

## **Supporting Information**

### **Structured nanoporous-gold/Al-fiber: Galvanic deposition preparation and reactivity for oxidative coupling of methanol to methyl formate**

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## TOF Calculation

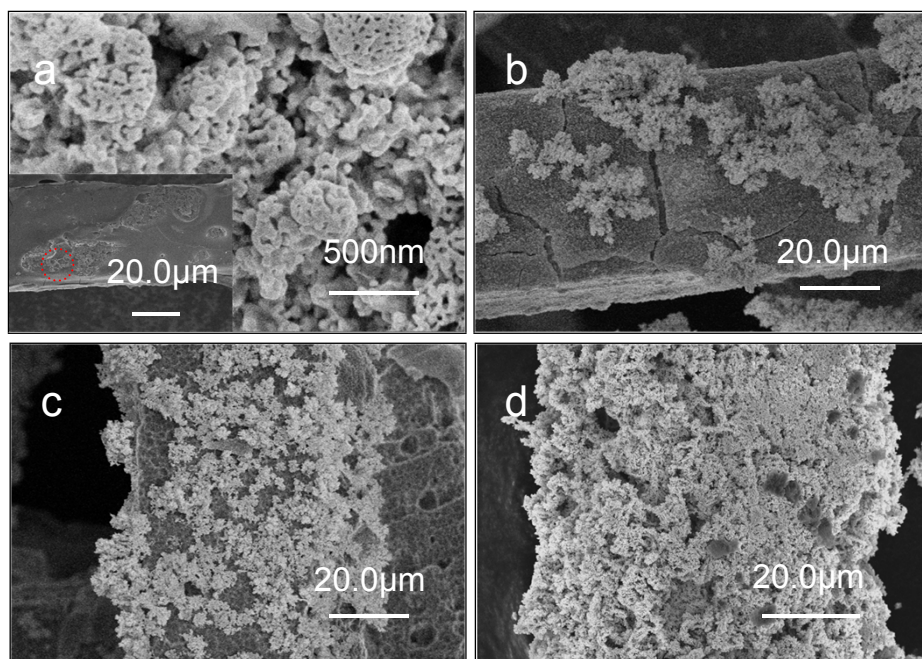
In order to further assess the catalytic activity, so called turnover frequencies (TOFs) which is defined as the ratio of product molecules per active site of catalyst and time are calculated. The number of product molecules per time (mol/s) is expressed by the flow of CH<sub>3</sub>OH (F, L/s) times  $\alpha$  (the yield of methyl formate gas), divided by the molar volume of gas ( $V_m$ , L/mol), assuming ideal behavior. The number of active sites is counted as active sites per surface area N (mol/m<sup>2</sup>) times the surface area of NPGs (A, m<sup>2</sup>). Accordingly, the TOF can be expressed by:

$$TOF = \frac{\text{Product Molecules}}{\text{Active Sites} \cdot \text{Time}} = \frac{F \cdot \alpha}{V_m \cdot N \cdot A}$$

Calculation example is demonstrated in the following. The flow of reactant CH<sub>3</sub>OH gas F is set to 10 ml/min. A catalyst with low residual Ag content NPG-4/Al-fiber (m=0.2 g) is used, in which the content of NPG is 8 mg and NPG surface area is 7 m<sup>2</sup>/g. At 140 °C, about 32% of the methanol is converted and the selectivity of methyl formate is 96%, thus the yield of methyl formate  $\alpha$  accounts to 0.15. It is supposed that every surface atom is an active site as an upper limit (the actual number will be lower). We considered that the density of surface atoms for the energetically most stable Au (111) surface is  $1.4 \cdot 10^{19}$  atoms/m<sup>2</sup> [S1]. Then the lower limit for the TOF can be calculated as:

$$TOF = \frac{\frac{10}{1000 \cdot 60} (L/s) \cdot 0.15}{22.4 (L/mol) \cdot \frac{1.4 \cdot 10^{19} \left( \frac{\text{atoms}}{\text{m}^2} \right)}{6.023 \cdot 10^{23} \left( \frac{\text{atoms}}{\text{mol}} \right)} \cdot 0.008 (g) \cdot 7 (m^2/g)} = 0.90 \text{ s}^{-1}$$

[S1] A. Wittstock, V. Zielasek, J. Biener, C. M. Friend and M. Bäumer, *Science*, 2010, **327**, 319-322.



**Fig. S1** SEM images of the NPG/Al-fiber catalyst samples with varied Au-loadings. (a) NPG-1/Al-fiber, the inset is an overview at low magnification and red-circle part is observed at high magnification. (b) NPG-2/Al-fiber. (c) NPG-3/Al-fiber. (d) NPG-4/Al-fiber

**Table S1.** Amount of adsorbed oxygen on NPG-1/Al-fiber samples with varied Ag residues.

Ag residues (at.%)	Integration area of O <sub>2</sub> -TPD peak		
	Total	Peak centred at ~340 °C	Peak centred at ~435 °C
38	202	117	85
25	189	126	63
13	192	135	57