

## Supporting information

### **Exploring the Slow-Light Effect of Pt/TiO<sub>2</sub>-SiO<sub>2</sub> Inverse Opal on Photocatalytic Nonoxidative Coupling of Methane**

*Xiaoyi Feng, Kai Kang, Yang Wu, Jinlong Zhang, Lingzhi Wang\**

Key Laboratory for Advanced Materials and Institute of Fine Chemicals,  
School of Chemistry and Molecular Engineering, East China University of  
Science and Technology, 130 Meilong Road, Shanghai 200237, P. R.  
China.

\*Corresponding Author. Email: [wlz@ecust.edu.cn](mailto:wlz@ecust.edu.cn)

## Experiment Section

**Materials.** Sodium dodecyl sulfate (SDS), potassium persulfate (KPS) and styrene were purchased from LingFeng Chemical Reagent. Polyethylene oxide–polypropylene oxide–polyethylene oxide (P123) was obtained from Sigma-Aldrich. Titanium tetrachloride ( $\text{TiCl}_4$ ) and titanium (IV) isopropoxide (TTIP) were purchased from Aladdin. Chloroplatinic acid hexahydrate was obtained from Macklin. Tetraethyl orthosilicate (TEOS) and ethanol was purchased from Titan.

**Synthesis of PS opal template.** Polystyrene (PS) opals were prepared as hard templates to generate macropores. First, 0.60 g SDS and 0.45 g KPS were dissolved in 420 mL of mixed deionized water and ethanol at room temperature. Under nitrogen atmosphere, the solution was heated to 344 K, and then 36 mL of styrene was injected into the solution. The mixture was stirred for 19 h at 344 K. Finally, the white colloidal suspension was obtained. The diameter of PS opals was determined by the ratio of water to ethanol. PS sphere with the diameters of 170, 250 and 335 nm were synthesized with the water/ethanol volume ratios of 2.50, 2.18 and 1.60, respectively.

**Fabrication of ordered PS arrays (solid).** The prepared PS colloidal suspension was transferred into beakers with the fluid level height of about 50.0 mm. The beakers were kept in a 353 K oven until the liquid was dried out. The samples were named as PS-170, PS-250 and PS-335.

**Fabrication of ordered PS arrays (film).** 500.00  $\mu\text{L}$  of PS emulsion was dispersed into 25.0 mL of water. Three pieces of quartz slides were immersed vertically into the solution. The beakers were kept in 353 K atmosphere until the liquid was dried out.

**Preparation of MATS, HTS inverse opals, METS and NTS (solid).** The hierarchical ordered  $\text{TiO}_2$ - $\text{SiO}_2$  (HTS) inverse opals were synthesized by the evaporation-induced self-assembly method. Generally, the  $\text{TiO}_2$ - $\text{SiO}_2$  precursor was prepared by mixing 2.0 g of P123, 30.0 mL of ethanol, 0.89 mL of TEOS, 0.53 mL of  $\text{TiCl}_4$ , and 3.30 mL TTIP. After the mixture was stirred for 4 h at room temperature, the PS microarray was soaked completely in the precursor, which was evaporated at 313 K and 55% relative humidity for 3 days. The obtained pieces were calcined at 773 K for 5 h with a heating rate of 1 K/min for 3 times. The samples denoted as HTS were collected and ground to powder for further use. For the preparation of macro-TS (MATS) and meso-TS (METS), PS and P123 were used as the macroporous and mesoporous templates. And NTS with no pore structure were synthesized without P123 and PS.

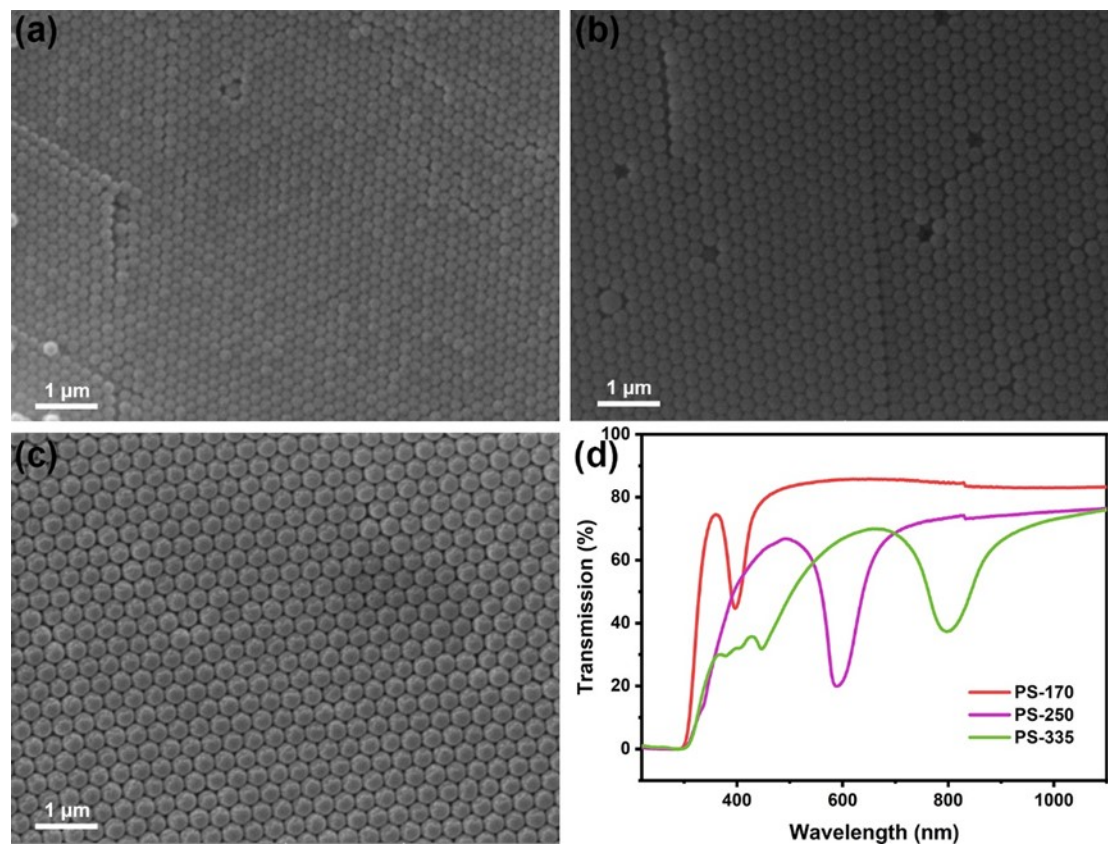
**Preparation of MATS inverse opals (film).** 100.00  $\mu\text{L}$  of the above precursor without P123 was dripped on the PS array films. Spin coating process was carried out at 2000 r/min for 40 s. The coated slides were kept at room temperature overnight and then calcinated at 773 K for 2 h with a heating rate of 1 K/min. The samples were marked as TS-170, TS-250 and TS-335.

**Synthesis of Pt/MATS, Pt/METS, Pt/HTS and Pt/NTS.** The samples were synthesized through loading Pt on  $\text{TiO}_2\text{-SiO}_2$  by the photodeposition method. Typically, ca. 250.0 mg of TS was dispersed in 20.0 mL of water and 20.0 mL ethanol. After that, 6.6 mL of 2.0 g/L  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  aqueous solution was added to the mixture. The mixture was stirred for 45 min and then irradiated by a 300-W xenon lamp for 1 h. The product was obtained by centrifuging, then washed with ethanol and water 3 times and dried in 353 K oven overnight.

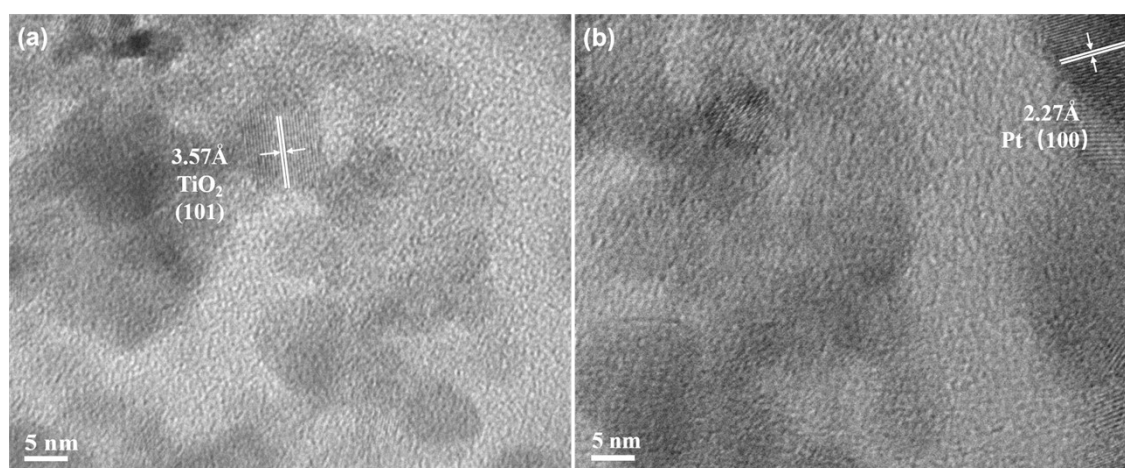
**NOCM Reaction.** The photocatalyst as ground powder (40.0 mg, 30.0 mg, 10.0 mg, 5.0 mg) or film (10.0 mg, 5.0 mg, 2.0 mg) was put into a quartz reaction vessel (45.0 mL), where the quantity uncertainty is within  $\pm 0.2$  mg. The vessel was sealed by clips and vacuum treatment. Afterward, 1.0 mL of pure methane (99.99%) was injected into the vessel by a gas injection needle. The vessel was irradiated by a 300 W Xe lamp (light power density =  $210 \text{ mW}/\text{cm}^2$ ) for 2 h. Before the photocatalytic NOCM reaction, all the samples had been evacuated in a tube furnace at 393 K for 4 h to remove the adsorbed water and other molecules. The hydrocarbon products were analyzed by gas chromatography (GC) with a flame-ionization detector (FID). Hydrogen was analyzed by GC with a thermal conductivity detector (TCD). The relative detection deviation was less than 5% for GC.

**Instruments and Characterization.** The morphology was characterized by transmission electron microscopy (TEM, JEM1400) and high-resolution transmission electron microscopy (HRTEM, JEM2100). Powder X-ray diffraction (XRD) characterization of all samples was performed on a Rigaku D/MAX 2550 diffractometer (Cu K radiation,  $\lambda = 1.5406 \text{ \AA}$ ) operating at 40 kV and 40 mA; data were collected in the range of  $10\text{--}80^\circ$  ( $2\theta$ ). The scanning electron microscopy (SEM) analysis was performed using a TESCAN Nova III scanning electron microscope. The BET surface area measurement was performed by  $\text{N}_2$  adsorption at 77 K using an ASAP2020 instrument. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha system with Al  $\text{K}\alpha$  radiation ( $h\nu = 1486.6 \text{ eV}$ ). The shift in the binding energy owing to the relative surface charging was corrected using the C 1s level at 284.6 eV as an internal standard. UV-Vis spectrophotometer (Shimadzu UV-2450) was used to analyze the absorption and transmission spectra of the samples. The electrochemical measurement was performed on an electrochemical analyzer (Zahner, Zennium) at room temperature. 5 mg of sample was dissolved in 0.5 mL of ethanol, and then 20.00  $\mu\text{L}$  of solution was dropped on the FTO glass within an area of  $1 \text{ cm}^2$  and

dried at room temperature. The transient photocurrent response of the different samples was determined in a 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution under irradiation of a 300-W Xe lamp with UV reflector. The Brunauer-Emmett-Teller (BET) surface area measurement was carried out over 100 mg of sample by N<sub>2</sub> adsorption at 77 K using an ASAP2020 instrument.



**Figure S1.** SEM images of PS opal films with sphere diameters of (a) 170 nm, (b) 250 nm and (c) 335 nm; (d) transmission spectra of the PS opal films.



**Figure S2.** HRTEM images of Pt/MATS-170.

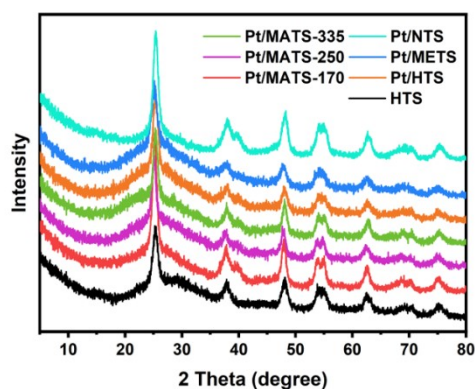


Figure S3. XRD patterns of HTS, Pt/MATS, Pt/HTS, Pt/METS and Pt/NTS.

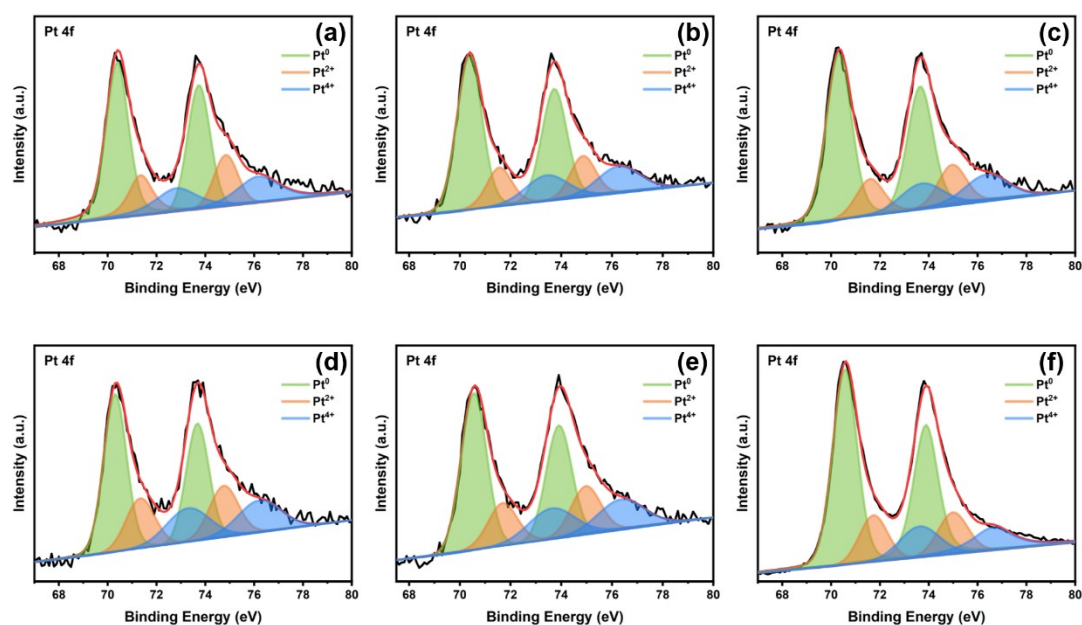


Figure S4. The Pt 4f XPS fine spectra of (a) Pt/MATS-170, (b) Pt/MATS-250, (c) Pt/MATS-335, (d) Pt/HTS, (e) Pt/METS, (f) Pt/NTS.

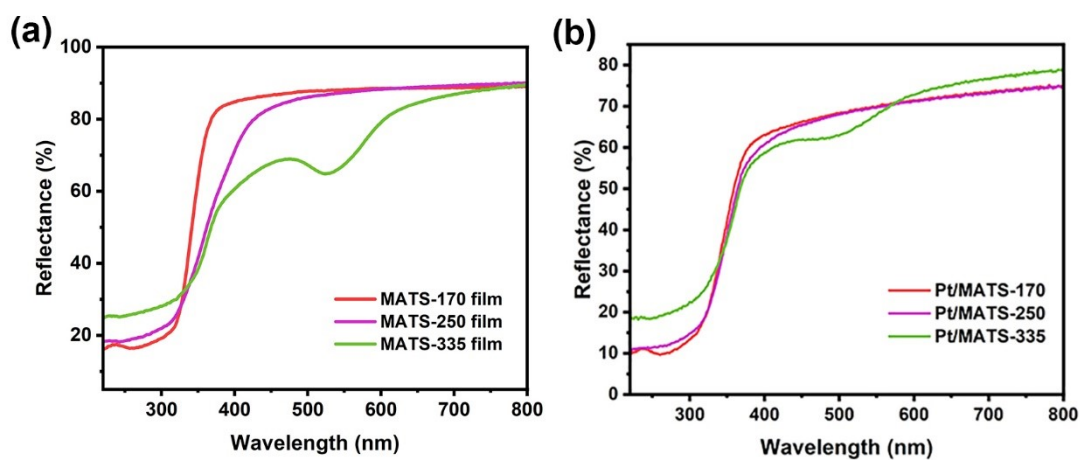


Fig S5. UV-Vis diffuse reflection spectra of (a) MATS and (b) Pt/MATS films.

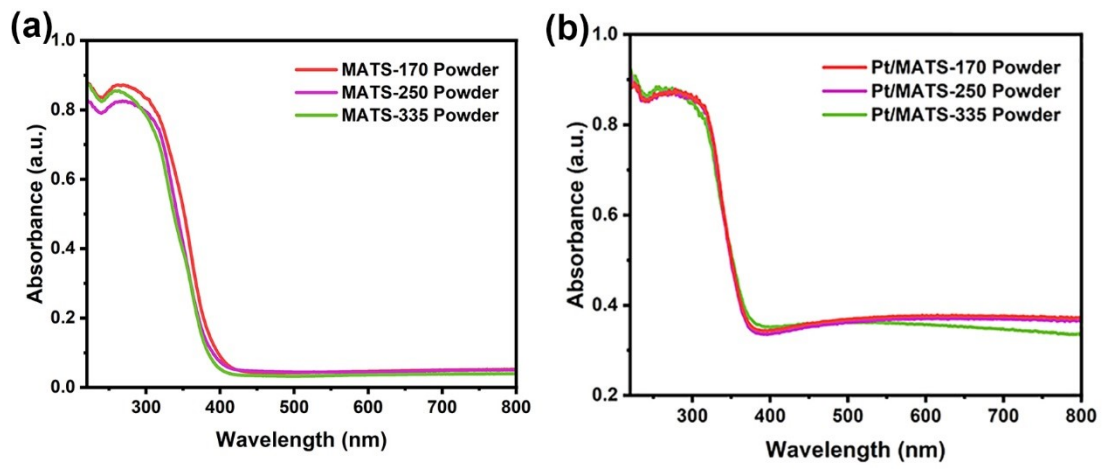
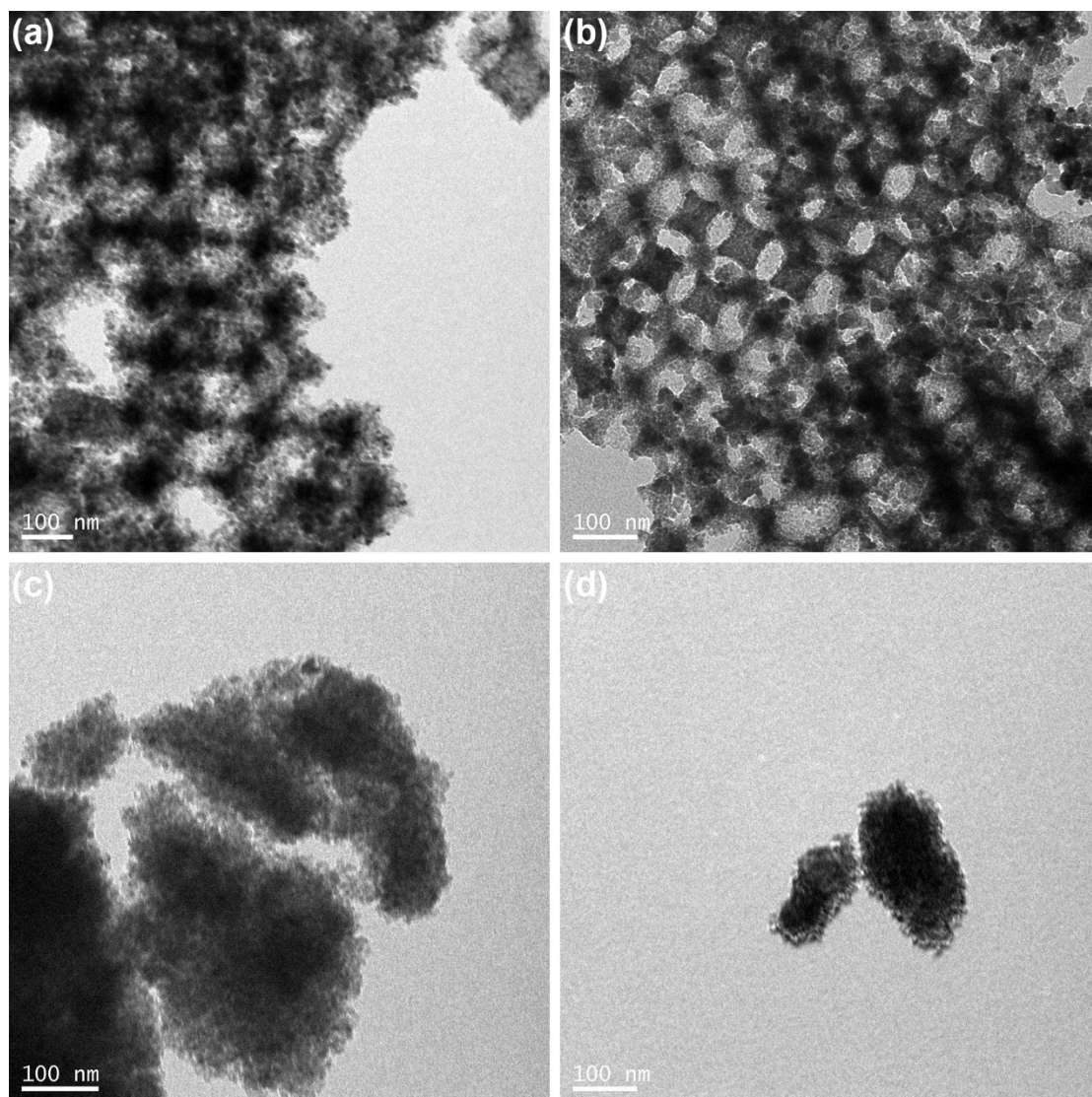
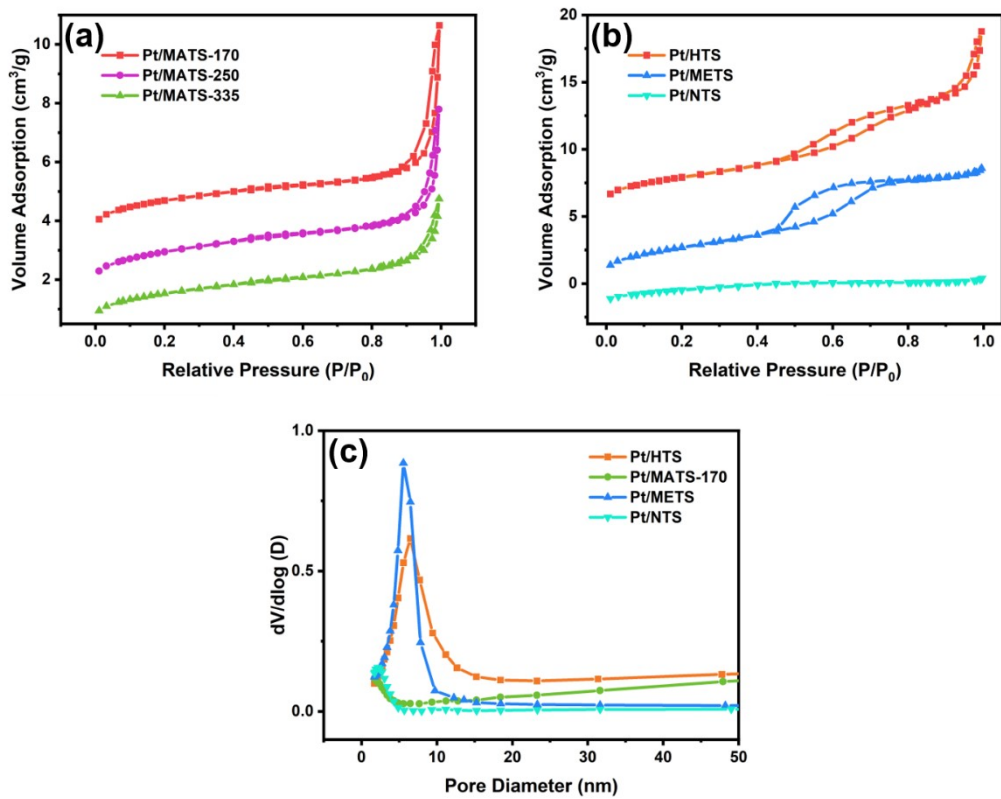


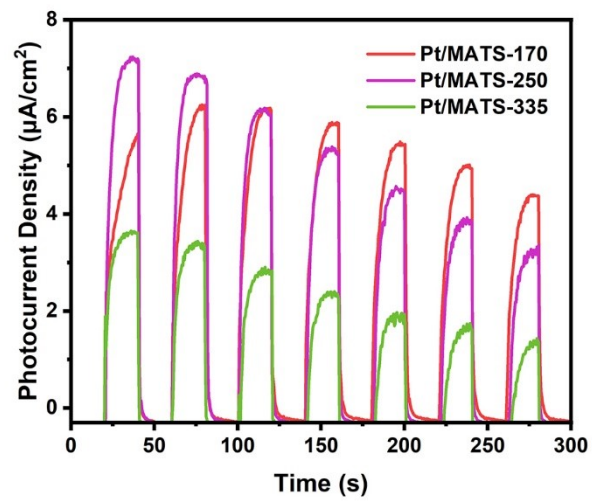
Fig S6. UV-Vis absorption spectra of (a) MATS and (b) Pt/MATS powders.



**Figure S7.** TEM images of (a) Pt/HTS; (b) Pt/MATS; (c) Pt/METS; (d) Pt/NTS.



**Figure S8.** Nitrogen adsorption–desorption isotherms of (a) Pt/MATS; (b) Pt/HTS, Pt/METS, Pt/NTS. Pore size distributions of (c) Pt/HTS, Pt/MATS-170, Pt/METS, Pt/NTS.



**Figure S9.** Transient photocurrent responses of Pt/MATS.



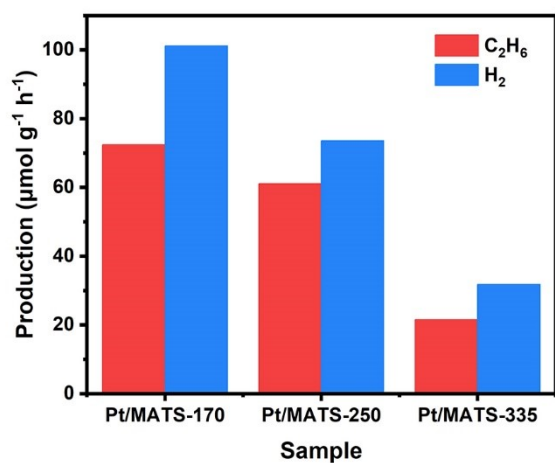


Figure S10.  $C_2H_6$  and  $H_2$  production from the photodriven NOCM reaction over Pt/MATS.

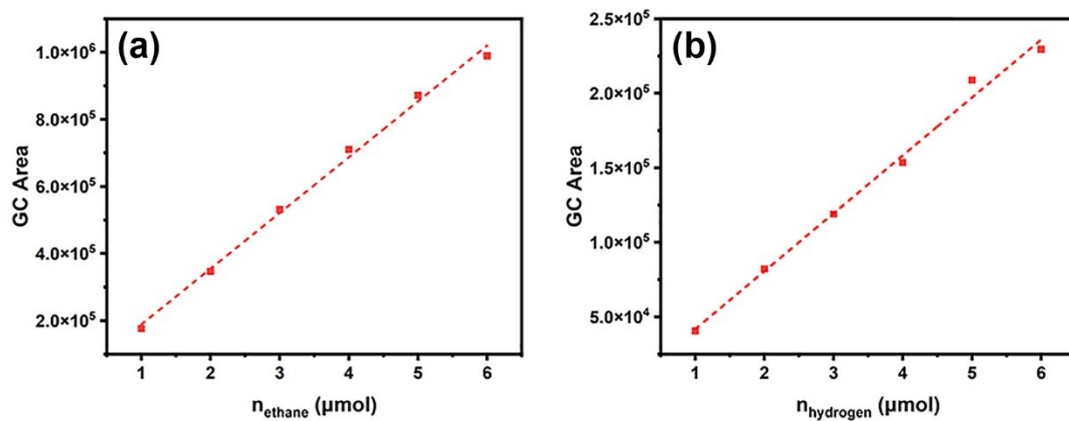
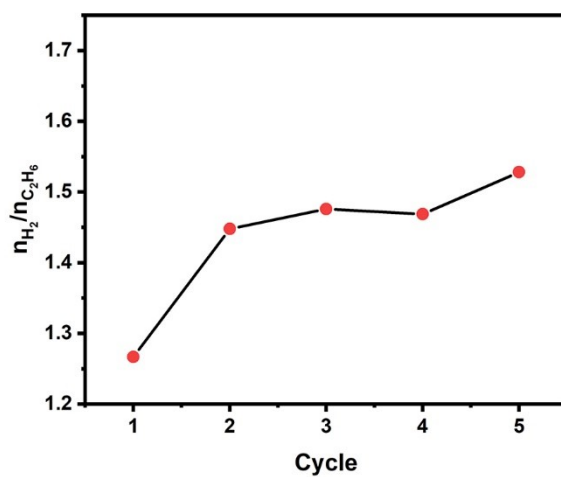


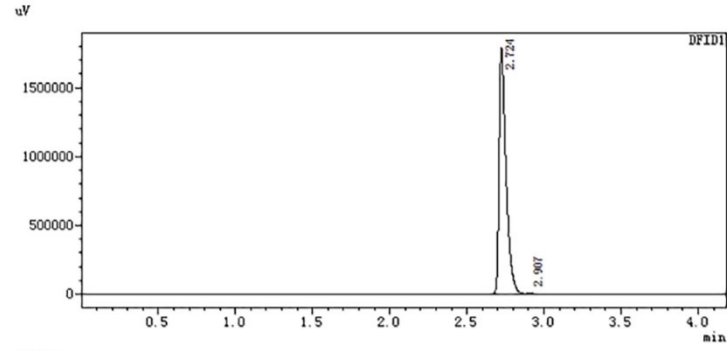
Figure S11.  $H_2/C_2H_6$  ratio for the cyclic NOCM reaction over Pt/MATS-170.

Figure S12. Calibration curves of (a)  $C_2H_6$  and (b)  $H_2$ .

<样品信息>

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 方法文件名 : GC - 副本 - 副本.gcm  
 批处理文件名 :  
 样品编号 : 1 样品类型 : 未知  
 进样体积 : 1 uL  
 分析日期 : 2021/7/14 星期三 下午 20:57:32 分析者 : System Administrator  
 处理日期 : 2021/7/14 星期三 下午 21:02:25 处理者 : System Administrator

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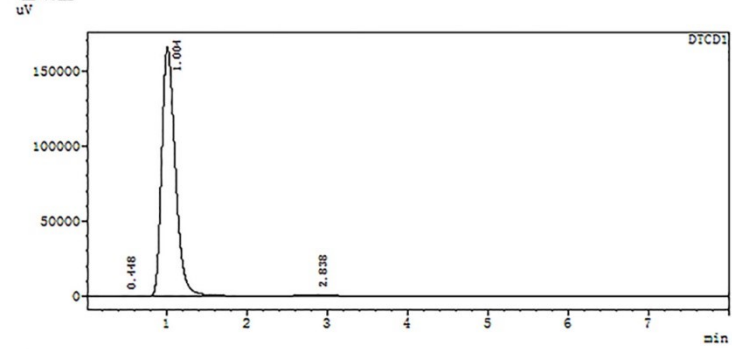
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1	2.724	5881035	1788994	93.483		■	
2	2.907	30553	9089	0.537		▼	
总计		5891588	1798084				

Figure S13. GC chromatograms of C<sub>2</sub>H<sub>6</sub> produced by 2 mg Pt/MATS-170 film.

<样品信息>

样品名 : TEST02-氢气-20190511  
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 方法文件名 : GC - 副本 - 副本.gcm  
 数据文件名 :  
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 进样量 : 1 uL  
 分析日期 : 2021/10/10 星期日 上午 11:12:09 分析者 : System Administrator  
 处理日期 : 2021/10/10 星期日 上午 11:20:15 处理者 : System Administrator

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峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	0.448	1025	184	0.000			
2	1.004	1958337	165901	0.000			
3	2.838	23169	1093	0.000			
总计		1982532	167137				

Figure S14. GC chromatograms of H<sub>2</sub> produced by 2 mg Pt/MATS-170 film.

**Table S1.** Surface Pt content of samples

Sample	Pt/MATS-170	Pt/MATS-250	Pt/MATS-335	Pt/HTS	Pt/METS	Pt/NTS
Surface Pt content	0.58%	0.58%	0.59%	0.43%	0.47%	3.20%

**Table S2.** BET surface area of samples

Samples	Pt/MATS-170	Pt/MATS-250	Pt/MATS-335	Pt/HTS	Pt/METS	Pt/NTS
BET surface area (m <sup>2</sup> /g)	129	128	118	235	256	122

**Table S3.** Results of AQY for methane conversion at 365 nm light

Sample	Pt/MATS-170	Pt/MATS-265	Pt/MATS-335
Light power density	38 mW/cm <sup>2</sup>		
H <sub>2</sub> production (mol)	0.0221	0.0189	0.0153
AQY (%)	2.65*10 <sup>-4</sup>	2.26*10 <sup>-4</sup>	1.83*10 <sup>-4</sup>

The Apparent quantum yield (AQY) can be calculated as:

$$AQY = \frac{N_{reacted}}{N_{incident}} \times 100\%$$

We use produced hydrogen to calculate the reacted electrons. The number of the reacted electrons is:

$$N_{reacted} = 2 \times n_{H_2} \times 6.02 \times 10^{23}$$

The number of the incident photons is:

$$N_{incident} = \frac{Pt}{hv} = \frac{Pt\lambda}{hc}$$

In the equation, t is the time (s), h is Planck's constant, v is the light frequency, and c is the speed of light in free space. The light power is:

$$P = IS$$

The projected area of the reactor was a rectangle with a length of 40 mm and a width of 25 mm. Therefore, the irradiated area (S) is:

$$S = 4.0 \times 2.5 = 10 \text{ cm}^2$$

Take the estimation of the AQY of Pt/MATS-170 at 365 nm as an example:

$$N_{incident} = 38 \times 10 \times 10^{-3} \times 4 \times 3600 \times 365 \times 10^{-9} \div (3 \times 10^8 \times 6.626 \times 10^{-34})$$

$$AQY = 100\% \times 2 \times 0.0221 \times 6.02 \times 10^{23} \div (1 \times 10^{22}) = 2.65 \times 10^{-4}\%$$

**Table S4.** Recent works on photocatalytic NOCM reaction.

Sample	Condition	AQY	Reference
Ga <sub>2</sub> O <sub>3</sub>	300 W Xe lamp for 3 h; 0.2 g sample; 200 mol CH <sub>4</sub>	0.01% at 220–270 nm	1
(Zn <sup>+</sup> , Zn <sup>2+</sup> )-ZSM-5 <sup>-</sup>	150 W high-pressure Hg lamp for 8 h; 1 g sample; 200 mol CH <sub>4</sub>	0.55% at 300–400 nm	2
Pt/HGTS (2%)	300 W Xe lamp for 4 h; 0.2 g sample; 44.6 mol CH <sub>4</sub>	1*10 <sup>-4</sup> % at 350 nm	3
Ag-HPW/TiO <sub>2</sub>	Hamamatsu LC8–06 Hg-Xe stabilized irradiation lamps for 7 h, 0.1 g samples; CH <sub>4</sub> = 0.3 MPa	3.5 % at 362 nm	4
Pd/Ga <sub>2</sub> O <sub>3</sub>	(ASM401N, Asumi-Giken) 40 W low-pressure mercury lamp, 0.05 g samples; CH <sub>4</sub> flow rate = 20 mL min <sup>-1</sup>	3.5 % at 362 nm	5
Pt/MATS-170	300 W Xe lamp for 2 h; 0.005 g sample; 44.6 mol CH <sub>4</sub>	2.65*10 <sup>-4</sup> % at 365 nm	This paper

#### Reference

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2. L. Li, G.-D. Li, C. Yan, X.-Y. Mu, X.-L. Pan, X.-X. Zou, K.-X. Wang and J.-S. Chen, *Angewandte Chemie International Edition*, 2011, **50**, 8299-8303.
3. S. Wu, X. Tan, J. Lei, H. Chen, L. Wang and J. Zhang, *J Am Chem Soc*, 2019, **141**, 6592-6600.
4. X. Yu, V. L. Zholobenko, S. Moldovan, D. Hu and A. Y. Khodakov, *Nature Energy*, 2020.
5. S. P. Singh, A. Anzai, S. Kawaharasaki, A. Yamamoto and H. Yoshida, *Catalysis Today*, 2021, **375**, 264-272.