Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Construction of push-pull system in g-C_3N_4 for efficient photocatalytic hydrogen evolution under visible light

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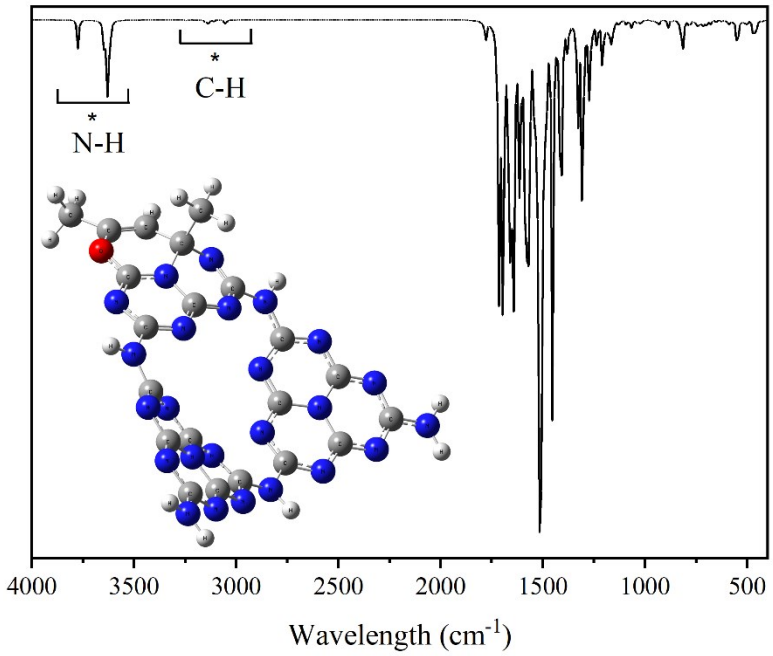


Figure S1 Infrared spectrum of UCN-*x*acac calculated by DFT

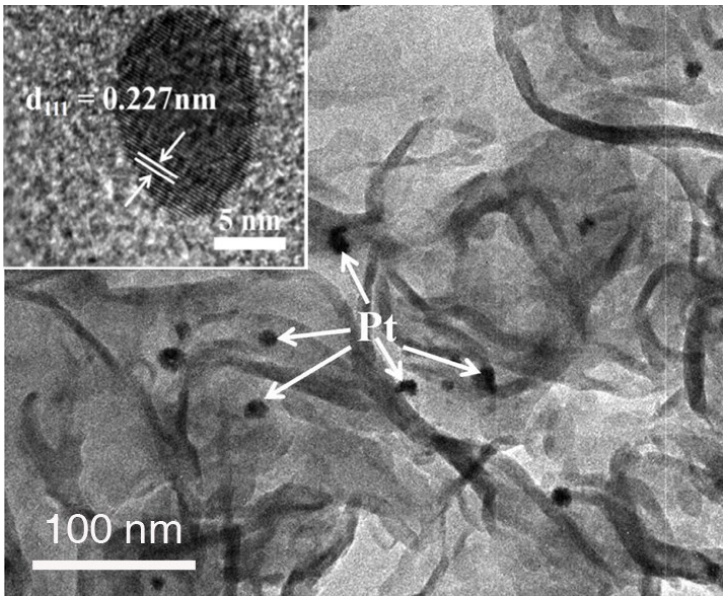


Figure S2 TEM images of 3% Pt photo-deposited on UCN-20acac photocatalyst. Inset shows the Pt nanoparticles with a lattice spacing of 0.227 nm.

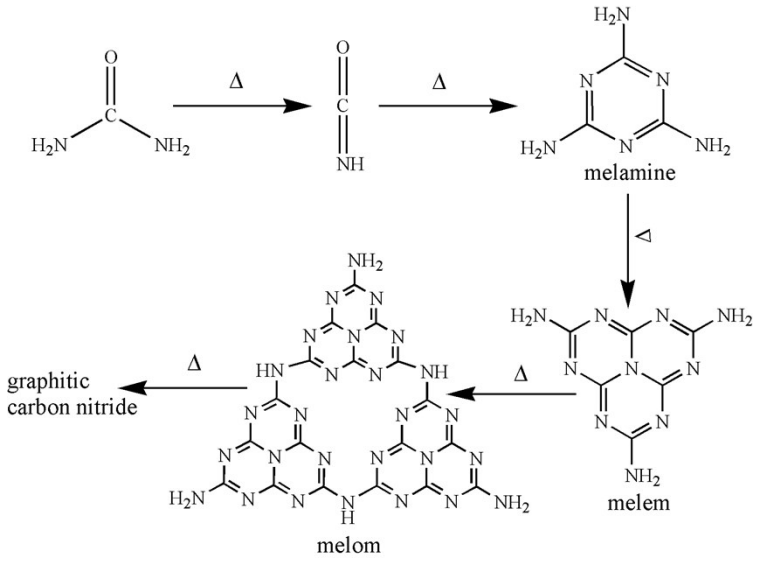


Figure S3 The formation mechanism of g-C_3N_4 by pyrolysis of urea [1-3].

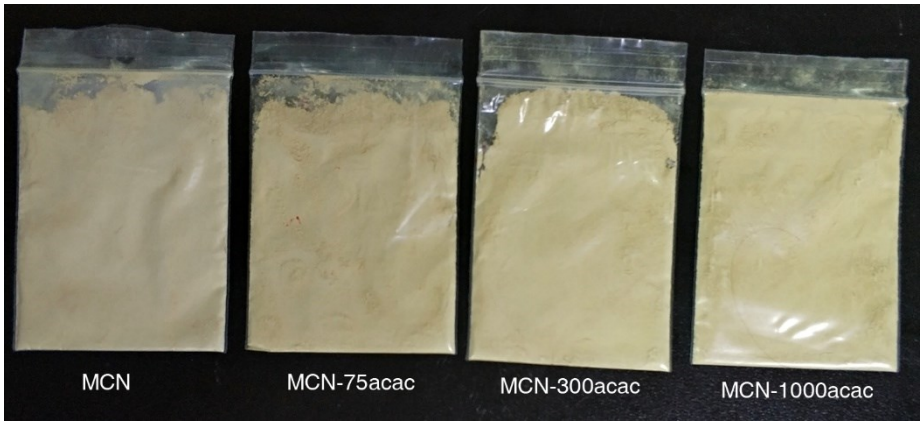


Figure S4 The color of MCN and MCN-*x*acac

Specifically, 5 g melamine and a designed amount of acetylacetone were charged in an alumina crucible with a cover, and then heated in a muffle furnace to 550 °C at a rate of 3 °C min^{-1} and kept at the temperature for 4 h. Pure g-C_3N_4 sample was obtained by direct polycondensation of melamine without the addition of acac. The sample was denoted as MCN. With the addition of acac, the as-prepared samples were denoted as MCN-*x*acac (*x*=75, 300 and 1000 μL). With the addition of acac into MA, it seems that there is no color difference occurring. Compared with the yellow MCN, the color of MCN-*x*acac only became slightly deeper (Fig. S4).

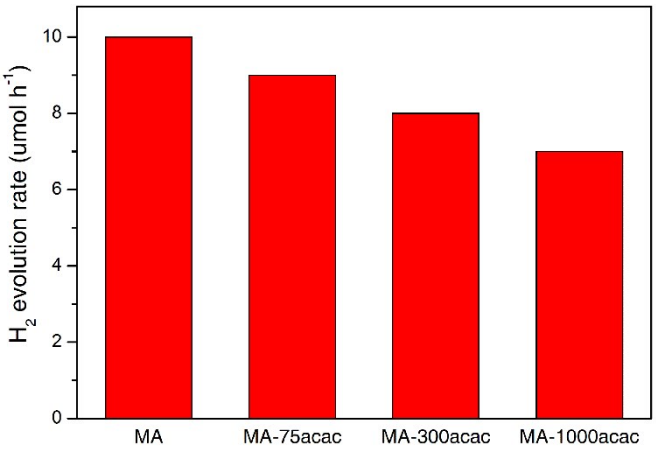


Figure S5 Hydrogen evolution rate over MCN and MCN-*x*acac under visible light (λ > 420 nm).

Furthermore, the hydrogen evolution rate (HER) of MCN and MCN-*x*acac samples were tested under visible light irradiation (Fig. S5). It is noted that the HER performance of MCN-*x*acac samples was not improved, even gradually deteriorated. The results indicated that melamine and its derivatives cannot react with acac effectively in the process of thermal polymerization, not to mention significantly improving the performance of hydrogen evolution. Taking in consideration of the structure feature of MA, we can infer that the fusion of acac doesn't proceed in the framework of tri-s-triazine, maybe just bonding with the terminal NH_2 of MA, On the other hand, in the case of fusion between urea and acac, we have confirmed that the -CH_3, -C=O- and -C=C- from acac are existed in the structure of UCN-*x*acac on the basis of the results of FTIR, NMR and XPS. The UCN-xacac samples exhibited significant improvement in HER. **In other words, the significant improvement in photocatalytic hydrogen evolution of UCN-*x*acac can be attributed to the fusion of acac in the framework of tri-s-triazine.**

Furthermore, previous studies have indicated that urea undergoes decomposition to NH_3 and HNCO gradually at 160 °C (Ref. 54, 55). Almost at the same temperature, acetylacetone is also evaporated. Compared with the large amount of urea, the acetylacetonate content is quite low in the system. Therefore, it is reasonable to infer that the evaporated acetylacetone will react with abundant HNCO to gradually incorporate into the framework of tri-s-triazine in the atmosphere of NH_3 and HNCO. The subsequent products of HNCO, such as melamine and its derivative, seemed difficult to react with acac.

Based on the above results and analysis, the proposed structure of products B is thus reasonable and the grafting procedure in Scheme 1 is considered the most possible.

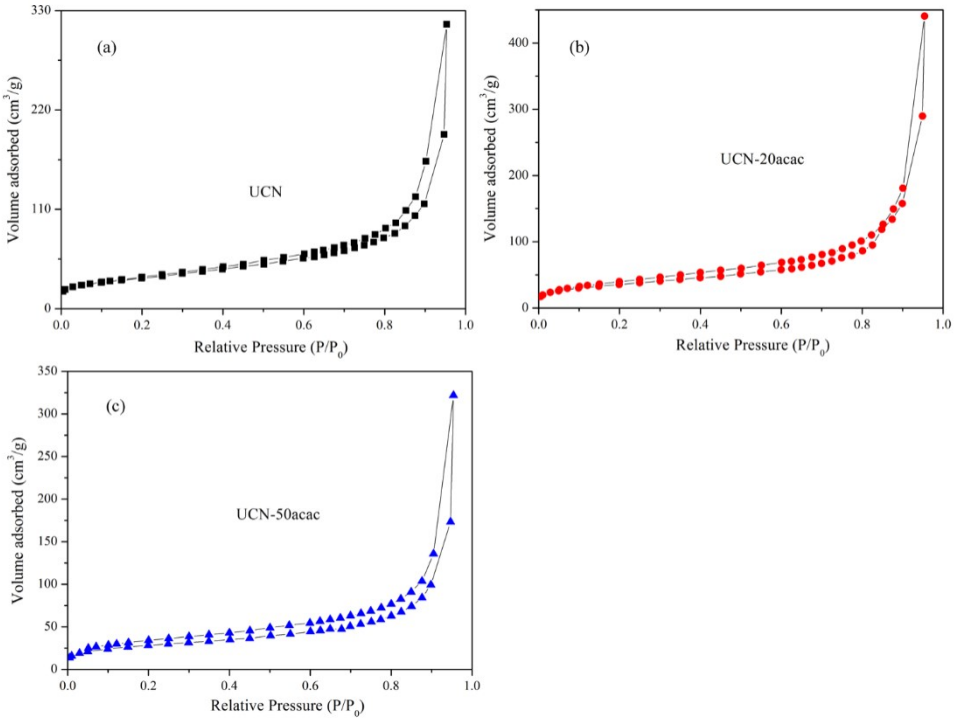
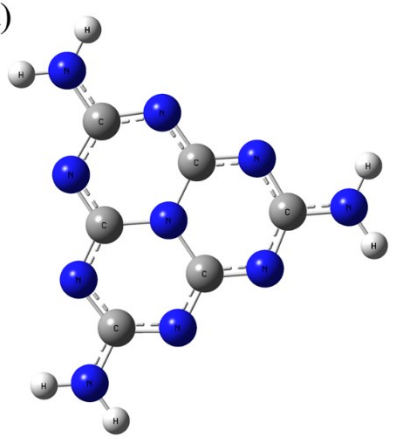
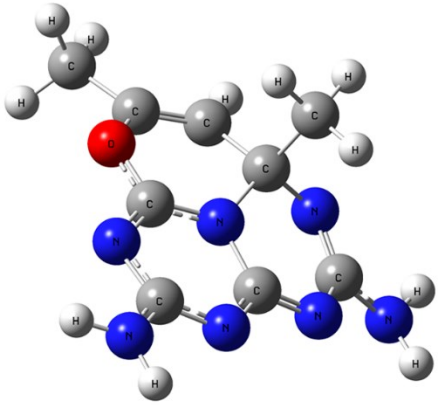


Figure S6 N_2 adsorption/desorption isotherms of UCN, UCN-20acac and UCN-50acac.

(a)

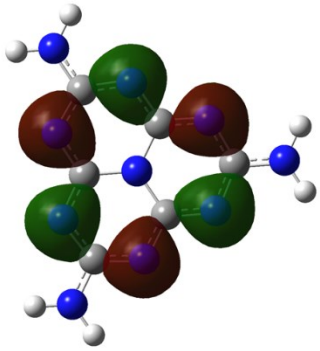


UCN

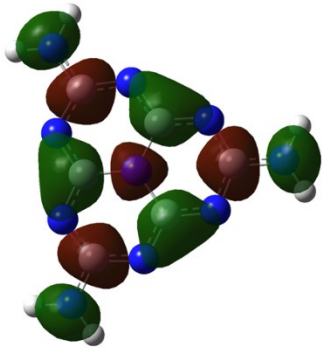


UCN-xacac

(b)



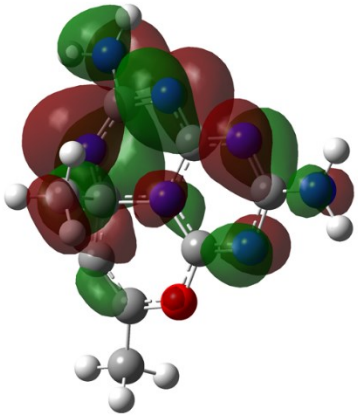
HOMO



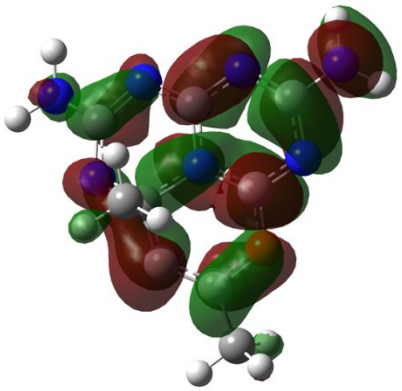
LUMO

UCN

(c)



HOMO



LUMO

UCN-xacac

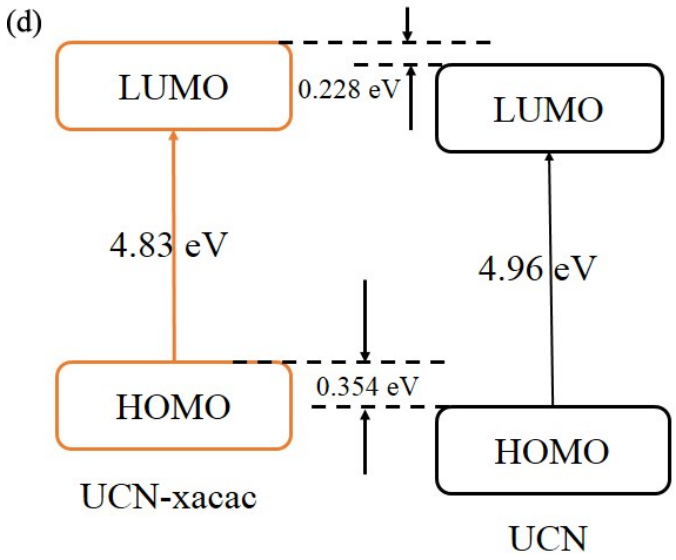


Figure S7 (a) the optimized polymeric monomer models of UCN and UCN-*x*acac; their corresponding electronic structure of HOMO and LUMO for (b) UCN and (c) UCN-*x*acac; (d) schematic diagram of HOMO and LUMO for UCN and UCN-*x*acac.

Table S1. BET specific surface area of UCN, UCN-20acac and UCN-50acac.

Catalyst	UCN	UCN-20acac	UCN-50acac
$S_{BET}(m^2/g)$	120.4	126.7	98.3

Table S2. Comparison of photocatalytic activity of the reported g-C_3N_4.

Catalyst	Light Source	Reaction Conditions	HER (μmol h^{-1})	Apparent quantum efficiency	Ref.
UCN-20acac	300 W Xe lamp, λ > 420 nm	3 wt% of Pt; Aqueous TEOA solution(10 vol%)	ca. 240	18.8 % (450 nm)	This work
UCN-BD	300 W Xe lamp, λ > 420 nm	3 wt% of Pt; Aqueous TEOA solution(10 vol%)	ca. 171	12.3% (450 nm)	[4]
PTI-C_3N_4	300 W Xe lamp, λ > 420 nm	3 wt% of Pt; Aqueous TEOA solution(10 vol%)	ca. 204	4.6% (450 nm) 15% (400 nm)	[5]
O-CN2	300 W Xe lamp, λ > 420 nm	1 wt% of Pt; Aqueous Lactic acid solution (10 vol%)	ca. 54	7% (450 nm) 13.2% (420 nm)	[6]
UCN-10	300 W Xe lamp, λ > 420 nm	3 wt% of Pt; Aqueous TEOA solution(10 vol%)	ca. 116.4	8.2% (450 nm)	[7]
UM3	300 W Xe lamp, λ > 420 nm	1 wt% of Pt; Aqueous Lactic acid solution (20 vol%)	ca. 179	12% (450 nm) 27.8% (420 ± 15 nm)	[8]
UCN-NA_{100}	300 W Xe lamp, λ > 420 nm	3 wt% of Pt; Aqueous TEOA solution (10 vol%)	ca. 102.1	5.6% (450 nm)	[9]
g-C_3N_4 (urea)	300 W Xe lamp, λ > 395 nm	3 wt% of Pt; Aqueous TEOA solution(13 vol%)	67	4% (450 nm) ca. 12.5% (420 nm) 26.5% (400 nm)	[10]
HCNS-1	300 W Xe lamp, λ> 420 nm	3 wt% of Pt; Aqueous TEOA solution(10 vol%)	224	7.5% (420 nm)	[11]
EY-mpg-C_3N_4	250 W high-pressure mercury lamp λ> 420 nm	1 wt% of Pt; Aqueous TEOA solution(15 vol%)	115.5	7.2% (460 nm)	[12]
g-C_3N_4 (urea and thiourea)	300 W Xe lamp, λ> 400 nm	1 wt% of Pt; Aqueous methanol solution (20vol%), pH=13.3 (KOH)	66.9	6.67% (400 nm)	[13]

MCN-1	300 W Xe lamp, $\lambda > 420$ nm	3 wt% of Pt; Aqueous TEOA solution (10vol%)	60.2	7.8% (420 nm)	[14]

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