure S4a. Diffuse reflectance UV-Vis spectra of the catalysts.



Figure S4b. Attenuated total reflection infra-red (ATR-IR) spectra of the catalysts.



**Figure S5.** (a) TEM image of Cat-1 showing the porous structure of *sg*-CN and inset showing selected area diffraction pattern indicating the amorphous nature of deposited Ni-species. (b) HRTEM image of Cat-1 after 8 days of continuous  $H_2$  production under photochemical conditions, (c) lattices of a selected dark particle and (d) corresponding FFT.



Figure S6. XPS studies of the catalysts for (a) Ni  $2p_{3/2}$ , (b) N 1s, (c) C 1s and (d) O 1s edges.



**Figure S7**. Long term photochemical hydrogen evolution profile of Cat-1 under 300 W Xe lamp irradiation with a cut off filter of 420 nm using TEOA as the sacrificial agent.



Figure S8. Ex situ EPR spectra of the catalysts compared with sg-CN.



**Figure S9a.** Temperature dependency of the EPR signals for Cat-1 with the temperature interval of 20 K.



**Figure S9b**. Temperature dependent magnetization M(T) calculated for different particle size of spherical Ni particles in comparison with the double integration of the Ni<sup>0</sup> signal of Cat-1.



**Figure S10.** Double integral of the CB-e<sup>-</sup> EPR signal of the catalysts during visible light irradiation (black) and after light switch-off (red). Background signals in the dark were subtracted. The inset shows an example of the analyzed CB-e<sup>-</sup> signal.

# References

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