

Supporting Information

Photocatalysis triggered CVD synthesis of graphene at low temperature

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Preparation of photocatalyst. CeO₂/Al₂O₃@graphene photocatalyst was prepared by co-precipitation method. A certain amounts of Al(NO₃)₃·9H₂O, Ce(NO₃)₃·6H₂O and graphene powder with a mass ratio of 200 : 5 : 1 were dissolved in deionized water (DI) and stirred mechanically for 60 min at 200 r/min rate at 50 °C. Then the NH₃·H₂O was added drop-wise to the solution while keeping a constant pH value of 9 and continuous stirring for 3 h. The products were obtained by centrifugation after aged for 6 h, washed with DI water for several times and then freeze-drying for 12 h. Finally, the obtained powder was calcined at 500 °C with a flow of 100 sccm Ar for 1 h to obtain the final products.

Synthesis of graphene. Experiments were carried out in a tube furnace with two heating zones. A piece of Cu foil (25 μm thick, purity >99.9%, Alfa Aesar, Product No. 46365) was ultrasonically cleaned in acetic acid, acetone, and isopropanol in sequence for 5 min to remove the oxide and organic impurities. The Cu foil was loaded into a quartz tube and heated to 1070 °C with the flow of 450 sccm Ar in atmospheric pressure. Subsequently, the Cu foil was annealed at 1070 °C with the flow of 450/30 sccm Ar/H₂ for 40 min. Then, the photocatalyst beforehand placed into the upstream position and

far away from the heating zone (Fig. S1) was irradiated with UV-visible light by a 300 W Xe lamp, and the CH₄/H₂ gas flow of 6/10 sccm was introduced to the CVD system for 5-180 min for graphene growth. Finally, the Cu foil was drawn out to rapidly cool down the sample to room temperature with a gas mixture of H₂/Ar.

Transfer of graphene. Typically, the graphene sample was transferred by a wet etching method using polymethyl methacrylate (PMMA) as mediated protector. For transfer, the PMMA was spin-coated on the graphene/Cu at a speed of 3000 r/min for 30 s. Then, the stack of PMMA/graphene/Cu was immersed into FeCl₃ aqueous solution to etch away the Cu metal after heating. Afterward, the residual stack was washed with DI water and transferred on a SiO₂/Si wafer, followed by heating at 70 °C for 10 min. Finally, the graphene/SiO₂/Si can be obtained after removing the PMMA by the dissolution in acetone.

Characterizations. OM images were collected with a BX51 optical microscope (Olympus, Japan). The surface morphology and structural properties of photocatalyst and graphene films were characterized by TEM (ThermoFisher Scientific Talos F200S), SEM (JEOL JSM-7800F) and AFM (Veeco Nanoscope IIIa). Raman spectra and mapping were obtained with a LabRAM HR Evolution (LabRAM HR Evolution) using 532 nm excitation wavelength. BET surface area and BJH analysis (Micromeritics ASAP 2020) were used to determine the total specific surface area and pore size distribution. The quality of photocatalyst was further characterized by XPS (Thermo Scientific Escalab 250Xi), steady/transient state fluorescence spectroscopy (Edinburgh FLS1000) and X-ray diffraction (XRD) (PANalytical B.V. Empyrean). The GC-MS data was acquired by GCMS-TQ8040.

Device Fabrication and Measurement. The electrical properties of the graphene were measured at room temperature in the atmosphere. We fabricated a graphene field effect transistor (FET) on a doped Si substrate with 300 nm of SiO₂. The photocurrent response measurements and electrochemical impedance spectra (EIS) were conducted in a three-electrode system on a CHI 760E electrochemical workstation.

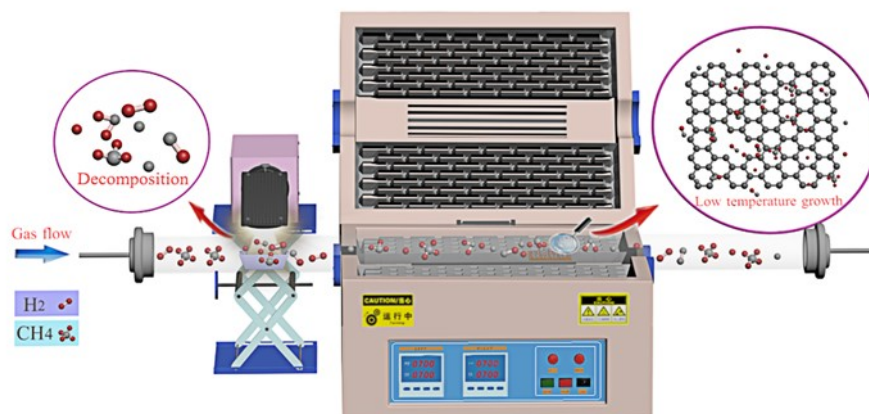


Fig. S1 Device diagram of graphene growth with the PTC-CVD approach.

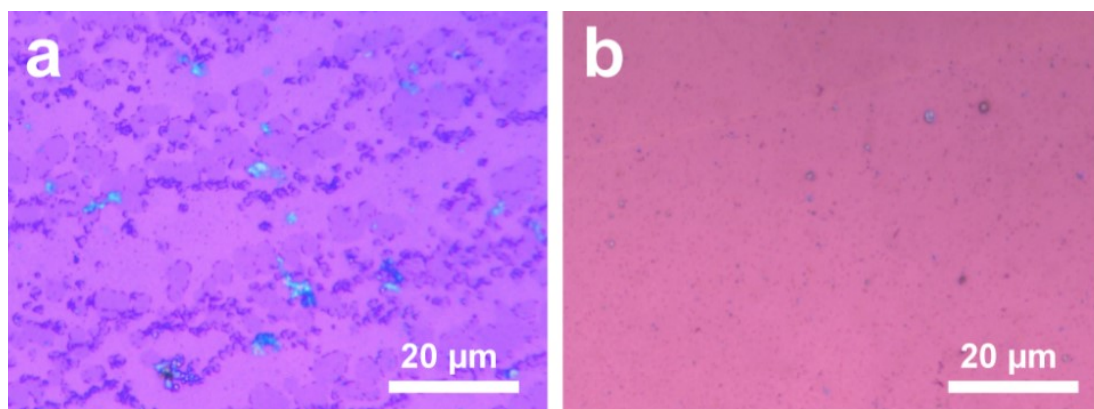


Fig. S2 The OM images of graphene films grown with (a) CeO₂/Al₂O₃ and (b) CeO₂/Al₂O₃@graphene as photocatalysts.

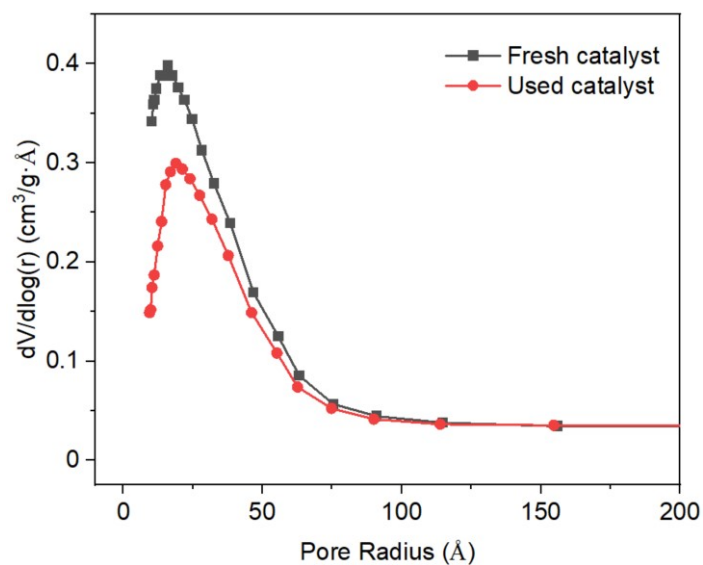


Fig. S3 BJH pore size distribution curves of fresh and used $\text{CeO}_2/\text{Al}_2\text{O}_3@\text{graphene}$ photocatalysts.

Table S1 Atoms ratios of $\text{CeO}_2/\text{Al}_2\text{O}_3@\text{graphene}$

Data Sources	Al/Ce		$\text{Ce}^{3+}/\text{Ce}^{4+}$	
	Fresh	Used	Fresh	Used
Feed	37.5:1	37.5:1	/	/
EDS	77.7:1	/	/	/
XPS	31.2:1	34.3/1	0.28	0.30

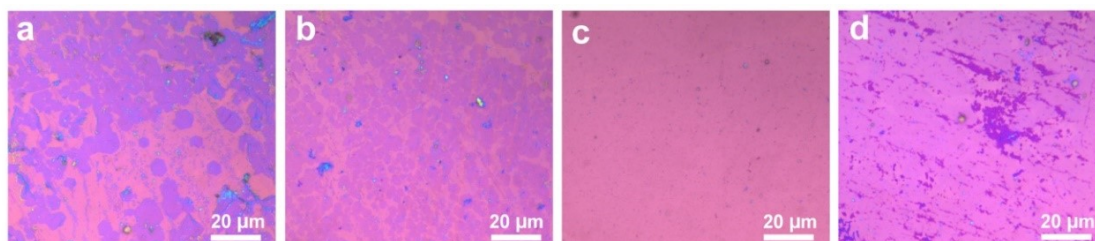


Fig. S4 Optical microscopy images of graphene films transferred on the SiO_2/Si wafers at different growth temperatures. (a) 600 °C, (b) 650 °C, (c) 700 °C, (d) 750 °C.

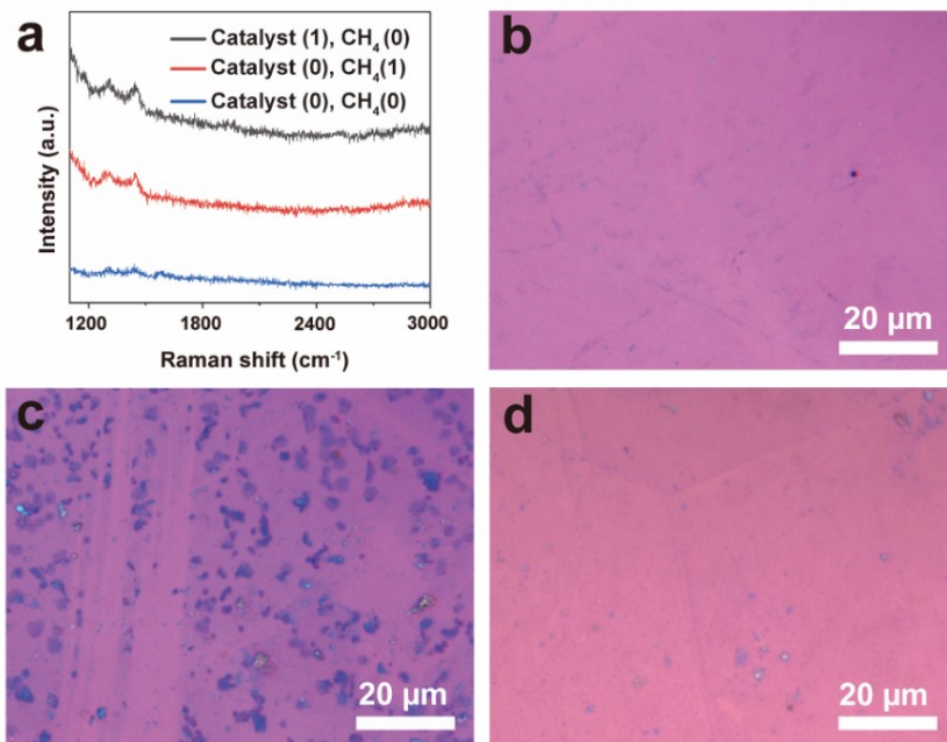


Fig. S5 Raman spectra (a) and optical microscopy images (b-d) of graphene films obtained using the present method. 1 represents the presence of photocatalyst or CH_4 during the growth phase, and 0 represents the absence of photocatalyst or CH_4 during the growth phase. (b) With $\text{CeO}_2/\text{Al}_2\text{O}_3$ @graphene photocatalyst (1) and without CH_4 (0); (c) Without $\text{CeO}_2/\text{Al}_2\text{O}_3$ @graphene photocatalyst (0) and with CH_4 (1); (d) Without $\text{CeO}_2/\text{Al}_2\text{O}_3$ @graphene photocatalyst (0) and without CH_4 (0).

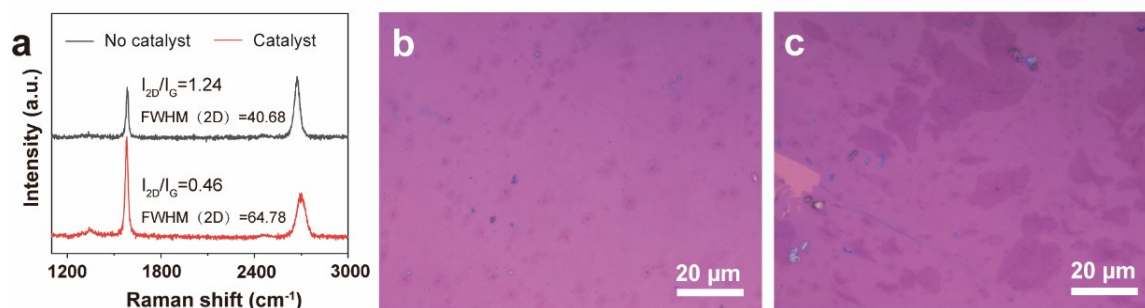


Fig. S6 (a) Raman spectra and (b-c) OM images of graphene films at conventional growth temperature of $1050\text{ }^\circ\text{C}$. (b) The graphene CVD growth without the $\text{CeO}_2/\text{Al}_2\text{O}_3$ @graphene photocatalyst; (c) The graphene CVD growth with the $\text{CeO}_2/\text{Al}_2\text{O}_3$ @graphene photocatalyst. Note: the CVD growth time is 5 min with the $\text{Ar}/\text{H}_2/\text{CH}_4$ gas flowrates of 450 sccm / 10 sccm / 1 sccm after 40 min annealing of Cu foil with the Ar/H_2 gas flowrates of 450 sccm / 10 sccm.

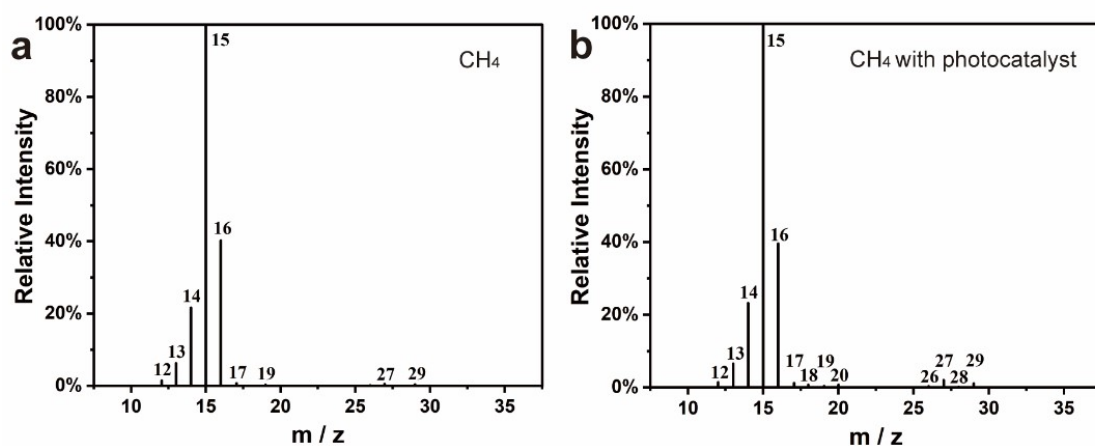


Fig. S7 The ex-situ GC-MS data of pure CH₄ gas (a) and its decomposition products after photocatalysis (b).

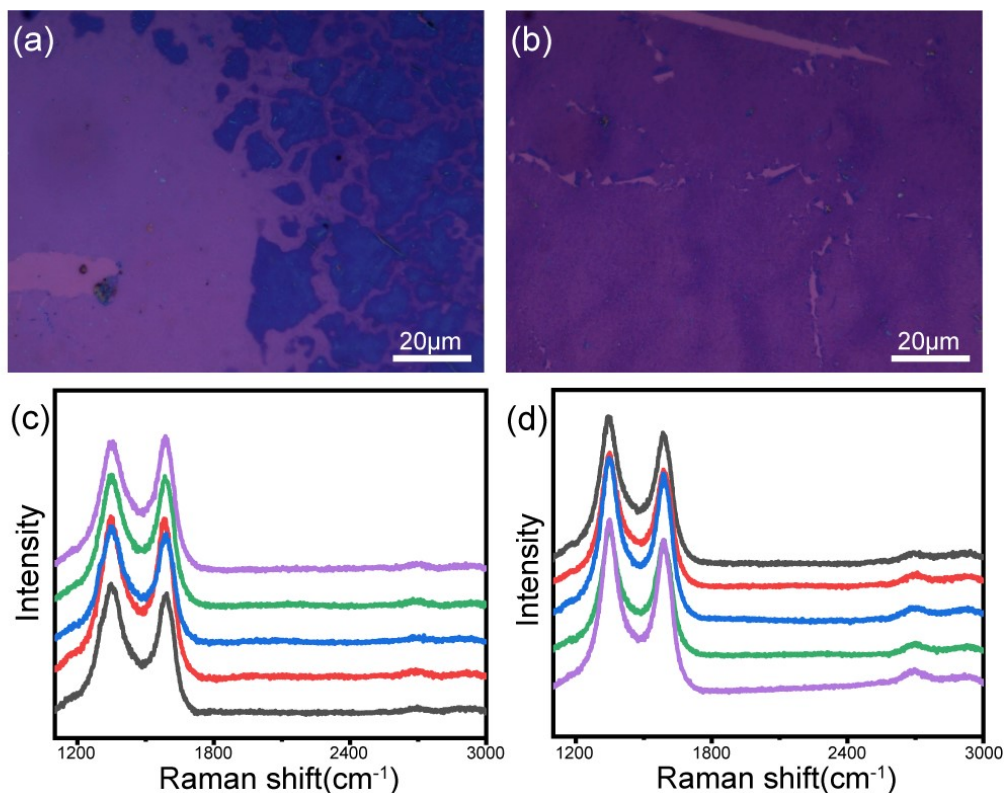


Fig. S8 The OM images and Raman spectra of CVD-grown carbon films with 6 sccm ethane (C₂H₆) as direct carbon source at 700 °C. (a), (c) The Cu foil was directly annealed at 700 °C; (b), (d) The Cu foil was first annealed at 1070 °C and then cooled down to 700 °C for CVD growth with our standard growth parameters used for our PT-CVD. Note that the flowrates of Ar and H₂ gases and temperature procedure used were the same as that for PTC-CVD to give direct comparison.

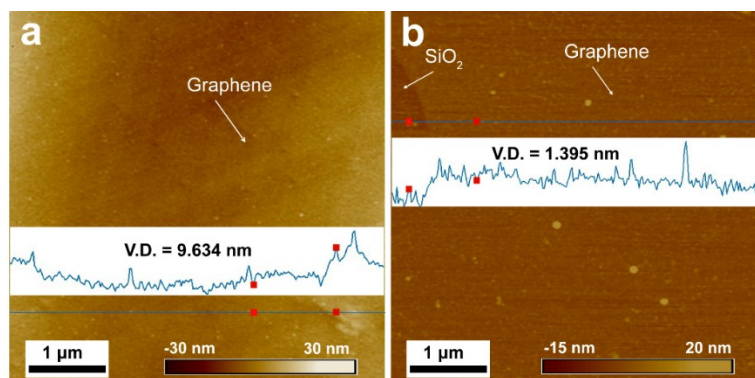


Fig. S9 Enlarged AFM images of graphene films (a) on Cu growth substrate and (b) transferred on a foreign SiO₂/Si substrate.

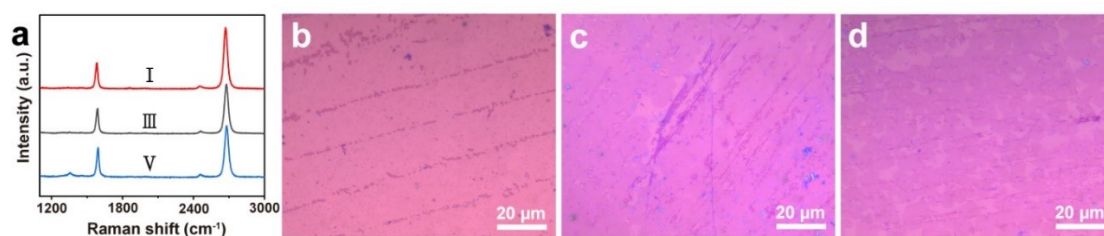


Fig. S10 Comparison for recyclability of CeO₂/Al₂O₃@graphene photocatalyst. (a) Raman spectra. Optical microscopy images, (b) use for first time, (c) use for three times, (d) use for five times.