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?

Arindam Indra, Prashanth W. Menezes, Kamalakannan Kailasam, Dirk Hollmann, Marc Schröder, Arne Thomas, Angelika Brückner and Matthias Driess*
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.\[S1\]

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-Kα (λ = 1.5418 Å). The solid-state $^{13}$C\{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 ≈ 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$_2$.6H$_2$O, 250 mg sg-CN and 50 mL TEOA/H$_2$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±1 °C. The solid material formed was then centrifuged out, washed several times with H$_2$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$_2$.6H$_2$O, 250 mg sg-CN and 50 mL TEOA/H$_2$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±1 °C. The solid material formed was centrifuged out, washed several times with H$_2$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$_2$.6H$_2$O, 250 mg sg-CN and 50 mL H$_2$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±1 °C. The obtained solid material was then centrifuged out, washed several times with H$_2$O/EtOH and dried at 50 °C in the oven for 24 h in order to acquire Cat-3.

**Table S1. Description of the catalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Description</th>
<th>Amount of total [Ni] by ICP (%)</th>
<th>Amount of [Ni] in surface by XPS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-1</td>
<td>sg-CN + Ni$^{2+}$ + TEOA + light irradiation for 48 h</td>
<td>0.73</td>
<td>0.12</td>
</tr>
<tr>
<td>Cat-1R</td>
<td>Cat-1 after recycling</td>
<td>0.62</td>
<td>0.06</td>
</tr>
<tr>
<td>Cat-2</td>
<td>sg-CN + Ni$^{2+}$ + TEOA + 48 h stirring in dark</td>
<td>0.53</td>
<td>0.03</td>
</tr>
<tr>
<td>Cat-3</td>
<td>sg-CN + Ni$^{2+}$ + light irradiation for 48 h</td>
<td>0.10</td>
<td>0.03</td>
</tr>
</tbody>
</table>
EPR studies:

In situ EPR measurements in X-band (microwave frequency \( \approx 9.8 \text{ GHz} \)) 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. 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 \( 1 \times 10^4 \), 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\(^-\). \( g \) 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; \( g = 2.0036 \pm 0.00004 \)). 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. \( > 320 \text{K} \)

and 2. \( < 320 \text{K} \)

Due to strong anisotropy below 320 K, the Langvin equation\(^{[S2,S3]} \) 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\(^-\) signal.

\[
M(t)=M_s(T)\cdot L(x) \tag{S1}
\]

\[
L(x)=\coth(x)-x^{-1} \tag{S2}
\]

\[
x=M_s(T) \cdot V \cdot H \cdot k^{-1} \cdot T^{-1} \tag{S3}
\]

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 m² 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 $^{13}$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 H₂ 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$^0$ signal of Cat-1.
Figure S10. Double integral of the CB-e⁻ 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⁻ signal.

References

