Supporting Information

Kinetically Controlled Synthesis of Nanoporous Au and their Enhanced Electrocatalytic Activity for Glucose-based Biofuel Cells

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The evolution of NPG in a water-ice bath

Figure S1. The temporal morphology evolution of the Au nanocrystals in a water-ice bath. The FE-SEM images of the Au nanocrystals obtained with maturation time of (A) 3 h, (B) 6 h, (C) 9 h, (D) 12 h, (E) 15 h, and (F) 18 h, respectively.

The morphology of the Au nanocrystal could be kinetically controlled by simply varying the aging time in a water-ice bath. It was observed that varied morphologies of the Au nanocrystals (Figure S1) were obtained depending on the reaction time, and their corresponding compositions were traced by XRD patterns (Figure S2). The evolution structure of the Figure S1A is foam and composed of interconnected networks of ultrathin wire-like structures. The size of NPs or nanowires is less than 10 nm. Figure S1A1 shows TEM image of the as-prepared initial Au nanowires. Careful

observation confirms that unlike the randomly agglomerated structures, the present Au nanostructure does not show single NP separated well from each other but fused together. To illustrate the detailed features and mechanism, a HR-TEM analysis was thus carried out. Actually, HR-TEM was conducted to characterize the materials in detail and to unravel the assembly state of the Au NPs in this stage. As shown in Figure S1A2, the crystalline domains containing lattice planes with inter-planar distances of about 0.235 nm are assigned to the (111) plane of face centered cubic metallic Au, and are widely distributed on the product. The branch-like segment is typically formed by two or more particles attaching together via a common crystallographic orientation, and the grain edges of coalescence are illustrated clearly (Figure S1A2). Thus ultrathin wire-like structures with irregular shapes exhibit the particular character of crystal growth by orientation attachment mechanism. At the same time, the orientation attachment among the Au NPs would lead to a series of dislocations or grain boundaries generating.

As the reaction proceeds (6 h), more and more Au atoms are reduced, and they preferentially adsorb onto the nanowires, and then form nanochains (Figure S1B). Because AuCl₄⁻ is adsorbed in a noncharged state and can be preferentially bound onto the Au particles surface, compared with citrate.^[1] Apparently, the increase in diameter steadies the nanochains, and promotes the formation of network structure. Considering that the network structure has typical dimensions on a similar size scale as the diameter of the nanochain, we conclude that the network is formed directly from the oriented attachment of nanochains (Figure S1C). This Au network structure, however, was found to be contradictory with the previous morphology evolution of Au nanocrystal, which is a reversible aggregation of unstable primary particles in the beginning followed by a redispersion of these primary particles in the final stage of the reaction.^[2]

Later, with the aging time increased to 12 h, NPG structures are obtained, as can be seen from Figure S1D. It was remarkable that the nanosponges are made of porous, interconnected networks and abundant curves, demonstrating a large amount of highindex surfaces and active sites. The size of the ligaments creating the nanoporous networks area is in the range of 50-80 nm. And the porous structures merge with pores due to nonideal attachment of the nanochains or nanowires. As the color of the reaction solution started to change into yellowish-brown, NPG inclines to fuse together to form a larger porous Au structures by oriented attaching (Figure S1E). Then, the larger porous Au structures set about "sealing" the pore, *i.e.* the increment of the non-porous area, with more reaction time (Figure S1F). At the same time, the overall morphology of porous Au structures began to assemble relatively uniform nanosheets (NSs). Finally, if the aging time is long enough, we believe that the almost non-porous and integrated NSs will appear by oriented attaching mechanism.



Figure S2. The XRD patterns of the Au nanocrystals obtained with different reaction time.



Figure S3. HR-TEM image and crystal defects in NPG.



Figure S4. HR-TEM image and grain boundary in the NPG.



Figure S5. The colour evolution of the reaction solutions at different times. The reaction solution represents the mixed solution of Au(III) and Na₃Cit with 0 mg, 28.3 mg, 45.3 mg, 56.6 mg, 67.9 mg, and 84.9 mg Na₂CO₃•10H₂O, respectively.



Figure S6. CV profiles in the presence of 10 mM glucose for Turkevich Au and NPG in pH=7.4 PBS buffer solution at 298 K.



Figure S7. Tafel plots of NPG at different temperature.

Table S1. Comparison of electrochemical surface area of the Au nanostructures obtained in 0.1 MNaOH at 298 K.

	Charge	Electrochemical	
	(C cm ⁻² mg ⁻¹)	surface area (m ² g ⁻¹)	
Au NPs	0.57857	120.03	
NPG	0.60357	125.22	
Au NSs	0.43929	91.14	
Turkevich-Au NPs	0.06139	12.74	
Au NSs Turkevich-Au NPs	0.43929 0.06139	91.14 12.74	

Table S2. Comparison of Tafel slops in different region on NPG at different temperature in 0.1 M NaOH recorded at 20 mV s⁻¹ in the presence of 10 mM glucose.

	278 K	288 K	298 K	310 K	323 K
	(mV/dec)	(mV/dec)	(mV/dec)	(mV/dec)	(mV/dec)
Region I	290.3±3.4	311.7±6.7	208.7±2.6	284.2±6.3	254±3.4
Region II	669.9±8.4	495.4±6.5	438.2±3.8	450±5.8	387.5±7.6

Notes and References

- S. Biggs, P. Mulvaney, C. F. Zukoski, F. Grleser, J. Am. Chem. Soc. 1994, 116, 9150-9157.
- [2] B.-K. Pong, H. I. Elim, J.-X. Chong, W. Ji, B. L. Trout, J.-Y. Lee, J. Phys. Chem. C 2007, 111, 6281-6287.