

## Electronic Supporting Information

# Direct Photocatalytic Hydrogen Evolution from Water Splitting Using Nanostructures of Hydrate Organic Small Molecule as Photocatalysts

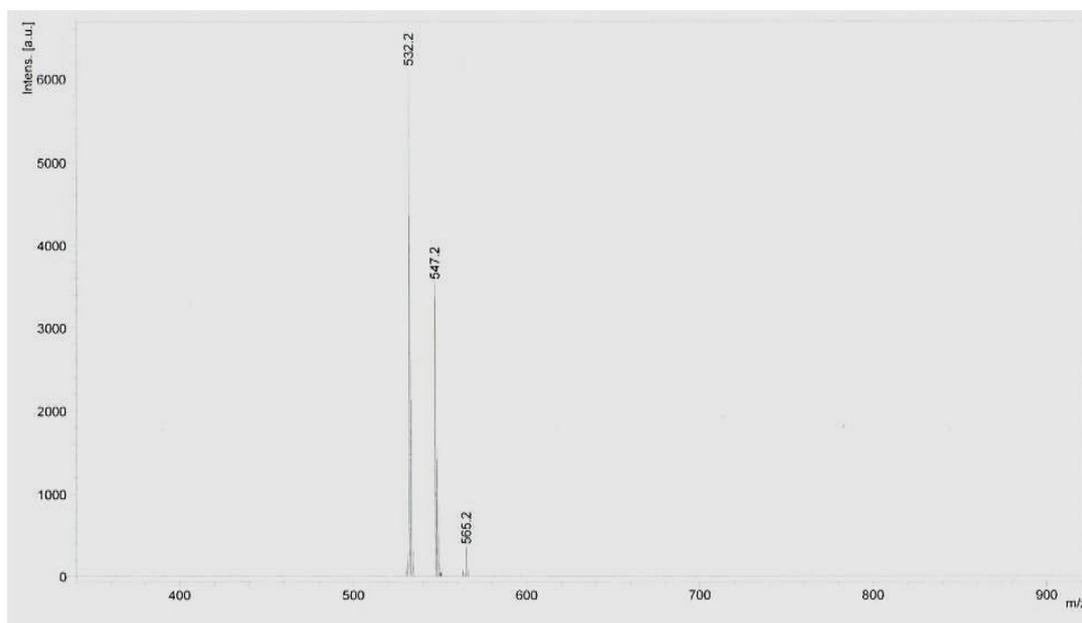
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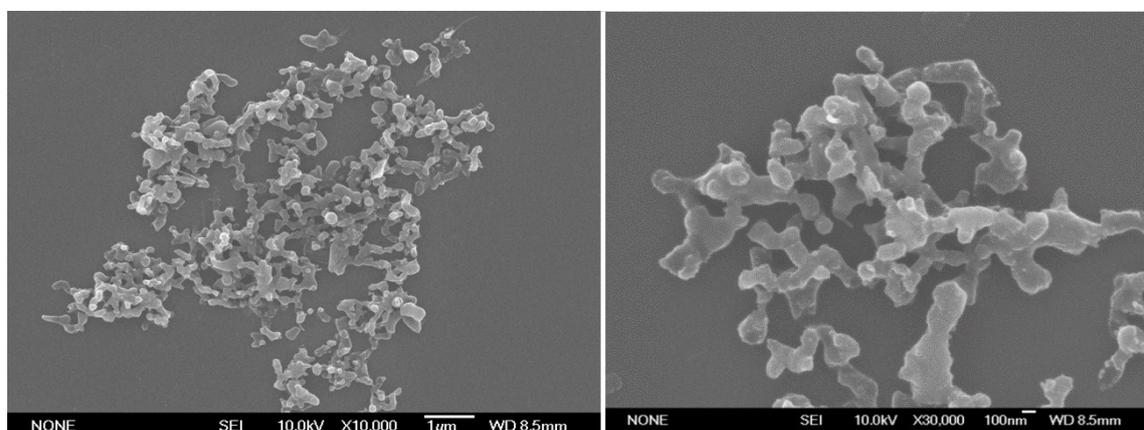
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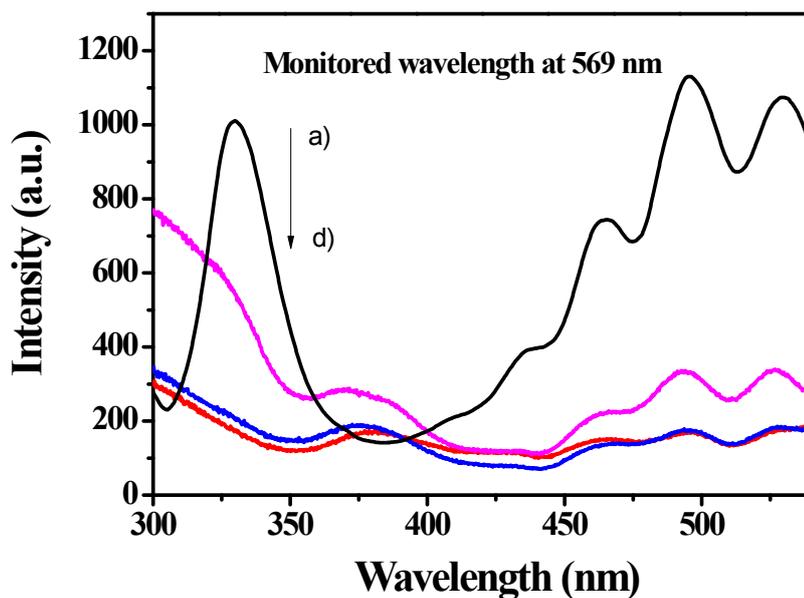
\*E-mail: jnyao@iccas.ac.cn.



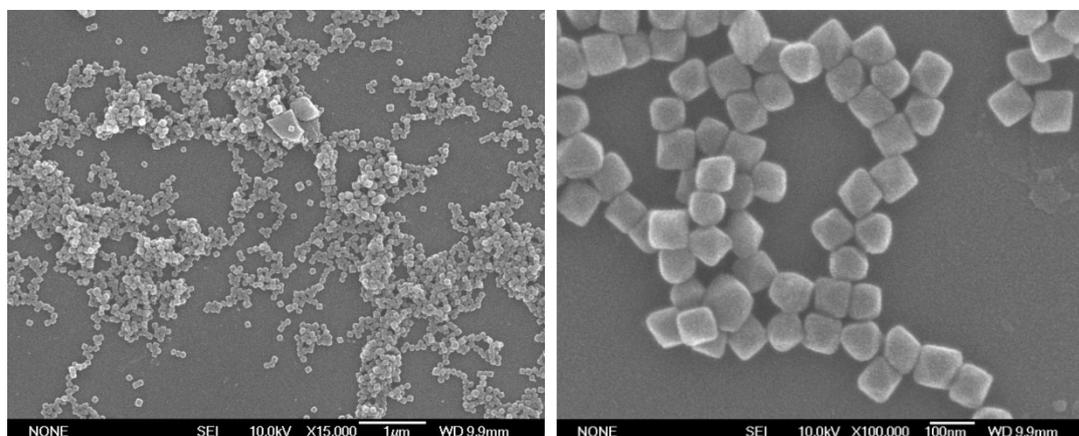
**Fig. S1** MALDI-TOF Mass spectra of rubrene nanoparticles. Calculation for  $C_{42}H_{28}$  ( $M^+$ ),  $m/z$ , 531.7 ; found, 532.2. The peaks at 547.2 should be  $C_{42}H_{27}O$  , which results from the oxidation of rubrene in air.<sup>1</sup>



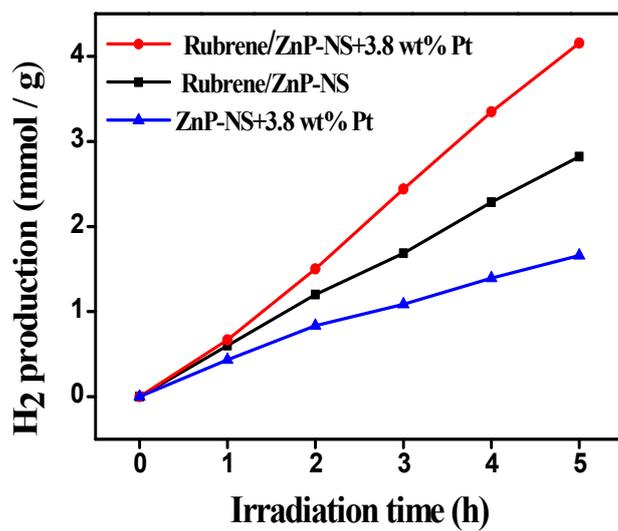
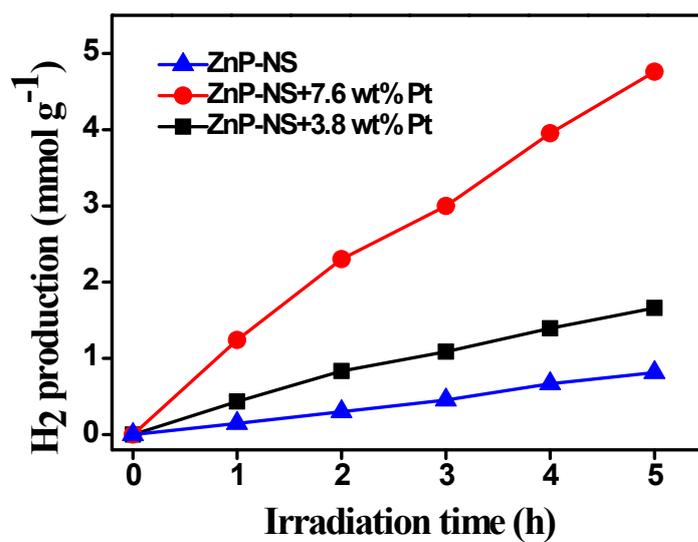
**Fig. S2** SEM images of rubrene nanoparticles with the average size of ~200 nm obtained after 1 mL of 1 mM rubrene perchlorate was rapidly injected into 3 mL of ultrapure water.



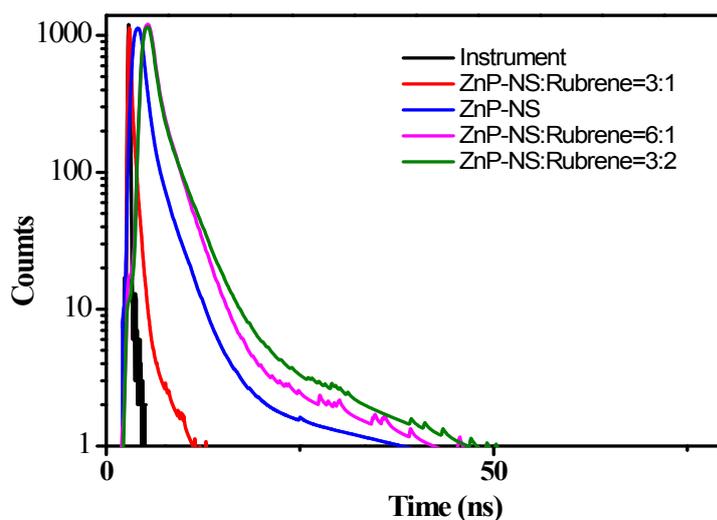
**Fig. S3** The excitation spectra in aqueous dispersion system monitored at 569 nm. a) rubrene nanoparticles and the nanostructure of Rubrene/ZnP-NS with different molar ratio of b) 2:3, c) 1:3 and d) 1:6.



**Fig. S4** SEM images of ZnP octahedron nanoparticles(ZnP-NPs) with the average size of ~80 nm obtained after 1 mL of 1 mM ZnP perchlorate was rapidly injected into 3 mL of ultrapure water including 6 mM CTAB and aged for one hour.



**Fig. S5** Time course of photocatalytic hydrogen evolution of ZnP-NS and Rubrene/ZnP-NS (1:3) nanostructure with and without Platinum (Pt).



**Fig. S6** Fluorescence decay profiles of sole ZnP-NS and ZnP-NS in Rubrene /ZnP-NS composite with molar ratio of 2:3, 1:3 and 1:6. The system was monitored at 643 nm upon the excitation wavelength of 350 nm.

**Table S1.** Fluorescence decay times of the fluorescence of sole ZnP-NS and ZnP in Rubrene/ZnP-NS composite with molar of 2:3, 1:3 and 1:6. The system was monitored at 643 nm upon the excitation wavelength of 350 nm.

Molar ratio of ZnP/rubrene	$\tau_1$		$\tau_2$		$\tau_3$		$\tau^a/\text{ns}$
	ns	% <sub>1</sub>	ns	% <sub>2</sub>	ns	% <sub>3</sub>	
1 : 0	0.61	69.4	2.52	25.2	45.83	5.3	3.49
6 : 1	0.48	44.8	2.16	51.6	20.93	3.7	2.10
3 : 1	0.41	46.1	1.93	49.1	14.91	4.8	1.85
3 : 2	0.59	50.2	2.67	44.2	19.43	5.1	2.47

<sup>a</sup> Average fluorescence lifetime,  $\tau^a = (\tau_1\%_1 + \tau_2\%_2 + \tau_3\%_3) / 100$

1 C. Kloc, K. J. Tan, M. L. Toh, K. K. Zhang, Y. P. Xu, *Apply. Phys. A-mater.*, 2009, **95**, 219-224.