Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for

Gold Nanoparticles Confined in the Interconnected Carbon Foams with High Temperature Stability

Min Wang, Jiping Ma, Chen Chen, Fang Lu, Zhongtian Du, Jiaying Cai, and Jie Xu*

Dalian National Laboratory for Clean Energy, State Key Laboratory of Catalysis

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 (P.R. China)

*Corresponding author: E-mail: **xujie@dicp.ac.cn**

Experimental Section

Au nanoparticles: A $HAuCl_4$ solution (2 g, 1 wt%) was added to deionized water (50 mL). The resultant solution was stirred under reflux. Then, a sodium tartrate solution (5 mL, 38.8 mM) was added and the system was refluxed for 30 min. Finally, the resultant colloid was cooled to room temperature and 50 nm gold nanoparticles were obtained. For 13 nm gold nanoparticles, the synthetic conditions were the same as described above except using sodium citrate as reduction reagent instead. For the synthesis of 6 nm gold nanoparticles, a $HAuCl_4$ solution (2 g, 1 wt%) and a sodium tartrate solution (4 mL, 38.8 mM) were added to deionized water (100 mL), finally a $NaBH_4$ solution (1 mL, 0.145 wt%) was added and gold nanoparticles were formed.

Au@SiO_2 core-shell particles: A fresh solution of polyvinylpyrrolidone (0.3 mL, 12.8 mg/mL) was added to a previously prepared gold solution. The resultant mixture was stirred for 24 h to allow complete adsorption of the polymer on the gold surface. Then, the solution was centrifuged and the supernatant was removed. The volume of the concentrated colloid was then adjusted to 9 mL by dilution with water. The colloid was ultrasonicated for 5 min, followed by addition of ethanol (28.5 mL) and concentrated ammonia solution (0.8 mL, 28 – 30 wt% NH_3 in water). Afterwards, a solution of tetraethylorthosilicate (1 mL) in ethanol (19 mL) was added. The reaction mixture was then stirred for additional 12 h at room temperature. The resultant colloid was centrifuged and washed with water and ethanol and dried at 353 K.

Au@Carbon foam: The as-prepared Au@SiO_2 core-shell particles (0.2 g) were pressed into pellet at 6 MPa. The particles were sintered slightly at their points of contact by heating the pellets to 773 K for 3 h in order to provide pore connectivity in the carbon replica. Then, the particles templates were immersed in a carbon precursor solution containing sucrose (0.25 g), sulfuric acid (0.06 g, 98%) and water (2 mL).The water solvent was evaporated under vacuum at 323 K for 2 h allowing the carbon precursor filling into the void spaces between silica nanoparticles. Next, the sugar–silica template was first heated to 373 K at a rate of 1 K/min for 3 h and then heated to 423 K at a rate of 1 K/min for 5 h to pre-carbonization of the sucrose. Complete carbonization was accomplished by heating the composite in a tube oven to 1073 K at a rate of 2 K/min for 3 h under N_2 atmosphere. Finally, the silica was etched away by overnight dissolution in aqueous HF (5 mL, 48%) to leave gold nanoparticles trapped inside the voids and the obtained materials are dried at 353 K. The gold content of Au@CF was 3.19 wt%.

Au/Carbon foam: The carbon foam was prepared as the same with Au@Carbon foam except using pure silica nanoparticles as template. The silica nanoparticles with diameter of 100 nm were prepared using reversed microemulsion method according to our previous paper.[1] A gold solution with a diameter of 13 nm was prepared as discussed above and then the carbon foam was added. The resultant solution was stirred under reflux for 5 h, followed by centrifugation and washing with water and ethanol. The gold content of Au/CF was 3.78 wt%.

Glycerol oxidation: Glycerol oxidation was performed in a 50 mL autoclave reactor with an internal Teflon insert. Typically, glycerol (2.5 mmol), NaOH (10 mmol) dissolved in water (4.5 g) and catalyst (0.05 g) were added into the reactor.

Then, upon heating to 60 ^{o}C, the reactor was charged with 0.3 MPa O_2 under magnetic stirring. The pressure was kept constant during the reaction by feeding O_2. Analysis of products was performed on a Waters e2695 HPLC with a Waters UV-vis and refractive index detector. An aqueous solution of H_2SO_4 (0.04 M) was employed as the eluent and the flow rate was 0.5 mL/min.

Characterization: Microstructures of the materials were examined by transmission electron microscopy (TEM) on a FEI Tecnai G^2 Spirit electron microscope at an accelerating voltage of 120 kV and field-emission scanning electron microscopy (SEM) on a FEI Quanta 200F. Ultraviolet–visible spectroscopy (UV–vis) was collected on a Shimadzu UV-2550 spectrophotometer. The X-ray powder diffraction (XRD) patterns were obtained using Rigaku D/Max 2500/PC powder diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm).

Reference

1. M. Wang, C. Chen, J. P. Ma, J. Xu, *J. Mater. Chem.* 2011, **21**, 6962.

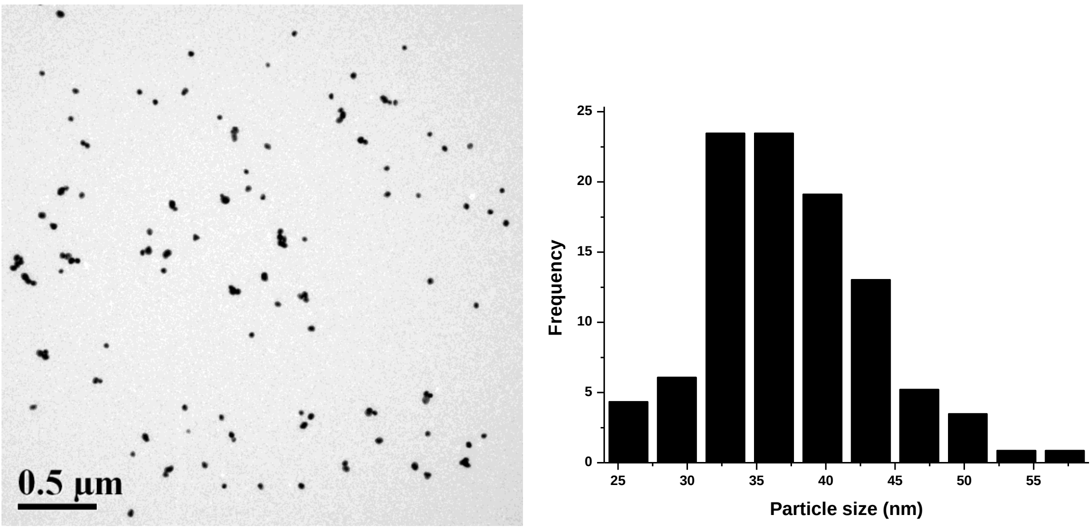

Fig. S1 Low magnification TEM image of gold nanoparticles and the particles size distribution.

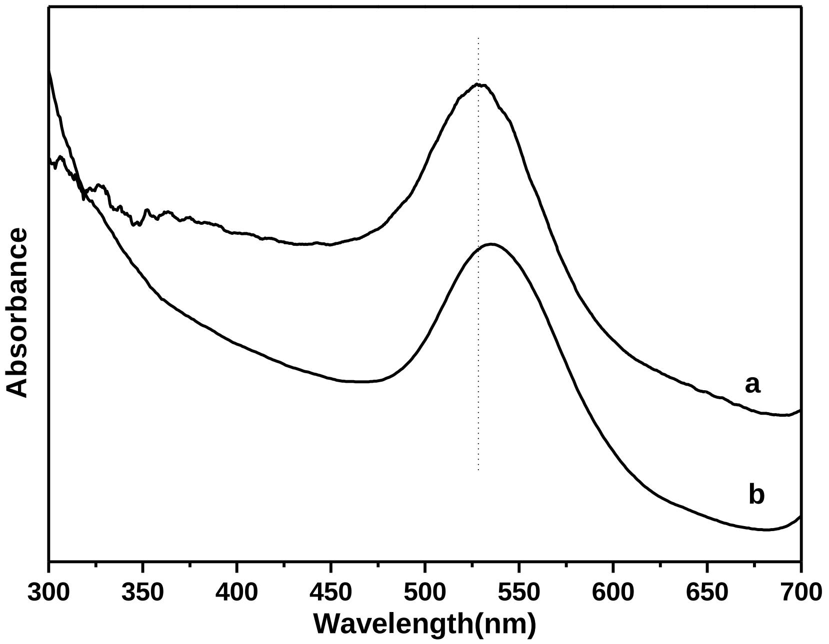

Fig. S2 UV-vis spectrum of (a) gold nanopartilces and (b) Au@ SiO_2.

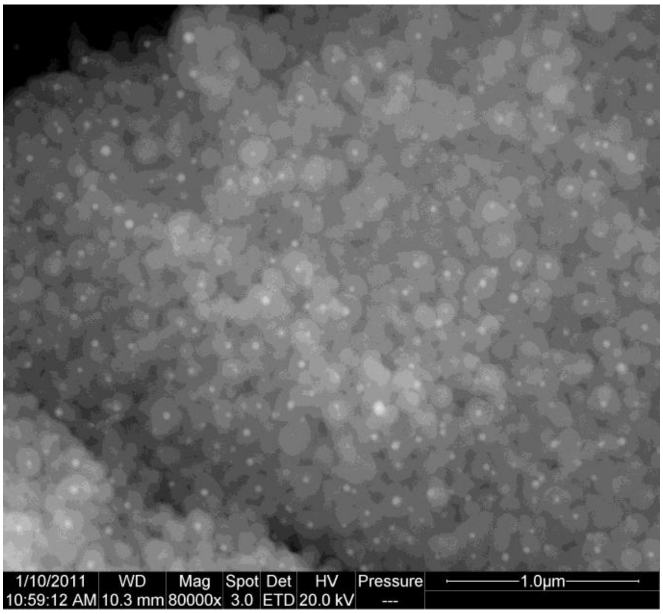

Fig. S3 SEM image of Au@ SiO_2.

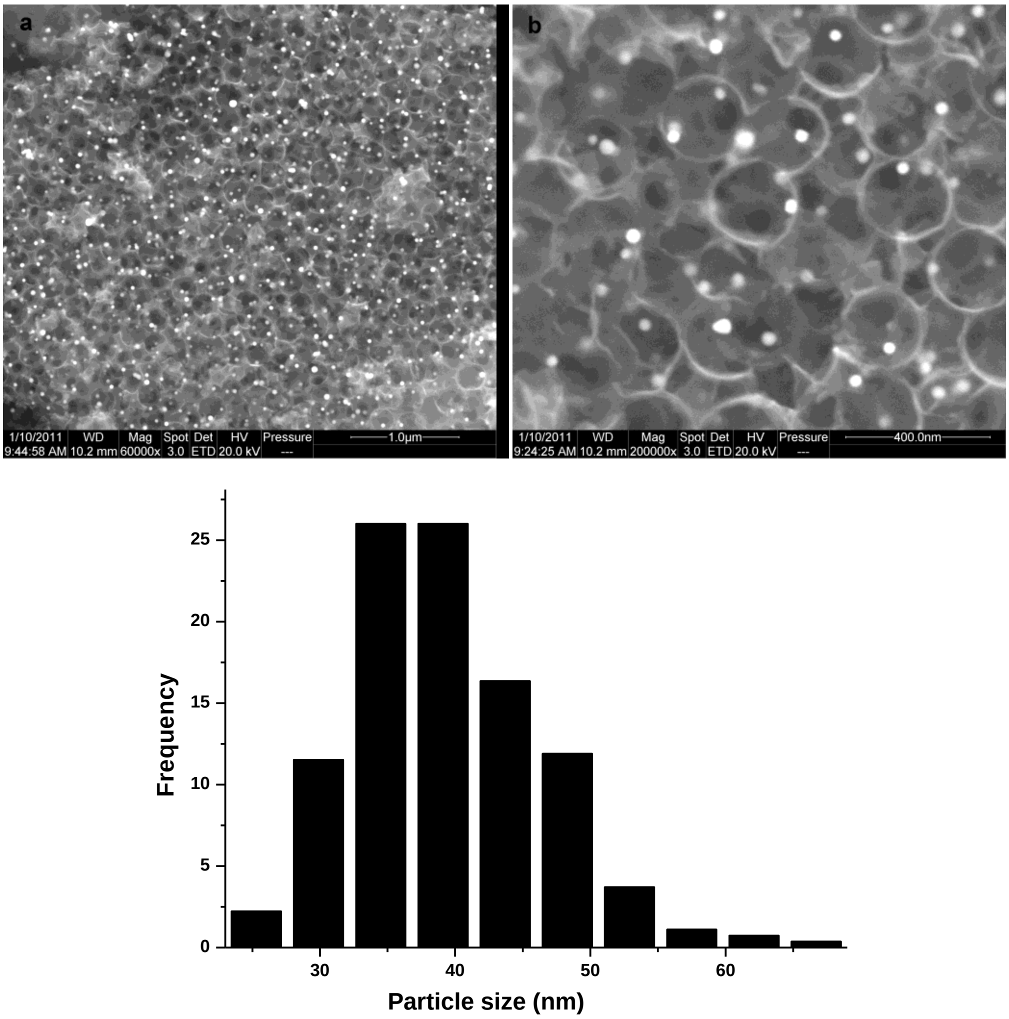

Fig. S4 Low magnification (a) and high magnification (b) SEM images of Au@C and the particles size distribution of gold nanoparticles.

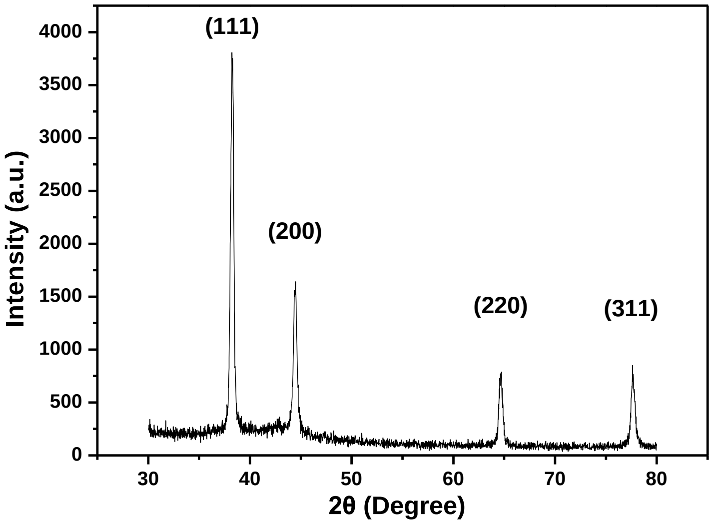

Fig. S5 XRD pattern of Au@CF.

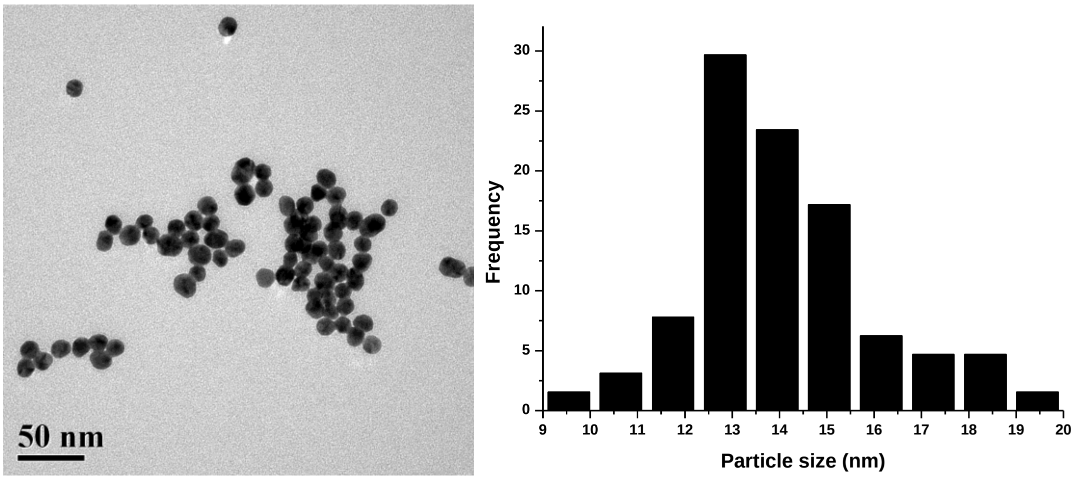

Fig. S6 Low magnification TEM image of gold nanoparticles and the particles size distribution.

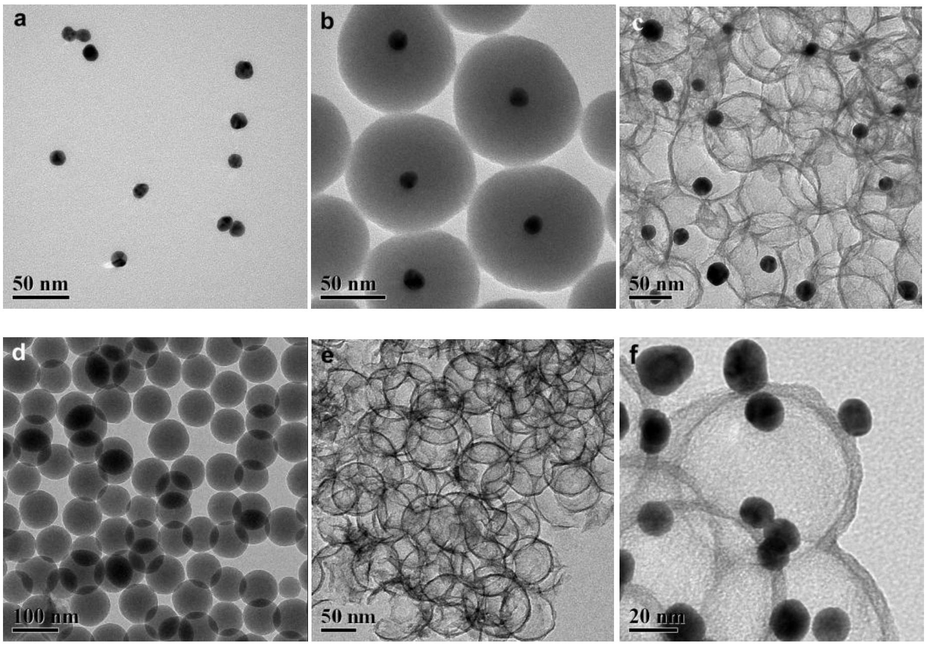

Fig. S7 TEM images of the materials in each step, (a) gold nanoparticles; (b) Au@SiO_2; (c) Au@CF; (d) SiO_2; (e) CF; (f) Au/CF.

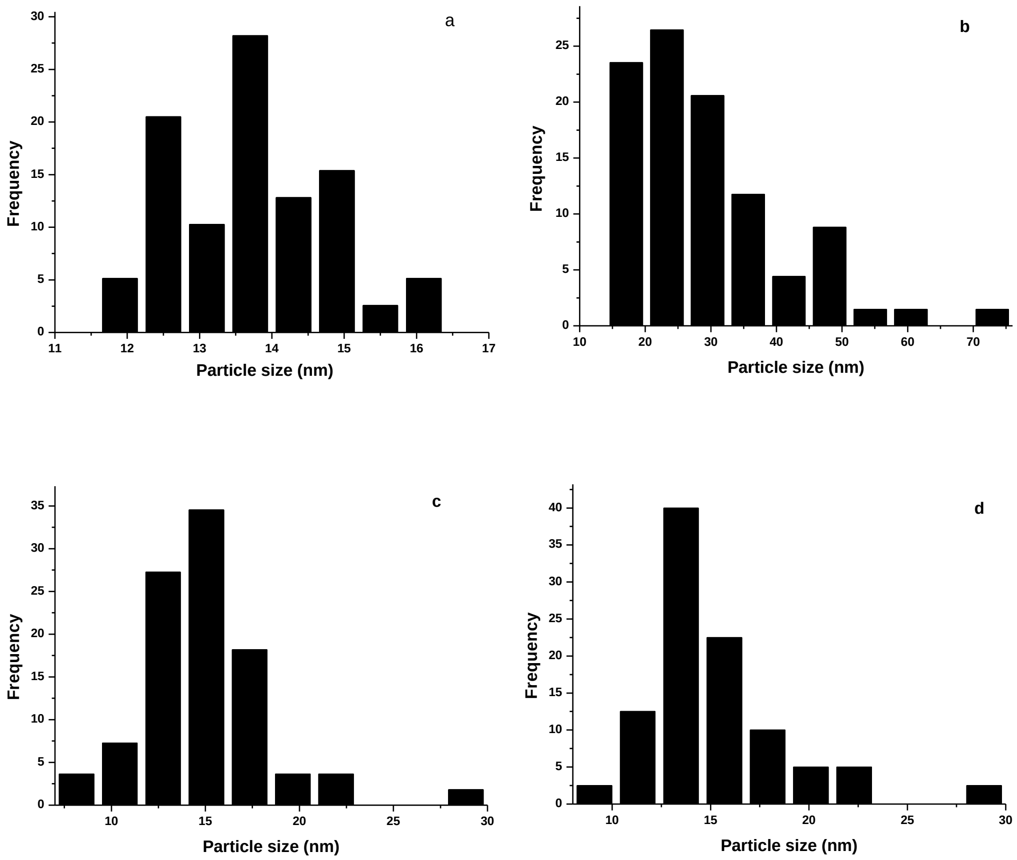

Fig. S8 Particle size distribution of Au/CF (a, b) and Au@CF (c, d) before (a, c) and after (b, d) thermal treatment.

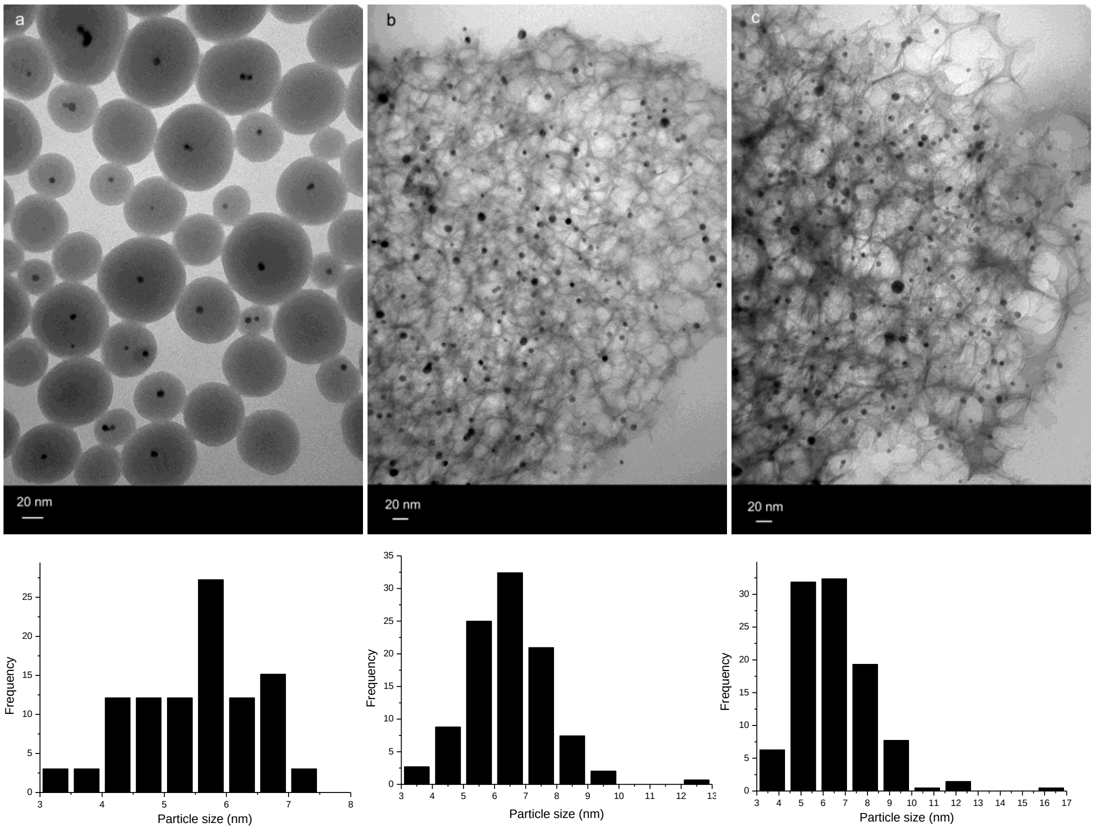

Fig. S9 TEM images and the gold particle size distributions of Au@SiO_2 (left), Au@CF before (middle) and after (right) thermal treatment

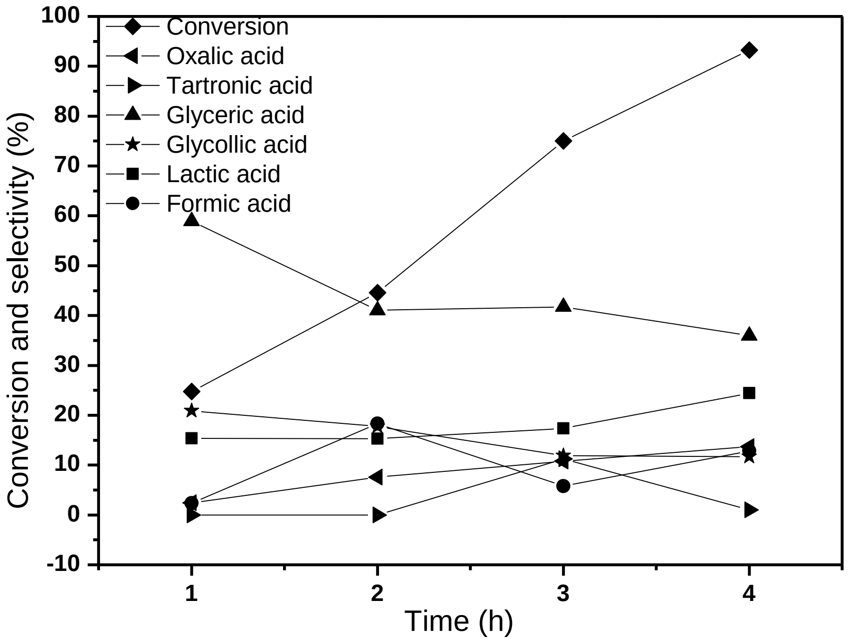

Fig. S10 The conversion and selectivity as the function of the reaction time for Au/CF.

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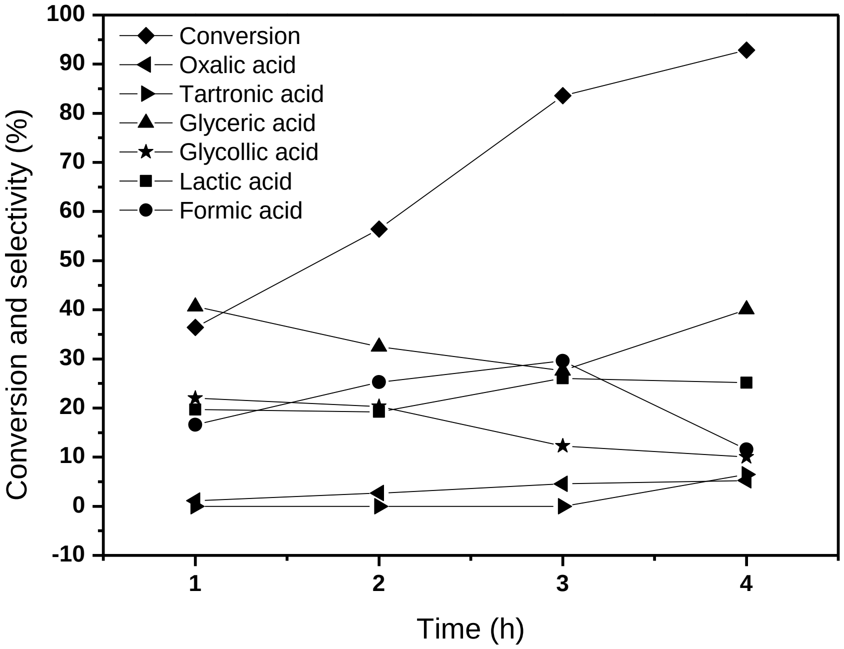

Fig. S11 The conversion and selectivity as the function of the reaction time for Au@CF.

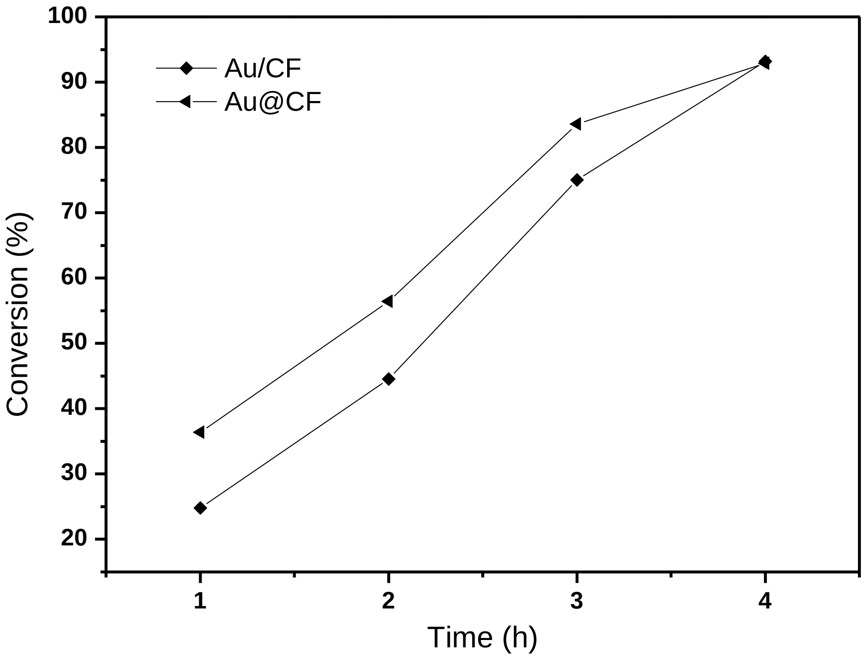

Fig. S12 The conversion of glycerol as the function of the reaction time.

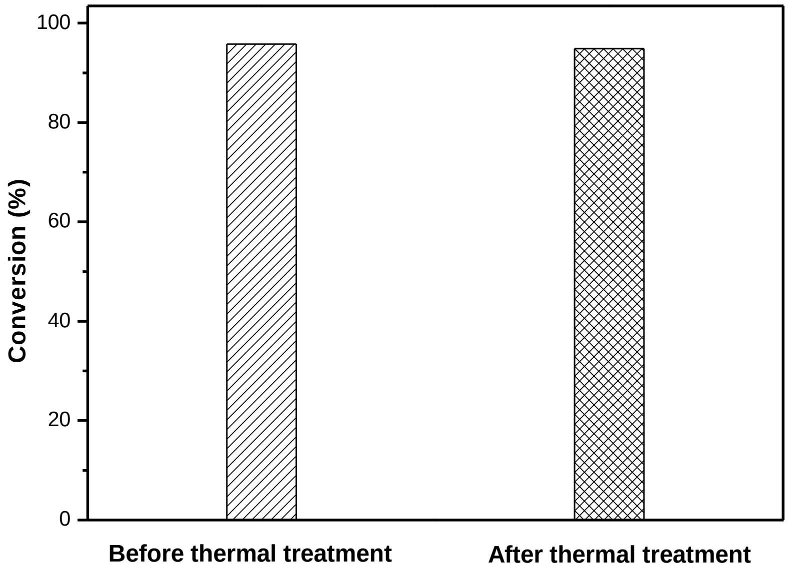

Fig. S13 The activity of Au@CF with 5 nm gold nanoparticles before and after thermal treatment in the oxidation of glycerol at 60 ^{o}C under 0.3 MPa dioxygen in 4 h.