

Selectivity regulation of Au/titanate by biochar modification for selective oxidation of benzyl alcohol

Xiya Chen^a, Hangwei Jiang^a, Danlan Cui^a, Kun Lu^a, Xiao Kong^a, Junmeng Cai^b, Shirui Yu^{c,d},
Xingguang Zhang^a *

¹ School of Materials and Chemistry, University of Shanghai for Science and Technology, 516 Jungong Road, Shanghai 200093, P.R. China.

² Biomass Energy Engineering Research Center, School of Agriculture and Biology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China.

³ Department of Food Science and Engineering, Moutai Institute, Luban Street, Renhuai 5645002, Guizhou, P.R. China.

⁴ Guizhou Health Wine Brewing Technology Engineering Research Center, Moutai Institute, Luban Street, Renhuai 564502, Guizhou, P.R. China.

*Corresponding authors: x.g.zhang@usst.edu.cn

Section 1. SEM images

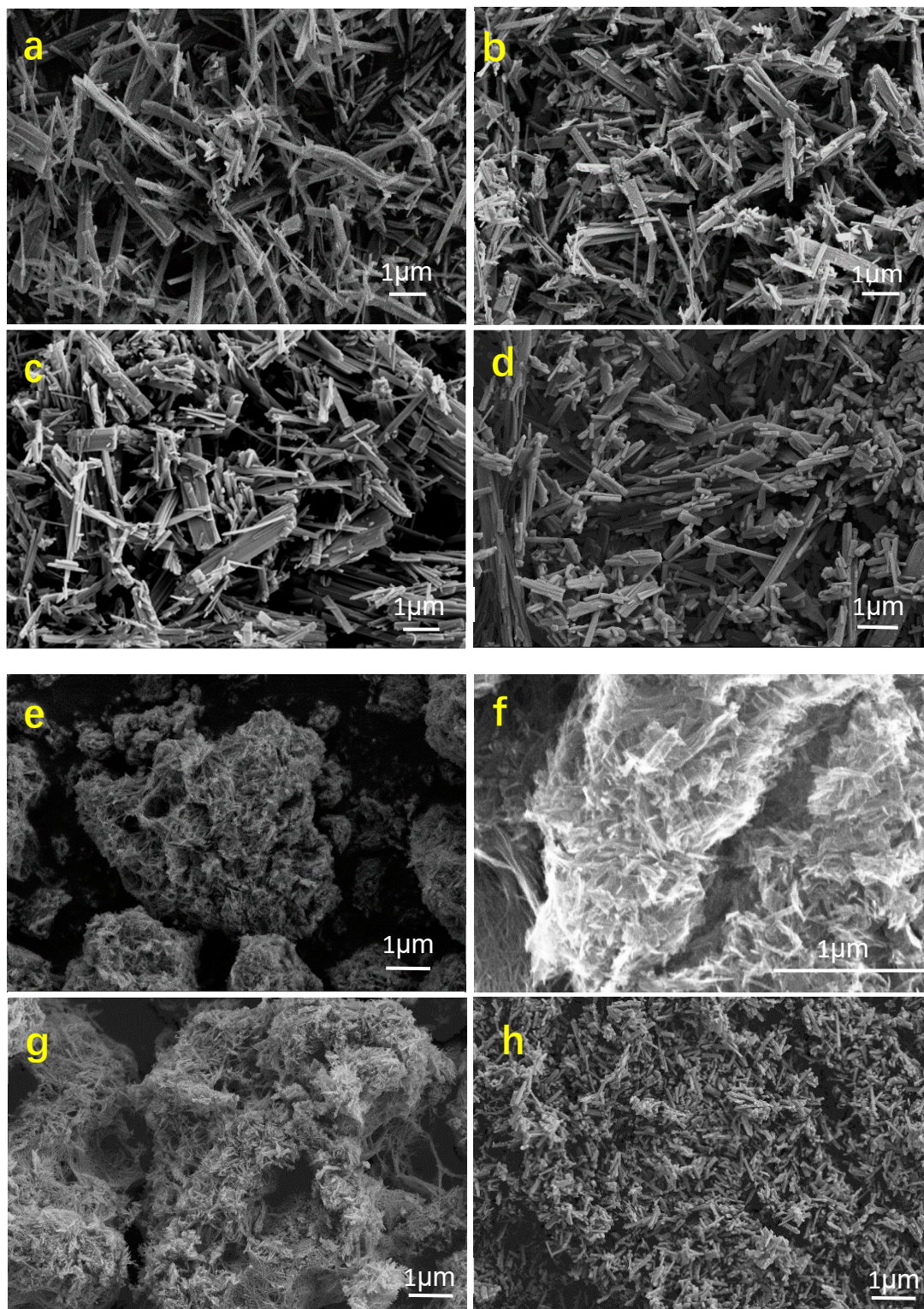


Fig. S1 SEM images of (a) Au/NaTiNT_s, (b) Au/NaTiNT_s-400Ar, (c) Au/NaTiNT_s-400Ar-400Air, (d) Au/NaTiNT_s-400Ar-800Air, (e) Au/BC_{0.25}@NaTiNT_s, (f) Au/BC_{0.25}@NaTiNT_s-400Ar, (g) Au/BC_{0.25}@NaTiNT_s-400Ar-400Air, (h) Au/BC_{0.25}@NaTiNT_s-400Ar-800Air.

Section 2. TEM images

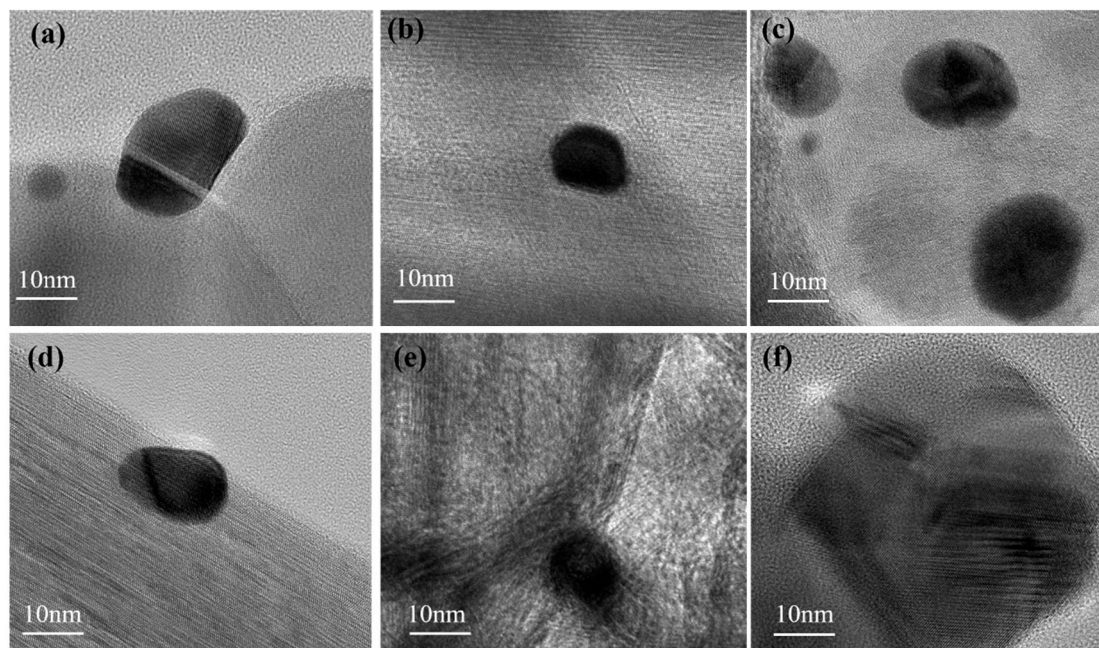


Fig. S2 TEM (a) Au/TiO₂-400Ar-400Air, (b) Au/NaTiNTs-400Ar-400Air, (c) Au/BC_{0.10}@NaTiNTs-400Ar-400Air, (d) Au/BC_{0.25}@NaTiNTs-400Ar-400Air, (e) Au/BC_{0.50}@NaTiNTs-400Ar-400Air, (f) Au/BC_{1.00}@NaTiNTs-400Ar-400Air

Section 3. XPS analysis of C1s and O1s over series of catalysts

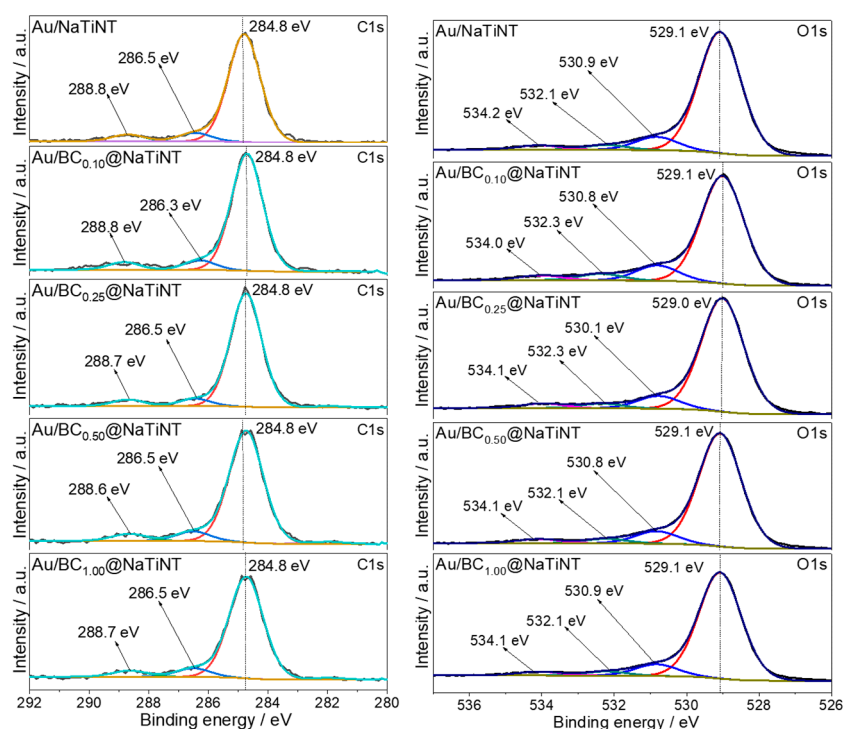


Fig. S3 XPS spectra of C1s (Left) and O1s (Right) over the catalysts of Au/NatTiNs and series of Au/BC@NatTiNs.

Note: all the catalysts were calcined at 400°C in Ar first and then at 400°C in air.

Table S1. The proportion analysis as quantified by XPS spectra

Items		C1s			O1s			
		C-C	C-O	O-C=O	Ti-O or Ti=O	O vacancy	O-H or ONa	O adsorbed
Au/TiO ₂	BE / eV	284.8	286.5	288.6	529.0	530.6	531.8	--
	Fraction %	91.5	5.4	3.1	86.6	11.6	1.8	--
Au/NatTiN	BE / eV	284.8	286.5	288.8	529.1	530.9	532.1	534.2
	Fraction %	87.6	6.9	5.5	84.0	8.6	3.8	3.6
Au/BC _{0.10} @NatTiN	BE / eV	284.8	286.3	288.8	529.1	530.8	532.3	534.0
	Fraction %	87.0	7.2	5.8	80.0	11.5	4.9	3.6
Au/BC _{0.25} @NatTiN	BE / eV	284.8	286.5	288.7	529.0	530.1	532.3	534.1
	Fraction %	89.1	5.8	5.1	83.7	9.4	3.5	3.4
Au/BC _{0.50} @NatTiN	BE / eV	284.8	286.5	288.6	529.1	530.8	532.1	534.1
	Fraction %	87.1	7.5	5.4	84.2	9.3	3.4	3.1
Au/BC _{1.00} @NatTiN	BE / eV	284.8	286.5	288.7	529.1	530.9	532.1	534.1
	Fraction %	87.4	7.4	5.2	84.3	9.3	3.3	3.1

Section 4. Comparison of reaction rates based on ICP tests

The actual content of Au on the prepared catalysts were detected by ICP-OES (**Table s2**). The results showed that the actual loading of Au on the surface of most catalysts was generally lower than the theoretical value. Based on the real loading of gold, the reaction rate of benzyl alcohol and the production rate of benzaldehyde were calculated as shown below.

Table S2. The reaction rate of benzyl alcohol and the production rate of benzaldehyde over typical catalysts

	In air	Au/TiO ₂ (0.64%)	Au/NaTiNT _s (1.00%)	Au/BC _{0.10} @NaTiNT _s (0.90%)	Au/BC _{0.25} @ NaTiNT _s (0.96%)	Au/BC _{0.50} @ NaTiNT _s (0.86%)	Au/BC _{1.00} @ NaTiNT _s (0.56%)
Reaction rate / mmol _{reactant} /(g _{Au} ·h)	200°C	338.9	199.3	203.7	79.2	77.5	71.4
	400°C	330.0	195.3	185.9	166.7	253.3	213.1
	600°C	285.4	172.6	162.2	163.2	14.8	10.7
	800°C	357.3	70.7	131.9	168.1	33.3	89.3
Production rate / mmol _{product} /(g _{Au} ·h)	200°C	266.7	103.4	147.7	73.7	76.7	70.7
	400°C	245.5	114.0	124.6	93.2	235.1	192.9
	600°C	218.9	114.1	118.6	91.6	14.7	10.6
	800°C	260.8	49.1	71.6	133.6	33.0	88.9

^a The nominal loading of gold was 1wt% and the real loading detected by ICP was given in the parentheses.

Reaction conditions: catalyst (100 mg), benzyl alcohol (4 mmol), toluene (20 ml), NaOH (0.4 mmol), reaction temperature oil bath 60°C, 6 h, air atmosphere. **Note.** All the catalysts were calcined in Ar first then were calcined in air.