## **Electronic Supplementary Information**

for

## Photocatalytic hydrogen evolution with Ni nanoparticles by using 2-phenyl-4-(1-naphthyl)quinolinium ion as a photocatalyst

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**Fig. S1.** Repetitive test of photocatalytic hydrogen evolution by photoirradiation of a mixed solution of phosphate buffer (pH 4.5) and MeCN [2.0 mL, 1:1 (v/v)] containing  $QuPh^+$ -NA (0.44 mM), NADH (1.0 mM) and NiNPs (6.6 nm, 12.5 mg L<sup>-1</sup>).



**Fig. S2.** (a) TEM image of NiO (5 – 20 nm) nanoparticles. (b) X-ray diffraction pattern of NiO nanoparticles compared with that reported in literature.<sup>S1</sup> (c) Repetitive test of photocatalytic hydrogen evolution by photoirradiation of a mixed solution of phthalate buffer (pH 4.5) and MeCN [2.0 mL (1:1)] containing QuPh<sup>+</sup>-NA (0.44 mM), NADH (1.0 mM) and NiO nanoparticles (12.5 mg L<sup>-1</sup>).

## Reference

S1. R. W. G. Wyckoff, *Crystal Structures 1 Second edition*, 85-237, Interscience Publishers, New York, NY, 1963.



**Fig. S3.** Powder X-ray diffraction pattern obtained from NiNPs with different sizes [(a) 6.6 nm, (b) 11 nm, (c) 36 nm; and (d) 210 nm] (The spectra were recorded by a Rigaku RINT 2000. Incident X-ray radiation was produced by a Cu X-ray tube, operating at 40 kV and 200 mA with Cu  $K_a$  radiation of 1.54 Å. A scanning rate was 2°/min from 20° to 80° in 2 $\theta$ .)



**Fig. S4.** Difference in magnetic properties between *hcp*-NiNPs and *fcc*-NiNPs. fcc-NiNPs are attracted to a magnet.



**Fig. S5.** Time courses of hydrogen evolution by photoirradiation of a mixed solution of buffer and MeCN containing QuPh<sup>+</sup>-NA (0.44 mM), NADH (1.0 mM) and different concentrations of NiNPs [6.6 nm, 6.3 mg L<sup>-1</sup> (green), 12.5 mg L<sup>-1</sup>(blue), 25 mg L<sup>-1</sup> (red)].



Fig. S6. DLS data of CuNPs just after preparation.