# Appendix A. Supplementary data

# Simply blending Ni nanoparticles with photocatalysts for efficient photocatalytic $H_2$ production

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**Preparation of Ni*x*@CN by photodeposition method**

CN (100 mg) and a certain amount of $NiCl_2$ $6H_2O$ (12.1, 28.3, 40.5 and 60.7 mg) were added into an aqueous solution (200 mL, 10 vol% TEOA) under magnetic stirring. Before photocatalytic reaction, $N_2$ was bubbled into the cell for 15 min to remove $O_2$. The temperature for photocatalytic reaction was kept at 35 ± 0.5 °C by thermostatic circulating water. A Xe lamp (300W) equipped without UV-cutoff filter was used as the light source. After the photocatalytic $H_2$ production experiment had proceeded for 2 h, the precipitates were collected using a centrifuge and washed with distilled water and alcohol 3 times, respectively. The washed precipitates were dried at 60 °C for 12 h. The obtained samples were labeled as Ni*x*@CN, in which *x*% (*x* = 3, 7, 10 and 15) was the mass ratio of Ni to CN.

**Evaluation of photocatalytic performance for Ni*x*@CN**

Photocatalytic $H_2$ production of Ni*x*@CN samples were performed in the similar procedure with the photodeposition process. While a Xe lamp (300W) equipped with a UV-cutoff filter ($\lambda$ > 420 nm) was used as the visible-light source, the amount of photocatalyst (Ni*x*@CN) was 50 mg, and the photocatalytic $H_2$ production experiment was proceeded for 6 h, the evolved $H_2$ was analyzed on a gas chromatograph (thermal conductivity detector, TDX-01 column, Ar as carrier gas) every 1 h.

The measurement of apparent quantum yield (AQY) for Ni7−CN was carried out under the above Xe lamp equipped with a band-pass filter (425 nm). The intensity of irradiated light was recorded from a spectrodiometer (Avantes AvaSpec-2048-USB2, Netherlands)

The AQY value was obtained by the following equation:

$$AQY(\%) = \frac{Number\ of\ reacted\ electrons}{Number\ of\ incident\ photons} \times 100\%$$
$$= \frac{Number\ of\ evolved\ H_2\ molecules \times 2}{Number\ of\ incident\ photons} \times 100\%$$

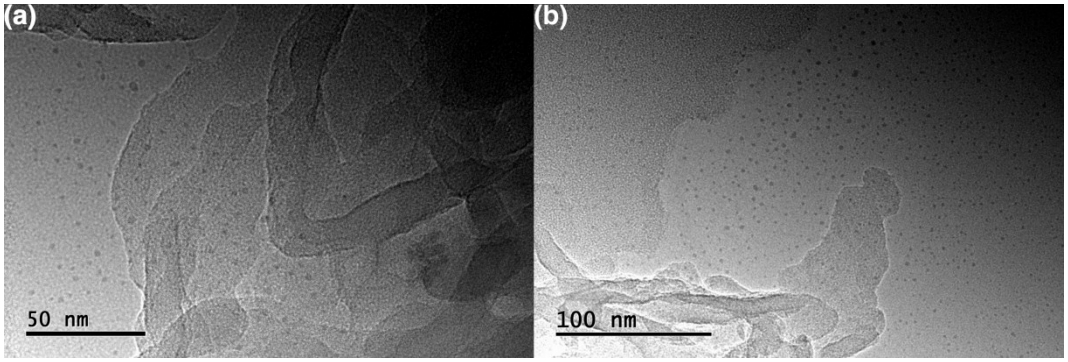


**Figure A.1.** (a, b) TEM images of Ni7−CN−R. Scale bar: (a) 50 nm and (b) 100 nm.

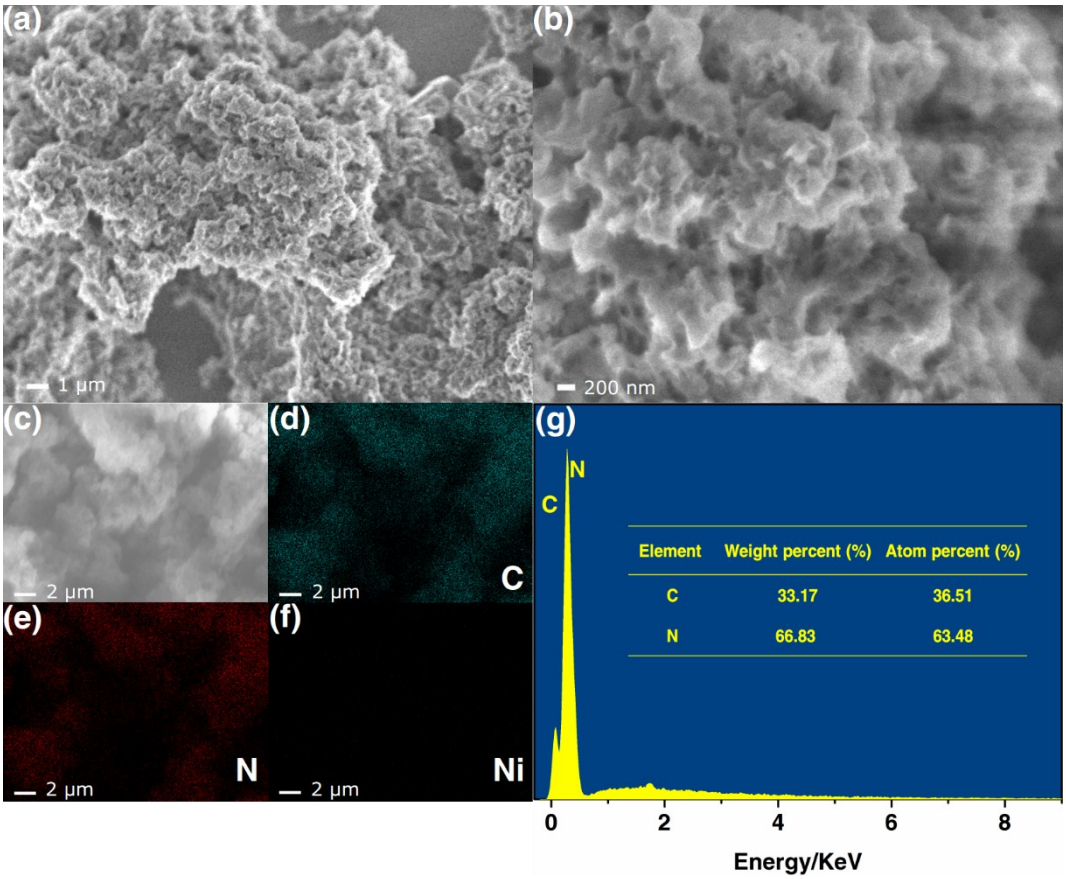


**Figure A.2.** (a) SEM and (b) high-resolution SEM images for Ni7−CN−R; (c) SEM image for Ni7−CN−R, and (d-f) corresponding elemental mapping images of (d) C, (e) N and (f) Ni elements for Ni7−CN−R, and (g) corresponding EDS result for Ni7−CN−R. Scale bar: (a) 1 μm, (b) 200 nm, (c-f) 2 μm.

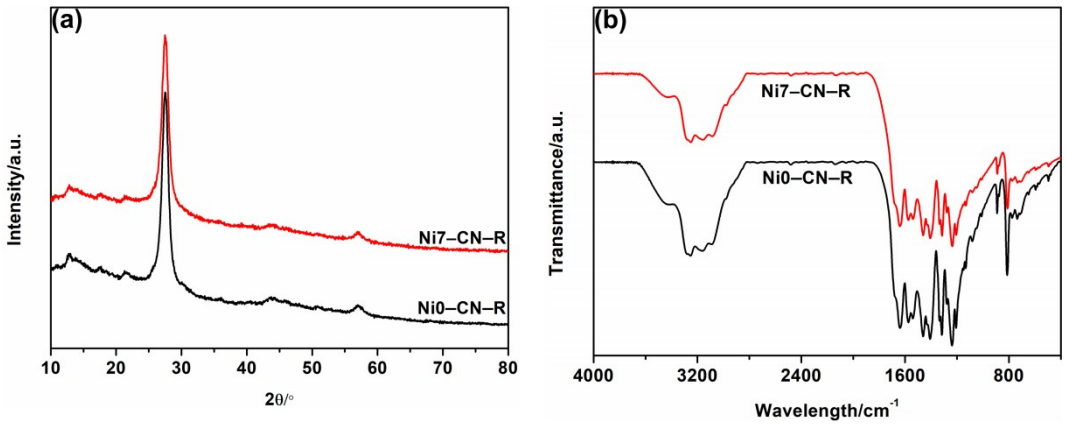


**Figure A.3.** (a) XRD patterns and (b) FTIR spectra for Ni0−CN−R and Ni7−CN−R.

The signals of Ni species were not observed in both XRD pattern and FTIR spectrum for Ni7−CN−R due to the low content of Ni NPs.

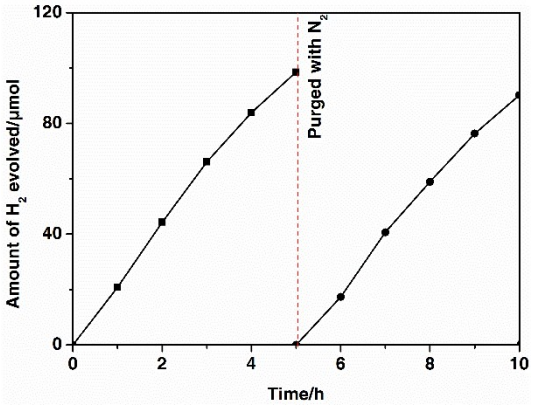


**Figure A.4.** Cyclic test of photocatalytic activity for Ni7−CN photocatalytic system.

Cyclic tests of photocatalytic activities for Ni*x*−CN photocatalytic systems, by taking Ni7−CN photocatalytic system as an example, showed that the photocatalytic activity showed little decay during two cyclic tests with each for 5 h (Fig. A.4), thus demonstrating the good stability for photocatalytic $H_2$ production.

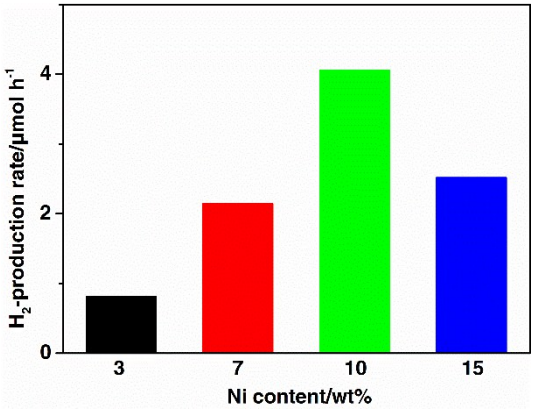


**Figure A.5.** Photocatalytic $H_2$-production activities for Ni*x*@CN samples ($x$ = 3, 7, 10 and 15).

**Table A.1.** Comparison between the simple blending method with other Ni loading methods for photocatalytic $H_2$ production over g-$C_3N_4$ modified with Ni cocatalyst. Photocatalyst amount (50 mg), sacrificial reagent (TEOA).

| Photoatalyst | Method | Light source (Xe lamp) | Ni amount (wt%) | Activity (μmol $h^{-1}$) | AQY (%) | Ref. |
|---|---|---|---|---|---|---|
| **g-$C_3N_4$** | **Blending** | **λ > 420 nm** | **7** | **22.04** | **2.06 (425 nm)** | **This work** |
| g-$C_3N_4$ | Photodeposition | λ > 420 nm | 10 | 4.06 | / | This work |
| g-$C_3N_4$ | Impregnation and reduction | λ > 420 nm | 2 | 5 | / | 1 |
| g-$C_3N_4$ | Solvothermal reaction | 500 W | 10 | 8.41 | / | 2 |
| Porous g-$C_3N_4$ | Solvothermal reaction | 500 W | 10 | 15.66 | / | 3 |

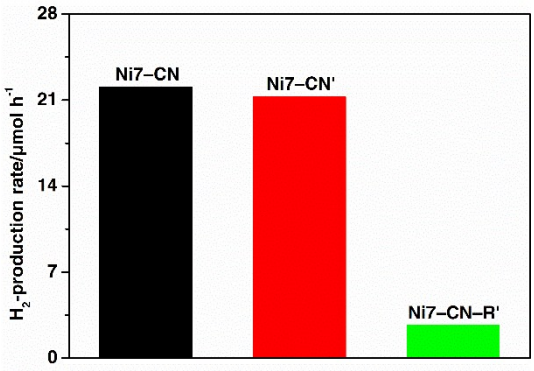


**Figure A.6.** Photocatalytic $H_2$-production activity for Ni7−CN, Ni7−CN' and Ni7−CN−R' photocatalytic system.

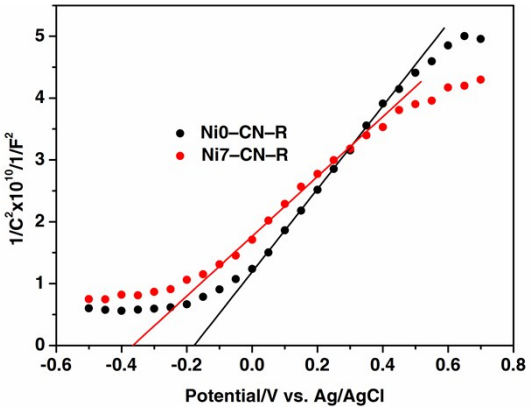


**Figure A.7.** Mott–Schottky plots of Ni0−CN−R and Ni7−CN−R samples.

**References**


1 G. Zhang, G. Li and X. Wang, *ChemCatChem,* 2015, **7**, 2864-2870.

2 L. Bi, D. Xu, L. Zhang, Y. Lin, D. Wang and T. Xie, *Phys. Chem. Chem. Phys.*, 2015, **17**, 29899-29905.

3 L. Bi, D. Meng, Q. Bu, Y. Lin, D. Wang and T. Xie, *Phys. Chem. Chem. Phys.*, 2016, **18**, 31534-31541.