Supplementary

1. More Information about the Dissolution of Cellulose in NaOH Solution:

The pretreated cellulose solution was neutralized with sulfuric acid solution (0.05 mol L^{-1}) and some solids were found to be regenerated out. After filtration, the solids were washed and dried, while the filtrate was further diluted with water to the volume of 1 L. Organic carbon content of the filtrate was determined to be ~418 mg L^{-1} by using total organic carbon analyzer (TOC-Vcpn, Shimadzu, Japan), suggesting ~19% of cellulose has changed into soluble content remaining in the solution.

The regenerated solids were analyzed by XRD for its structure information, as shown in Figure S1. For comparison, the raw cellulose was also detected. According to the results in previous references, the raw cellulose is attributed to cellulose I structure, while the precipitated crystalline is attributed to cellulose II structure [1–2]. Since cellulose with II structure is also very stable [2]. The regeneration of cellulose with II structure from solution indicates there still remain strong interactions between the cellulose molecules in NaOH solution.

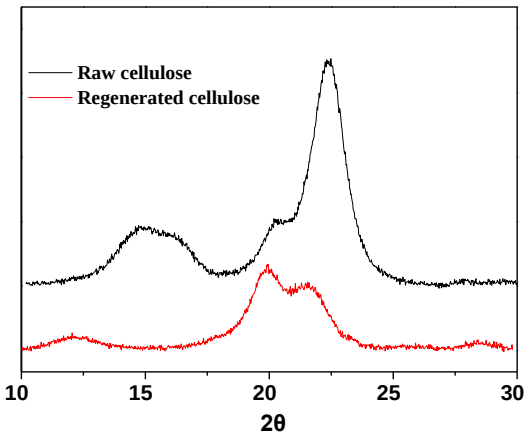

Figure S1. XRD of raw and regenerated cellulose.

2. TG/DSC Analysis for the Au/CA Electrode:

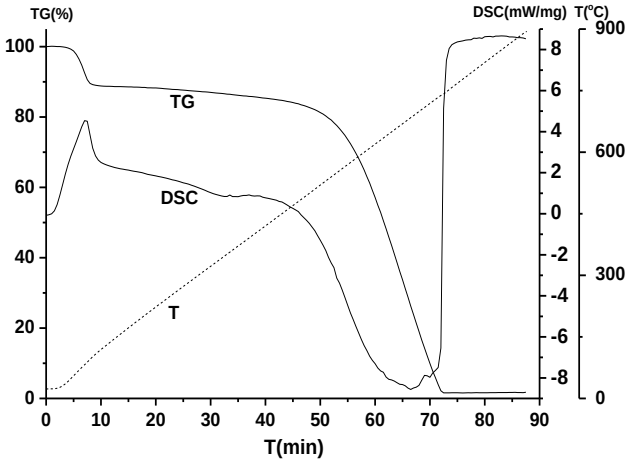

Figure S2. TG/DSC of Au/CA.

3. HPLC Analysis for the Acidified Electrolyte from Cellulose Electrochemical Transformation on Au/CA Anode:

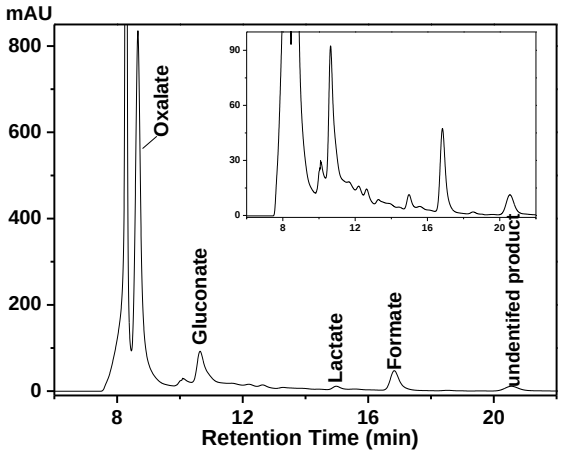

Figure S3. HPLC of the products from cellulose electrolysis.

4. IR Analysis for the CA Support with and without HNO_3 Activation:

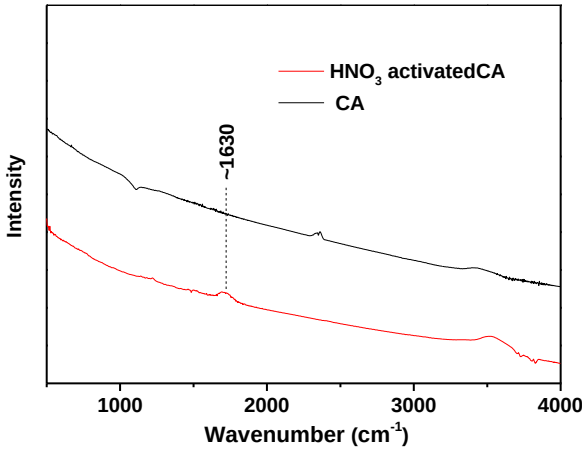

Figure S4. IR spectrum of CA and HNO_3 activated CA.

5. More Information for the Fundamental Electrochemical Reaction of Cellulose on Au/CA Electrode:

In order to obtain better understanding of the fundamental electrochemical reaction of cellulose on Au/CA electrode, cyclic voltammetry (CV) was performed in the pretreated cellulose-NaOH solution. However, the current is very high in the reaction process, making the adsorption/desorption and oxidation/ reduction peaks not apparent in the CV curve, as shown in Figure S4. This is due to the excellent electrical conductivity of CA support [3]. Considering that the electrochemical reactions of cellulose in NaOH solution were mainly taken place on the surface of Au nanoparticles electrocatalyst, we fabricated the nano-Au electrode through electrodeposition of Au nanoparticles on gold disk at a potentials of 0.8 V (*vs.* SCE) for 30 min. Subsequently, the CV measurement of cellulose in NaOH solution was performed on the nano-Au electrode, as shown in Figure S5. For comparison, it was also detected at Au disk electrode in the same condition. From Figure S5 we can see that, the fundamental electrochemical reactions of cellulose in NaOH solution are identical whether at Au or at nano-Au electrodes. However, due to deposited Au nanoparticles, the peak currents at nano-Au electrode were much higher than those at Au disk electrode, implying the higher active sites obtained in nano-Au electrode. In the CV curves, peak I at −0.1 V corresponds to the adsorption of OH^- on Au nanoparticles surface, and peaks III at 0.26 V and VI at −0.23 V correspond to the oxidation and

reduction of the Au nanoparticles. In addition, peak VI also corresponds to the desorption of OH^-. While peak II at 0.07 V corresponds to the oxidation of cellulose, and peak V at ~0 V corresponds to the desorption of the reaction products from the electrode surface. Simultaneously the cellulose was further oxidized at the revealed electrode surface [4].

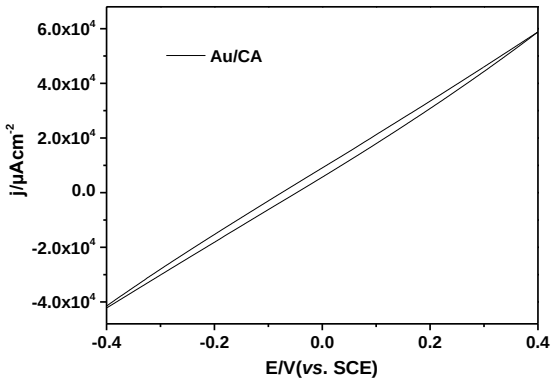

Figure S5. CV of Au/CA electrode in cellulose-NaOH solution at a scan rate of 50 mV s^{-1}.

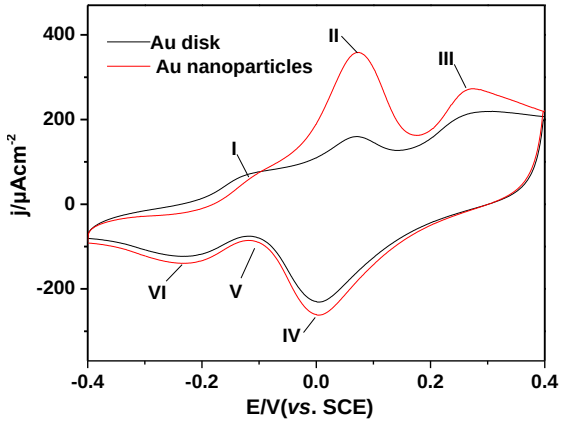

Figure S6. CV of nano-Au and Au disk electrode in cellulose-NaOH solution at a scan rate of 50 mV s^{-1}.

References

1. Chen, X., Chen, J.H.; You, T.T.; Wang, K.; Xu, F. Effects of polymorphs on dissolution of cellulose in NaOH/urea aqueous solution. *Carbohydr. Polym.* **2015**, *125*, 85–91.
2. Duchemin, B.J.C. Mercerisation of cellulose in aqueous NaOH at low concentrations. *Green Chem.* **2015**, *17*, 3941–3947.
3. Jin, Y.N.; Wu, M.F.; Zhao, G.H.; Li, M.F. Photocatalysis-enhanced electrosorption process for degradation of high-concentration dye wastewater on TiO_2/carbon aerogel. *Chem. Eng. J.* **2011**, *168*, 1248–1255.
4. Sugano, Y.; Latonen, R.M. Akieh-Pirkanniemi, M.; Bobacka, J.; Ivaska, A. Electrocatalytic Oxidation of Cellulose at a Gold Electrode. *ChemSusChem* **2014**, *7*, 2240–2247.