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Supplementary Materials for

Hydrogen production with ultrahigh efficiency under visible light by graphene well-wrapped UiO-66-NH_2 octahedrons

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Section 1. Materials and methods

All chemicals were obtained from commercial sources without further purification. Zirconium chloride, 2-aminoterephthalic acid and graphene oxide was purchased from Aladdin, Afa Aesar and Hengqiu Tech. Inc. respectively. GO sheets were grounded to powders under anhydrous environment before use.

Section 2. Experimental Section

2.1 Preparation of UiO-66-NH_2 octahedrons

In a typical synthesis^{S2} with some modification, $ZrCl_4$ (0.233g) and 2-aminoterephthalic acid (BDC-NH_2) (0.181g) were first dissolved in 102.1 mL N,N-dimethylformamide (DMF). Then acetic acid (22.9mL) was added into the solution, following the ultrasonic treatment for 20 min. The solution was then transferred into a 200mL Teflon-lined stainless steel autoclave and heated to 120ºC for 16h. After cooling to room temperature, the products were collected by centrifugation and wash three times with DMF to remove the excess reactants, then washed with methanol for three times to remove DMF, and finally heated at 150 ºC under vacuum for 12h.

2.2 Preparation of GOWU6N

Take 50wt% GOWU6N for example, 0.1g UiO-66-NH_2 octahedrons, 30ml deionized water and 1mL HCl were mixed in the glass vial and ultrasonic for 10min. Subsequence 0.05g GO powder was added to the system ultrasonic for 10min and stirred for 2h. Then products were collected by centrifugation at 5000 rpm and dried in air at 80 ºC. Other samples (1wt%, 10wt% and 200wt%) were prepared in the same way.

2.3 Preparation of DGO/U6N, CGO/U6N

0.1g UiO-66-NH_2 octahedrons, 30mL DMF were mixed in the glass vial ultrasonic for 10min and then 0.05g GO sheet added ultrasonic for 10min and stirred for 2h. Then products were washed with methanol for three times and collected after being dried at 80 ºC. The preparation of CGO/U6N were the same as UiO-66-NH_2 octahedrons, the only difference is before adding acetic acid, GO sheets were introduced in the solution of $ZrCl_4$, BDC-NH_2 and DMF and stirred for 12h. Finally, the three kind dried powers together with 30ml deionized water were transferred to 50 ml Teflon-lined stainless steel autoclave and heated to 120ºC for 12h and dried at 80 ºC. The samples were renamed as RGOWU6N, RDGO/U6N and RCGO/U6N respectively.

2.4 Preparation of ZIF-8 and graphene wrapped ZIF-8

The preparation of ZIF-8 was according to the previous method with some modifications [S8]. 0.375g $Zn(NO_3)_2 6H_2O$ and 0.205g 2-methyl-imidazole were dissolved into 50ml methanol respectively. Then the two solutions mixed with stirring for 2h. After that, the products were separated via centrifugation and then dried at 80 ºC. As mentioned before, in the preparation of RGOWU6N, graphene wrapped ZIF-8 was prepared by mixing 0.06g ZIF-8, 0.03g GO powders 1 ml HCl in 30ml deionized water. After stirring for 2h, the samples were gained by centrifugation and dried at 80 ºC.

2.5 Photocatalytic hydrogen production

Photocatalytic H_2 production reactions were carried out in a 200mL closed quartz flask reactor. The reactor was degassed for 1h to drive away the residual air. The photocatalytic hydrogen production was initiated by irradiating the suspension with a 300W xenon lamp (PLS-SXE300C) coupled with a UV cut-off filter (λ >420 nm). The gas products were analyzed periodically through a gas chromatograph (GC-9790Ⅱ) with a TCD detector. 5mg samples, 0.05g ErB or RhB and 28μL H_2PtCl_6 solution (1g H_2PtCl_6 dissolved in 40ml water, 5 wt% Pt) were used in the tests. In order to eliminate the mistake of the added amount of sacrifice reagent in parallel experiments, about 1L TEOA solution (3ml TEOA and 1L deionized water) and methanol solution (10ml methanol and 1L deionized water) was prepared before test. Each test needs 100ml solution and the tests of various amounts of ErB were also done.

The apparent quantum efficiency (QE) was measured at 420nm using the following equation:

$$x = \frac{2 \times \mathit{the\ number\ of\ evolved\ hydrogen\ molecules}}{\mathit{the\ number\ of\ incident\ photons}} * 100\%$$

Section 3. Characterization Section

Zeta potential of the samples was measured by ZETASIZER Nano-ZS980 from Malvern Instruments. Powder X-ray diffraction (Rigaku Ultima IV) was used to characterize the crystallinity and chemical composition of the materials studied. SEM images were gained by Hitachi S4700. TEM and HR-TEM images were taken on a FEI Tecnai G^2F30 transmission electron microscopy. The photoluminescence (PL, FLS980) emission spectra of samples were tested to investigate the recombination of photo-generated electron-hole pairs and UV-vis diffuse reflectance spectroscopy (DRS, Cary 5000) was used to measure the light absorption of the samples.

Table S1. Summary of recent reports on MOF-based photocatalysts.

Group	Time	Photocatalyst	Co-catalyst	Light source	Sacrificial reagent	Photosensitizer	H_2 production rate(umol/g/h)	Turnover number
He et al [S1]	2014	Zr-MOF	Pt	$\lambda>420$	TEOA	RhB	116.1	2.3[a]
Yuan et al [S2]	2015	Zr-MOF	Pt	$\lambda>420$	Methanol	ErB	460	17.4[b]
Xiao et al [S3]	2016	Zr-MOF	Pt	$\lambda>380$	TEOA	None	257.38	1.8[a]
Silva et al [S4]	2010	Zr-MOF	Pt	UV	Methonal	None	～740 (only active for 1h)	—[c]
Horiuchi et al [S5]	2012	Ti-MOF	Pt	$\lambda>420$	TEOA	None	<400	<1.6[a]
Pullen et al [S6]	2013	Zr-MOF	[FeFe]-(dcbdt)$(CO)_6$	Blue LED 470 nm	Ascorbate	$[Ru(bpy)_3]^{2+}$	～350	—[d]
Wen et al [S7]	2014	Cr-MOF	Pt	$\lambda>420$	TEOA	RhB	580	7.5[e]
In this work	2017	Zr-MOF/GOWU6N	Pt	$\lambda>420$	TEOA	ErB	21205.3/41396.4	82.8/161.7[a]

[a] The turnover number of per hour was calculated by the equation of TON=n(H_2)/n(Pt) based on Pt particles, the amount of H_2 was obtained according to the Experimental section of the cited papers based on the amount of practical used photocatalysts, [b] the data was obtained according to a 18h period test described by the author. [c] the specific amount of Pt was not described and [d] the co-catalyst was not Pt particles. [e] TON was corresponding to the maximum H_2 generation rate.

References

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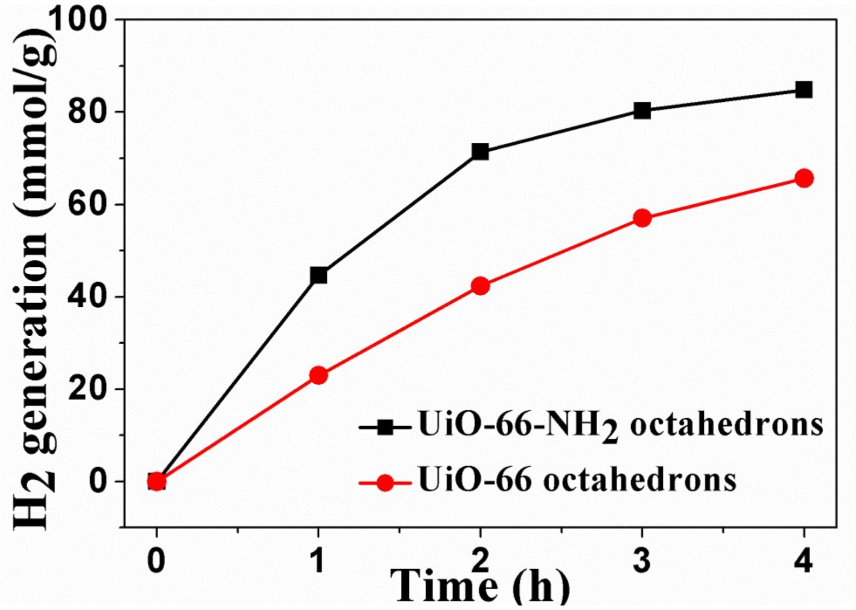

Figure S1. H_2 generation abilities of UiO-66-NH_2 and UiO-66 under the system of 0.05g ErB as sensitizer, TEOA as the sacrifice agent and Pt as co-catalyst.

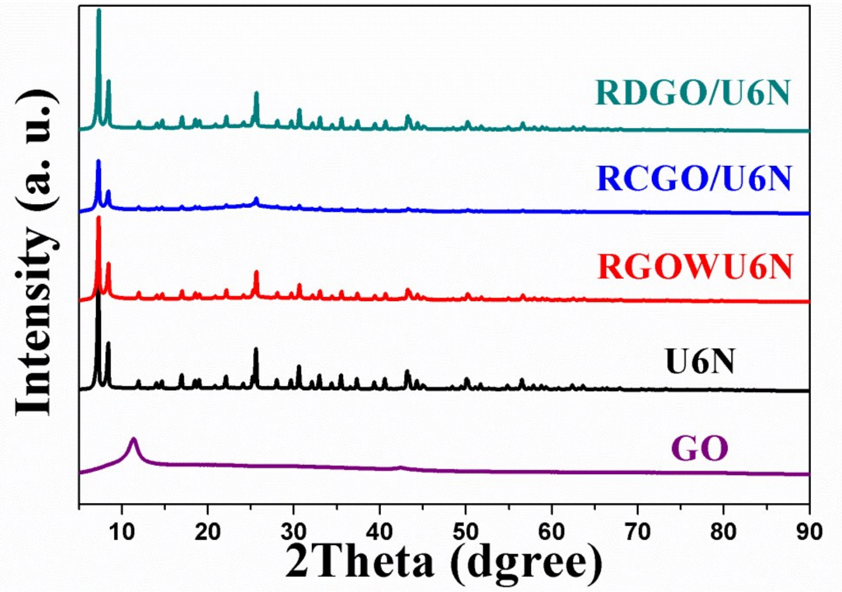

Figure S2. XRD patterns of the prepared samples.

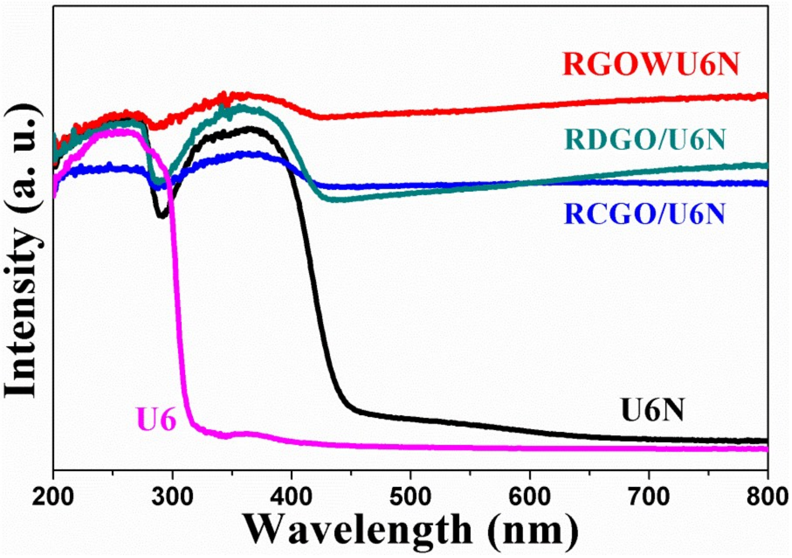

Figure S3. UV-vis diffuse reflectance spectra for UiO-66 octahedrons, UiO-66-NH_2 octahedrons, 50wt%RDGO/U6N, 50wt%RCGO/U6N and 50wt%RGOWU6N.

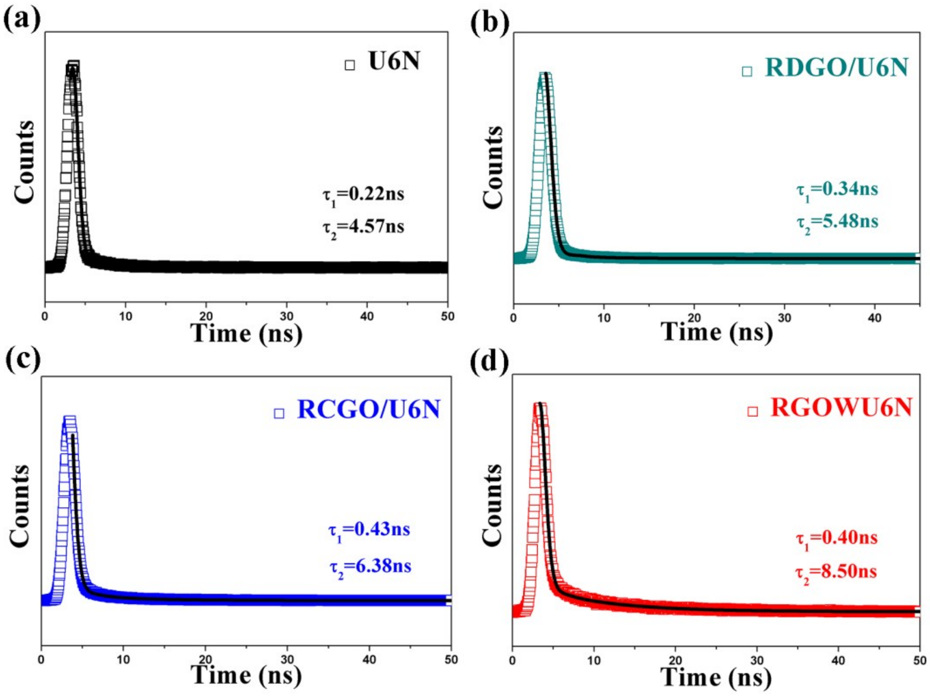

Figure S4. Decay and corresponding fit curves for UiO-66-NH_2 octahedrons (a), 50wt%RDGO/U6N (b), 50wt%RCGO/U6N (c) and 50wt%RGOWU6N (d).

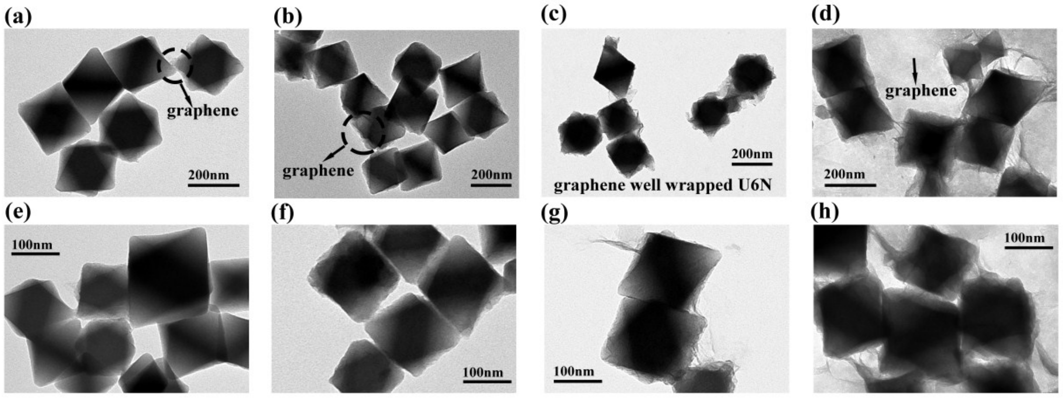

Figure S5. TEM images of RGOWU6N 1wt% (a) (e), 10wt% (b) (f), 50wt% (c) (g) and 200wt% (d) (h).

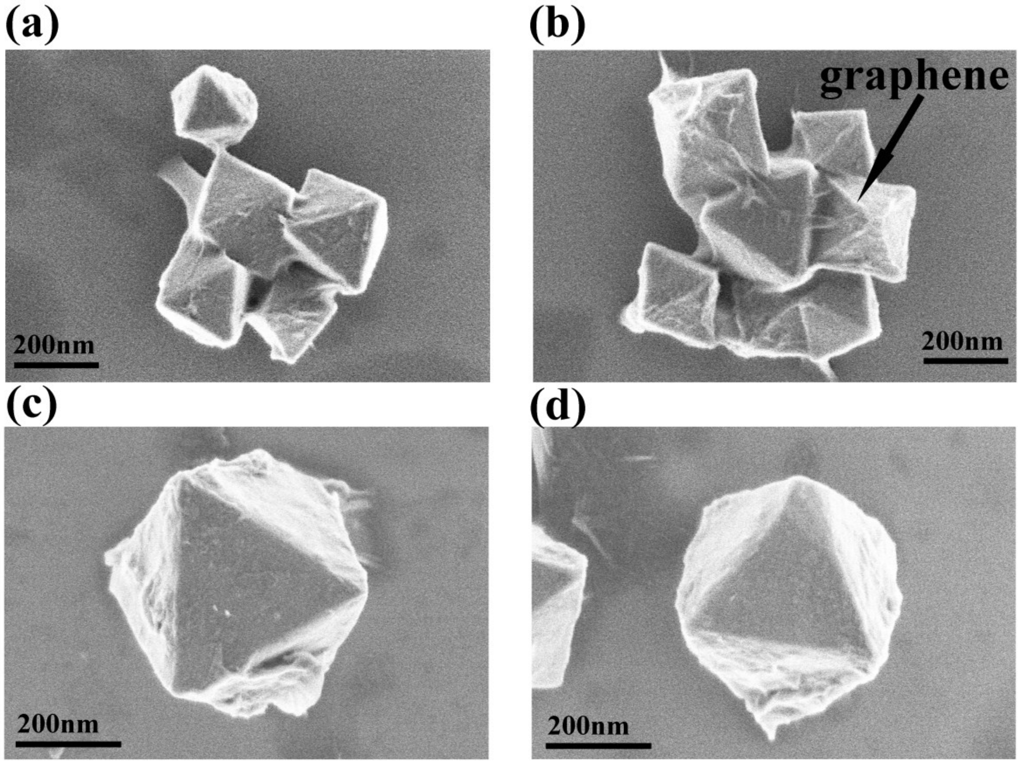

Figure S6. SEM images of 50wt% RGOWU6N.

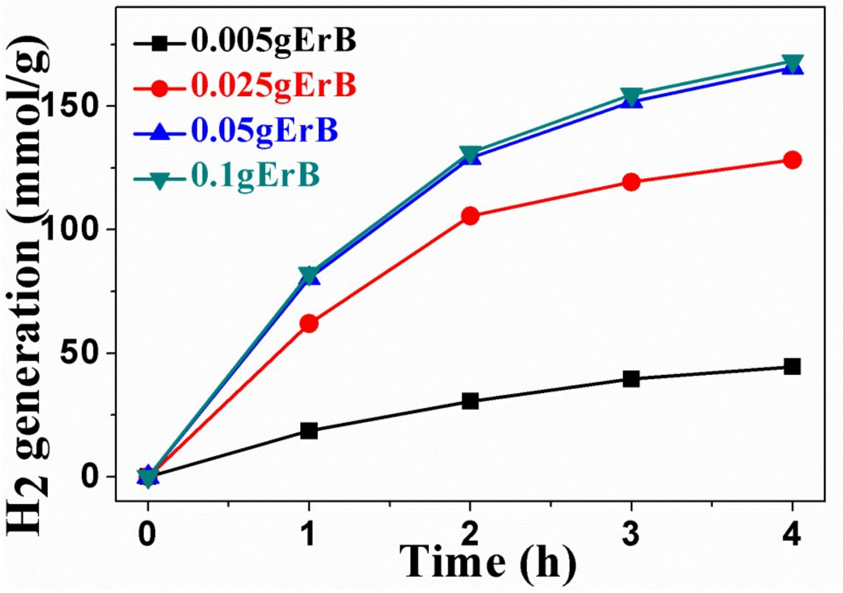

Figure S7. Water splitting performance with various amounts of ErB catalyzed by 50wt% RGOWU6N.

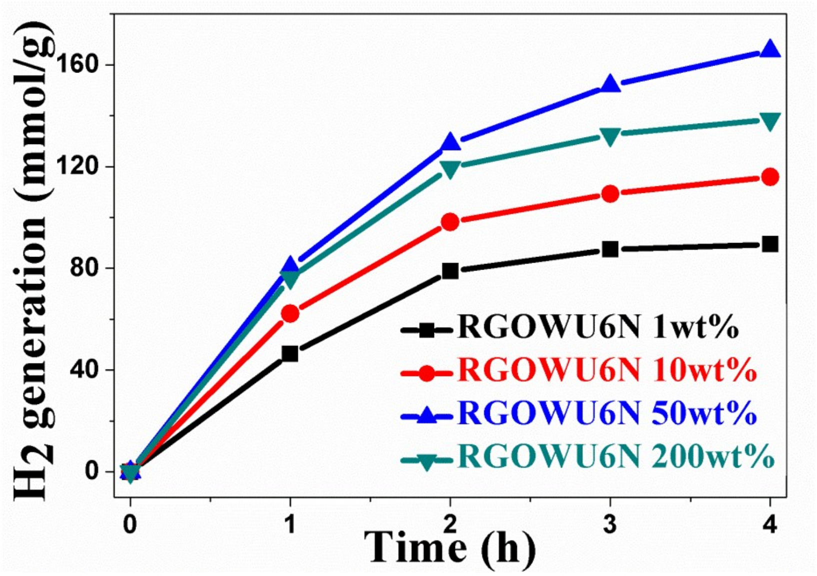

Figure S8. H_2 generation performance catalyzed by 1wt%, 10wt%, 50wt% and 200wt% RGOWU6N

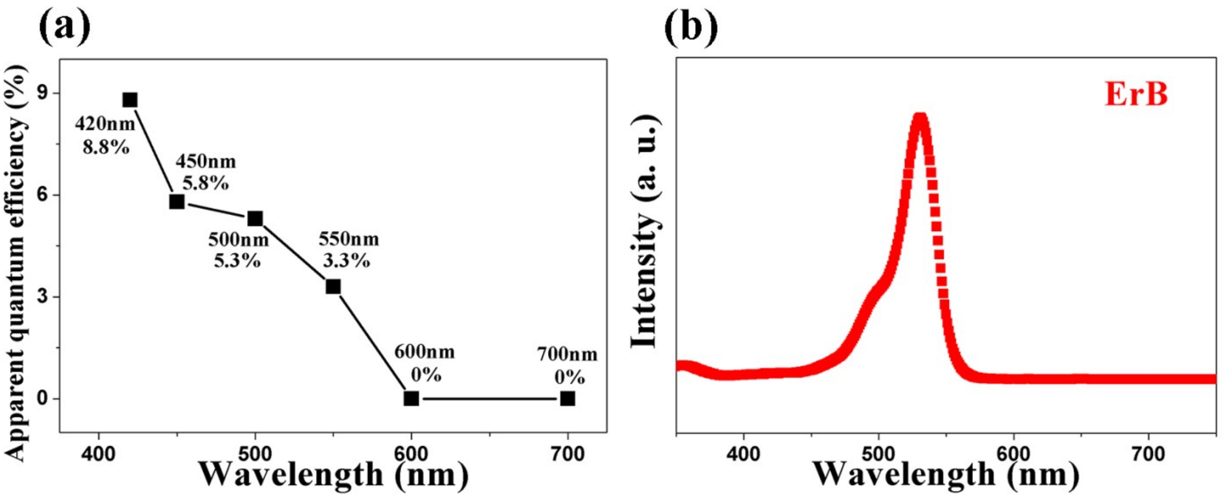

Figure S9. Quantum yield tests of 50wt% RGOWU6N (a) and UV-vis spectra of ErB (b).

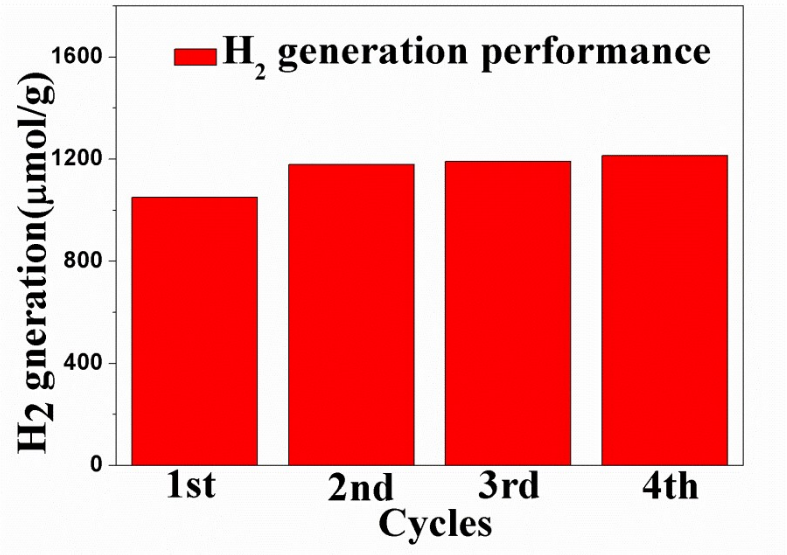

Figure S10. The recyclability of 50wt%RGOWU6N without Pt-cocatalyst to illustrate the stability of the designed structure.

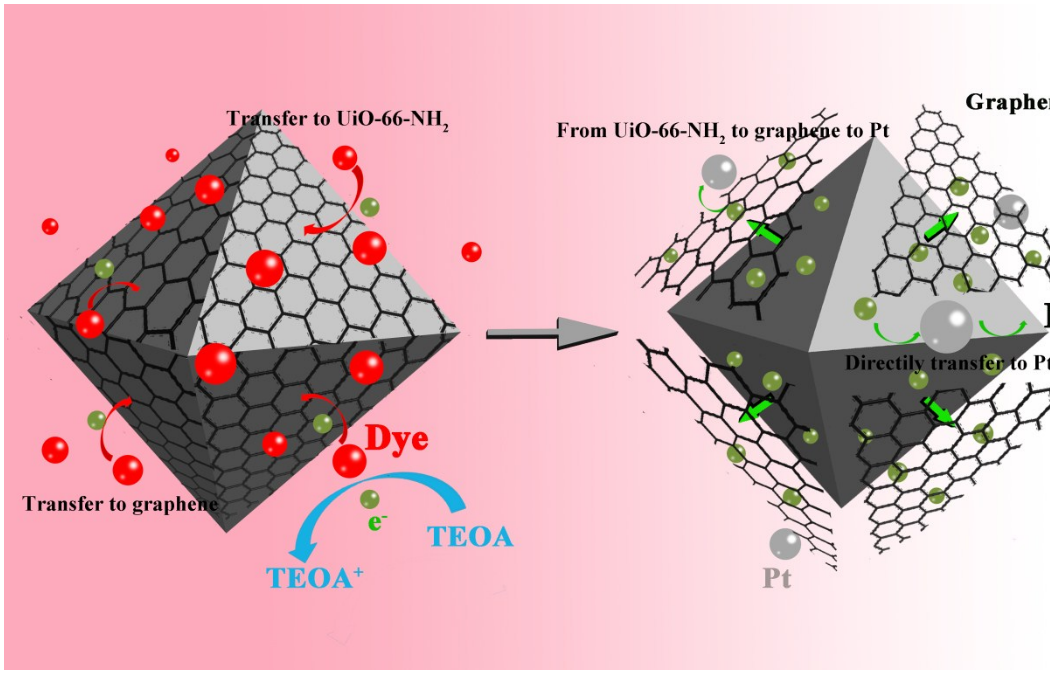

Figure S11. The proposed mechanism of multiple faces electron transfer for RGOWU6N.

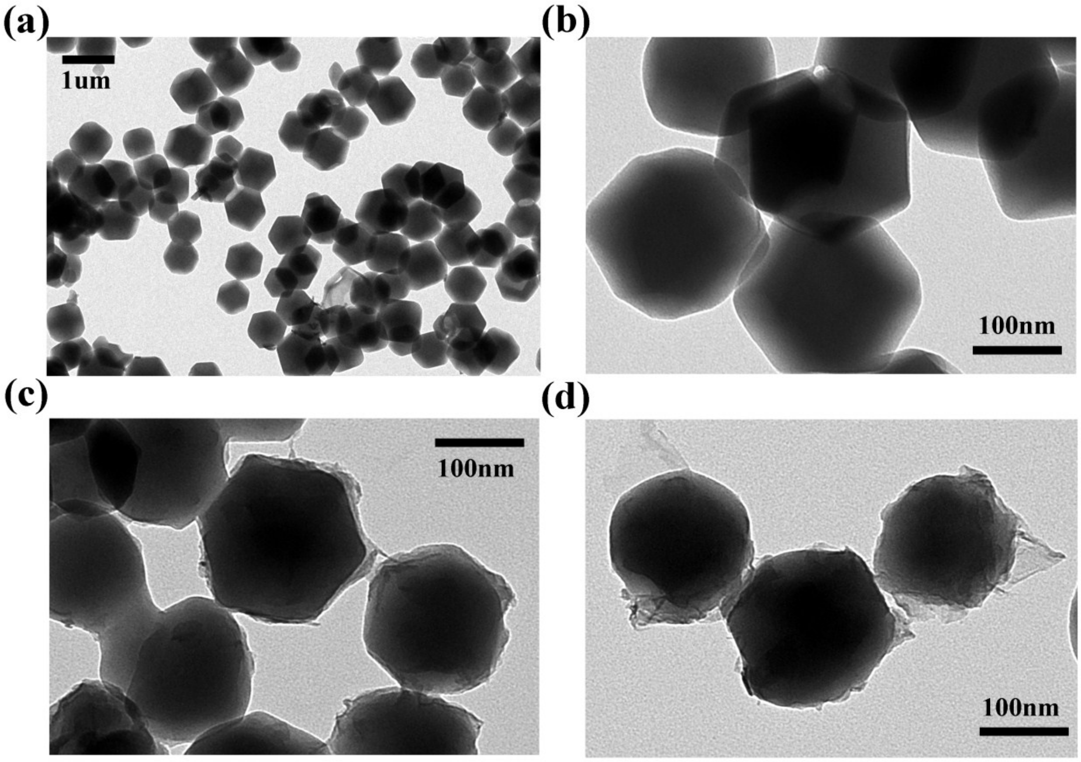

Figure S12. TEM images of ZIF-8 (a), (b) and graphene wrapped ZIF-8 (c), (d).