## Selective oxidation of methanol to methyl formate on catalysts of Au-Ag alloy nanoparticles supported on titania under UV irradiation †

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## LEGENDS

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catalysts	P25(g	$H_2O~(ml)$	NaBH <sub>4</sub> (g	AgNO₃(ml	HAuCl₄(ml)	Au/Ti(%	Ag/Ti(%
Au/TiO <sub>2</sub>	0.5	288	0.022	_	160	2.56	_
Ag/TiO <sub>2</sub>	0.5	96	0.0074	32	_	_	2.56
AuAg(1:3)/TiO	0.5	144	0.011	48	40	0.64	1.92
AuAg(1:1)/TiO	0.5	192	0.0145	64	80	1.28	1.28
AuAg(3:1)/TiO	0.5	240	0.0184	80	120	1.92	0.64

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Fig. s1 Schematic photocatalytic reactor.



Fig. s2 TEM images of (a) AuAg(1:3)/TiO<sub>2</sub> and (b) AuAg(3:1)/TiO<sub>2</sub>





**Fig. s3** Formation rate of methyl formate on catalysts calculated by per unit noble metal. (a) titania (TiO<sub>2</sub>), pure Au (Au/TiO<sub>2</sub>) and Ag (Au/TiO<sub>2</sub>) nanoparticles on titania, alloy nanoparticles with Au/Ag ratios of 1:1 (AuAg(1:1)/TiO<sub>2</sub>), 1:3 (AuAg(1:3)/TiO<sub>2</sub>) and 3:1 (AuAg(3:1)/TiO<sub>2</sub>) on titania; (b) AuAg(1:1)/TiO<sub>2</sub>-450C-5, calcined at 450 °C for 5 h, AuAg(1:1)/TiO<sub>2</sub>-UC, uncalcined catalyst, AuAg(1:1)/TiO<sub>2</sub>-A, dealloyed AuAg(1:1)/TiO<sub>2</sub>

The methyl formate formation rate in Fig. s3 was calculated by the equation (s1).

$$Fr = \frac{\rho VCS}{M \times 2 \times n} \quad (s1)$$

where

*Fr* formation rate,  $h^{-1}$ 

 $\rho$  concentration of methanol in feed gas, 13 mg.L<sup>-1</sup>

V flow rate of feed gas, 3 L.h<sup>-1</sup>

C conversion of methanol, %

*S* selectivity of methyl formate, %

M molecular weight of methanol, 32.04 g/mol

*n* millimole of noble metals in the catalyst (Au+Ag, mmol)



Fig. s4 XRD patterns of ZnO and AuAg(1:1)/ZnO

The UV-visible spectra of ZnO and AuAg(1:1)/ZnO are shown in Fig. s5. The absorption band from 450 nm to 600 nm caused by the LSPR effect can be observed in the pattern of AuAg(1:1)/ZnO. The band gap of this ZnO is 3,1 eV, which is almost equal to that of the titania used in this study.



Fig. s5 UV-visible spectra of ZnO and AuAg(1:1)/ZnO

The GC spectra of the photocatalytic reaction at 30 °C on AuAg(1:1)/ZnO and AuAg(1:1)/TiO<sub>2</sub> are shown in Fig. s6. Methyl formate is the main product and carbon dioxide is the main by-product on AuAg(1:1)/TiO<sub>2</sub>, in addition trace dimethoxy methane which accounts for about 0.005 vol.% of the flow gas can be observed on this catalyst. But this trace species is neglected because its amount is hard to accurately determined and close to the calculation error. Trace methyl formate can be observed on AuAg(1:1)/ZnO.



Fig. s6 GC spectra of AuAg(1:1)/ZnO and AuAg(1:1)/TiO<sub>2</sub>