Supporting Information

Influence of Carbon Content in Molybdenum Sulfides MoS_xC_y Obtained by Thermal Decomposition On Photocatalytical Hydrogen Generation

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METHODS

X-ray powder diffraction patterns were measured with a STOE-P diffractometer with CuKα radiation in transmission geometry. HRTEM images were recorded with Tecnai G^2-ST F30. The chemical composition was investigated with a EuroEA 3000. The samples were heated up to 1010 °C under an oxygen atmosphere. Specific surface areas were determined with nitrogen and krypton sorption measurements at 77 K applying the BET model. Photocatalytic reactions were carried out in a double-walled thermostatically controlled glass vessel that was loaded with 10 mg of MoS_xC_y, evacuated and back-filled with argon four times in order to remove other gases. Triethylamine (8 mL), distilled and degassed water (3 mL) and $[Ru(bpy)_3](PF_6)_2$ (1 mM) in acetonitrile (10 mL) were transferred *via* syringe. The mixture was stirred, set at 25 °C and the system was left to equilibrate for 15 min. The reaction was started by switching on the light source (275 W Xe-arc lamp with an optical cut-off filter $\lambda > 420$ nm). An Agilent Technologies 7890A gas chromatograph with a 60/80 Carboxen 1000 (Supelco) column and a TCD was used to qualify the gas. The amount of hydrogen was quantified with an automatic burette.

Preparation of $(NH_4)_2MoS_4$ and of $(NR_4)_2MoS_4$

$(NH_4)_2MoS_4$ was synthesized by dissolving $(NH_4)_6Mo_7O_{24}*4H_2O$ (0.024 mol) in 200 mL ammonia solution (25 %wt). H_2S was introduced to this solution. The product, red-green shimmery crystals were washed with cold distilled water, ethanol, and diethyl ether. The yield was 65 %. $((CH_3)_4N)_2MoS_4$ was synthesized by dissolving $(NH_4)_2MoS_4$ (0.012 mol) in 60 mL distilled water. $(CH_3)_4NBr$ (0.024 mol) was dissolved in 25 mL aqueous NaOH solution (1.0 M). The first solution was added to the second and a red solid immediately precipitated. The product was washed with distilled water. The yield was 86 %. $((C_3H_7)_4N)_2MoS_4$ was synthesized by dissolving $(NH_4)_2MoS_4$ (0.012 mol) in 60 mL distilled water. $(C_3H_7)_4NBr$ (0.024 mol) was dissolved in 18 mL aqueous NaOH solution (2.0 M). The first solution was added to the second and a red solid immediately precipitated. The product was washed with distilled water. The yield was 11 %.

Preparation of MoS_xC_y

MoS_xC_y photocatalysts were prepared by thermal decomposition of $(R_4N)_2MoS_4$ (R = -H_4 (C0), -CH_3 (C1), -C_3H_7 (C3), -C_6H_{13} (C6)) (0.4 to 1.0 g) at 350 °C for one hour with a heating rate of 100 °C / h in a rotary furnace under N_2 flow (200 cm^3 / min).

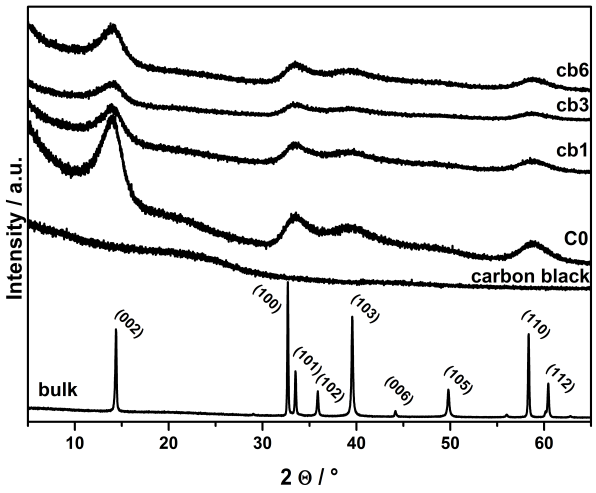
Preparation of mechanical mixtures

C_0 was mechanically mixed with carbon black (cb) and graphene (g) in a ball mill for 15 min. The compositions are given in Table 1.

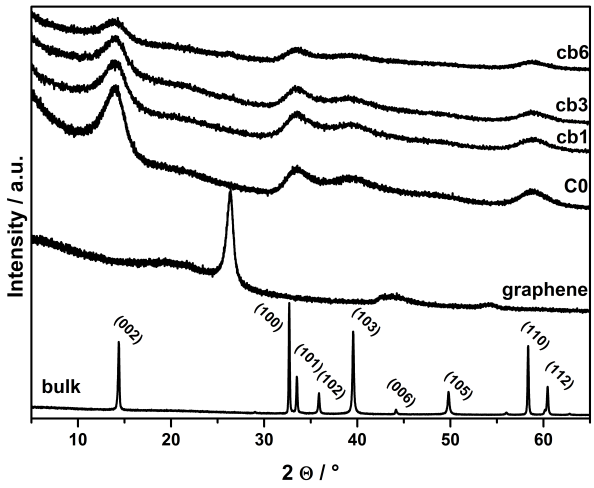
S.I. Table 1: Compositions of mechanical mixtures.

	m_{C0}/mg	m_{cb}/mg
cb1	197	2.7
cb3	190	10.0
cb6	179	22.8
	m_{C0}/mg	**m_g/mg**
g1	197	2.5
g3	190	9.6
g6	179	21.1

XRD patterns of mechanical mixtures

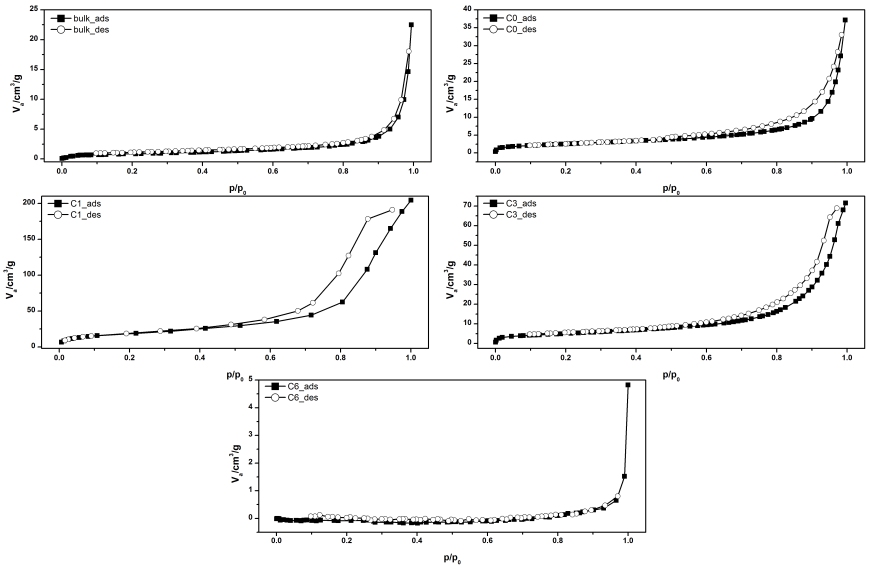


S.I. Figure 1: XRD patterns for mechanical mixtures of C_0 with carbon black (cb).



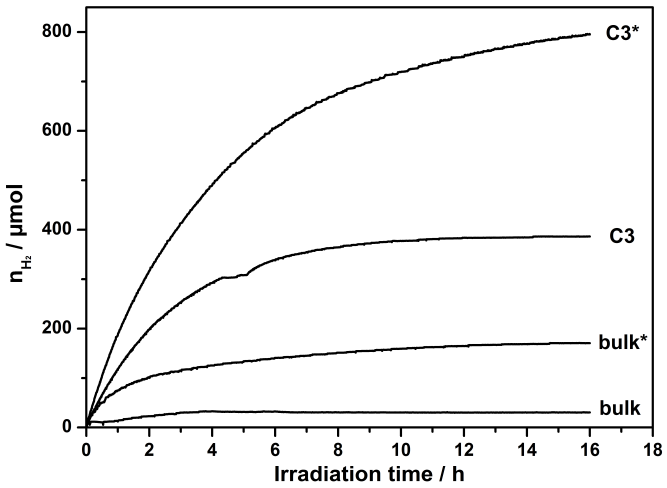
S.I. Figure 2: XRD patterns for mechanical mixtures of C_0 with graphene (g).

Nitrogen and krypton adsorption measurements

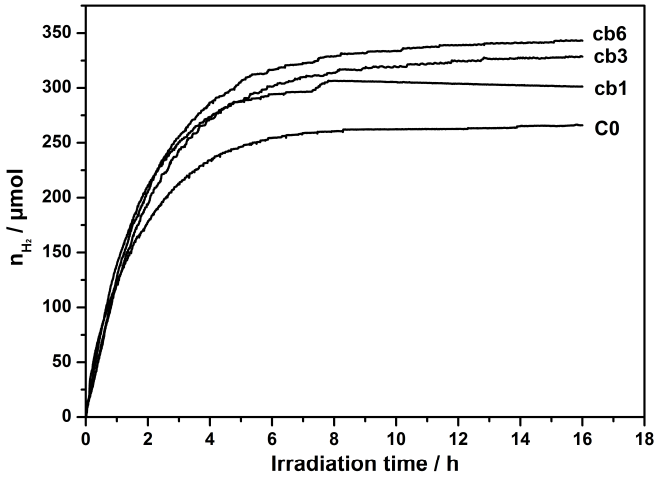


S.I. Figure 3: Nitrogen and krypton adsorption (ads) –desorption (des) isotherms of thermal decomposition products and of bulk MoS_2.

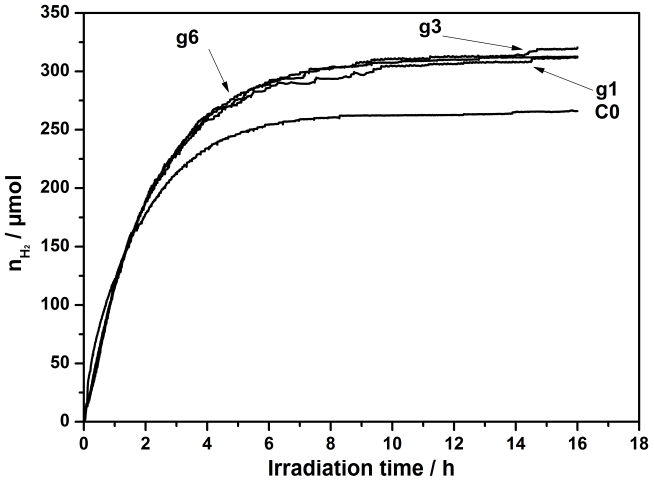
Photocatalytic hydrogen reaction



S. I. Figure 4: Kinetic studies of the photocatalytic hydrogen evolution reaction from a mixture containing triethylamine (8 mL), water (3 mL) and [Ru(bpy)3](PF6)2 (1 mM) in acetonitrile (10 mL). Additionally the C3* and bulk* samples were tested in an equal system applying $[Ir(pyb)_2(bpy)](PF_6)$ as sensitizer.



S. I. Figure 5: Kinetic studies of the photocatalytic hydrogen evolution reaction from a mixture containing triethylamine (8 mL), water (3 mL) and [Ru(bpy)3](PF6)2 (1 mM) in acetonitrile (10 mL) for C0 and its mechanical mixtures composed of carbon black (cb).



S. I. Figure 6: Kinetic studies of the photocatalytic hydrogen evolution reaction from a mixture containing triethylamine (8 mL), water (3 mL) and [Ru(bpy)3](PF6)2 (1 mM) in acetonitrile (10 mL) for C0 and its mechanical mixtures composed of graphene (g).