

Supporting Information

Table S1. Photocatalytic H₂ evolution using sacrificial agent (SaH) ^(a).

SaH	SaH/mmol	T/h ^(b)	Gas volume ^(c) /mL				Molar ratio			$H_2^{\max}$ $CO_2^{\max}$
			Total ^(d)	H ₂	CO ₂	CH ₄	H ₂ /1	CO ₂ /1	CH ₄ /1	
1a	0.25	31	37	26	11	0	4.7	1.9		$H_2^{\max} = 5.2$ $CO_2^{\max} = 2.1$
	0.50	68	62	44	18	0	4.0	1.6		
	0.75	69	76	54	22	0	3.2	1.3		
	1.00	77	78	56	22	0	2.5	1.0		
	1.25	77	97	69	28	0	2.5	1.0		
1b	0.25	23	23	16	6	0	2.8	1.0		$H_2^{\max} = 2.9$ $CO_2^{\max} = 1.0$
	0.50	70	27	20	7	0	1.8	0.6		
	0.75	68	40	30	10	0	1.8	0.6		
	1.00	71	52	39	13	0	1.7	0.6		
	1.25	47	65	49	16	0	1.7	0.6		
1c	0.25	20	32	23	9	0	4.1	1.6		$H_2^{\max} = 5.0$ $CO_2^{\max} = 1.8$
	0.50	51	68	49	19	0	4.3	1.7		
	0.75	29	91	65	26	0	3.9	1.6		
	1.00	94	121	86	35	0	3.9	1.5		
	1.25	58	125	89	36	0	3.2	1.3		
1d	0.25	27	62	48	14	0	7.3	0.5		$H_2^{\max} = 7.0$ $CO_2^{\max} = 2.0$
	0.50	50	87	68	19	0	5.4	0.9		
	0.75	68	109	85	24	0	4.8	0.6		
	1.00	73	135	105	30	0	4.2	0.3		
	1.25	75	153	119	34	0	3.9	0.3		
1e	0.25	48	20	20	0	0	3.6	0.0		$H_2^{\max} = 4.0$ $CO_2^{\max} = 0.0$
	0.50	51	40	40	0	0	3.6	0.0		
	0.75	58	50	50	0	0	3.0	0.0		
	1.00	68	58	57	0	1	2.5	0.0		
	1.25	79	68	67	0	1	2.4	0.0		
1f	0.25	24	25	21	4	0.2	3.7	0.7		$H_2^{\max} = 3.5$ $CO_2^{\max} = 0.7$
	0.50	29	40	33	7	0.3	3.0	0.6		
	0.75	78	63	53	11	0.4	3.1	0.6		
	1.00	78	97	81	16	0.6	3.6	0.7		
	1.25	72	104	87	17	1.3	3.1	0.6		
1g	0.25	45	43	33	10	0	5.9	1.0		$H_2^{\max} = 6.4$ $CO_2^{\max} = 1.8$
	0.50	52	84	66	19	0	5.9	0.8		
	0.75	48	113	88	25	0	5.4	0.7		
	1.00	90	139	108	31	0	4.8	0.7		
	1.25	113	166	129	37	0	4.2	0.8		
1h	0.25	96	20	18	2	0	2.4	0.4		$H_2^{\max} = 3.3$ $CO_2^{\max} = 0.5$
	0.50	66	29	26	3	0	1.8	0.2		
	0.75	66	60	55	5	0	2.3	0.3		
	1.00	72	55	49	6	0	1.8	0.3		
	1.25	64	58	57	1	0	1.8	0.0		

Table S1. Cont.

SaH	SaH/mmol	T/h ^(b)	Gas volume ^(c) /mL				Molar ratio			$H_2^{\max}$
			Total ^(d)	H ₂	CO ₂	CH ₄	H ₂ /1	CO ₂ /1	CH ₄ /1	CO ₂ ^{max}
1i	0.25	48	22	22	0.3	0	3.9	0.05		
	0.50	40	32	32	0.1	0	2.9	0.01		
	0.75	45	48	48	0.2	0	2.9	0.01		$H_2^{\max} = 4.0$
	1.00	88	56	56	0.1	0	2.5	0.01		$CO_2^{\max} = 0.0$
	1.25	135	64	64	0.2	0	2.3	0.01		
1j	0.25	19	20	20	0	0	5.3	0.1		
	0.50	96	48	48	0	0	3.7	1.7		
	0.75	69	56	56	0	0	3.2	1.2		$H_2^{\max} = 4.1$
	1.00	75	52	52	0	0	2.7	0		$CO_2^{\max} = 0.1$
	1.25	70	64	64	0	0	2.5	0		
1k	0.25	69	30	30	0	0	5.3	0		
	0.50	70	42	42	0	0	3.7	0		
	0.75	62	54	54	0	0	3.2	0		$H_2^{\max} = 4.6$
	1.00	77	60	60	0	0	2.7	0		$CO_2^{\max} = 0.0$
	1.25	120	67	67	0	0	2.4	0		
1l	0.25	72	14	14	0.4	0	2.4	0.07		
	0.50	71	28	28	0.1	0	2.5	0.01		
	0.75	62	35	34	0.3	0	2.1	0.02		$H_2^{\max} = 2.4$
	1.00	120	56	47	0.3	0	2.1	0.01		$CO_2^{\max} = 0.04$
	1.25	160	69	66	1.7	0	2.4	0.06		
1m	0.25	36	29	29	0	0	5.18	0		
	0.50	70	30	30	0	0	2.68	0		
	0.75	72	39	39	0	0	2.32	0		$H_2^{\max} = 3.3$
	1.00	96	37	37	0	0	1.65	0		$CO_2^{\max} = 0.0$
	1.25	97	48	48	0	0	1.71	0		
2a	0.25	23	11	16	6	0	1.1	1.1		
	0.50	27	22	25	11	0	1.0	1.0		
	0.75	40	34	37	17	0	1.1	1.0		$H_2^{\max} = 1.0$
	1.00	52	45	43	22	0	1.0	1.0		$CO_2^{\max} = 1.0$
	1.25	65	56	52	28	0	1.0	1.0		
2b	0.25	23	17	6	11	0	1.1	2.0	0.25	
	0.50	27	34	11	23	0	2.0	1.0	0.50	
	0.75	40	51	17	34	0	2.0	1.0	0.75	$H_2^{\max} = 1.0$
	1.00	52	68	23	45	0	2.0	1.0	1.00	$CO_2^{\max} = 2.0$
	1.25	65	85	28	57	0	1.0	2.0	1.25	
2c	0.25	10	26	15	10	0	2.8	1.8		
	0.50	14	51	31	20	0	2.8	1.8		$H_2^{\max} = 2.8$
	0.75	16	77	46	31	0	2.7	1.9		$CO_2^{\max} = 1.8$
	1.00	18	102	61	41	0	2.7	1.8		
	1.25	25	128	77	51	0	2.8	1.8		

Table S1. Cont.

SaH	SaH/mmol	T/h ^(b)	Gas volume ^(c) /mL				Molar ratio			$H_2^{\max}$ $CO_2^{\max}$
			Total ^(d)	H ₂	CO ₂	CH ₄	H ₂ /1	CO ₂ /1	CH ₄ /1	
2d	0.35	29	32	22	8	2	3.9	1.4	0.4	$H_2^{\max} = 2.9$ $CO_2^{\max} = 1.7$ $CH_4^{\max} = 0.27$
	0.50	44	43	29	11	3	2.6	1.0	0.3	
	0.75	55	54	34	14	4	2.1	0.8	0.2	
	1.00	62	56	33	18	6	1.4	0.8	0.3	
	1.25	72	59	34	20	5	1.2	0.7	0.2	
2e	0.25	48	31	14	15	2	2.6	2.6	0.4	$H_2^{\max} = 2.6$ $CO_2^{\max} = 2.7$ $CH_4^{\max} = 0.3$
	0.50	53	49	23	23	3	2.0	2.1	0.3	
	0.75	72	64	30	30	4	1.8	1.8	0.2	
	1.00	103	80	37	38	5	1.7	1.7	0.2	
	1.25	132	93	43	44	6	1.5	1.6	0.2	
2f	0.25	53	46	28	16	2	5.0	2.9	0.4	$H_2^{\max} = 3.3$ $CO_2^{\max} = 0.5$
	0.50	53	61	37	21	2	3.3	1.9	0.2	
	0.75	69	81	50	27	3	3.0	1.6	0.2	
	1.00	78	86	53	29	3	2.4	1.3	0.1	
	1.25	70	102	62	34	4	2.2	1.2	0.1	
2g	0.35	69	57	36	19	2	4.6	2.5	0.3	$H_2^{\max} = 4.9$ $CO_2^{\max} = 2.5$ $CH_4^{\max} = 0.3$
	0.50	53	69	44	23	3	3.9	2.1	0.2	
	0.75	53	79	52	24	3	3.3	1.4	0.2	
	1.00	75	105	67	35	4	3.0	1.6	0.2	
	1.25	75	133	84	45	5	3.0	1.6	0.2	
2h	0.50	49	65	37	25	3	3.3	2.3	0.3	$H_2^{\max} = 3.9$ $CO_2^{\max} = 2.7$ $CH_4^{\max} = 0.3$
	0.75	72	85	48	33	4	2.9	2.0	0.2	
	1.00	86	102	58	40	4	2.6	1.8	0.2	
	1.25	97	112	63	44	5	2.3	1.6	0.2	
2i	0.50	48	32	22	10	0	2.0	0.9		$H_2^{\max} = 2.3$ $CO_2^{\max} = 1.0$
	0.75	48	45	31	14	0	1.9	0.8		
	1.00	50	53	37	16	0	1.6	0.7		
	1.25	56	60	42	18	0	1.5	0.7		

^(a) After N₂ bubbling, an aqueous solution (150 cm³) containing varied amounts of SaH (0.25–1.25 mmol) and Pt/TiO₂ (100 mg; 1.25 mmol) was irradiated. ^(b) Irradiation time to reach the maximum gas volume. ^(c) The collected gas was analyzed by GLC. ^(d) The gas volume in mL collected by a mess cylinder. ^(e) Data were referred from [1].

Reference

1. Shiragami, T.; Tomo, T.; Matsumoto, T.; Yasuda, M. Structural dependence of alcoholic sacrificial agents on TiO₂-photocatalytic hydrogen evolution. *Bull. Chem. Soc. Jpn.* **2013**, *86*, 382–389.

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