

Supporting Information

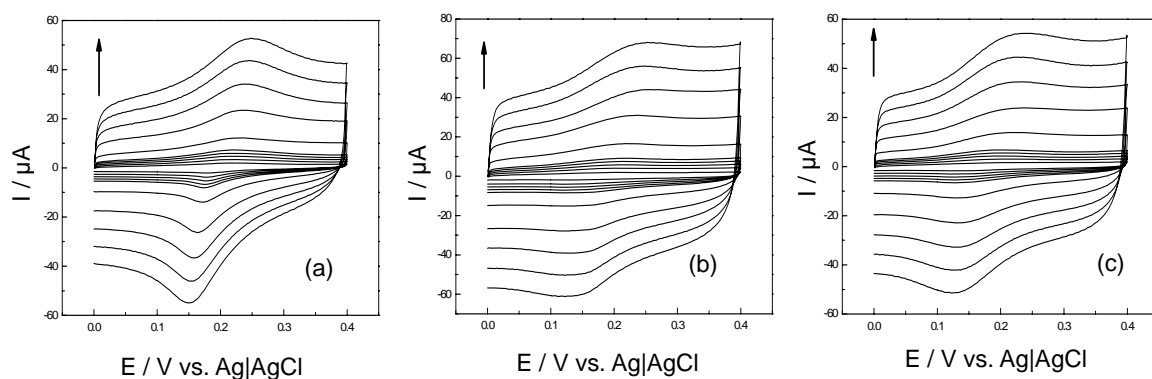


Figure S1. CVs of Au-NS/SOD (a), Au-NR/SOD (b), Au-NP/SOD (c) gold electrodes in 25 mM PBS (pH 7.2) at different scan rates: 10, 20, 30, 40, 50, 100, 200, 300, 400, 500 mV s^{-1} (from the inner to the outer).

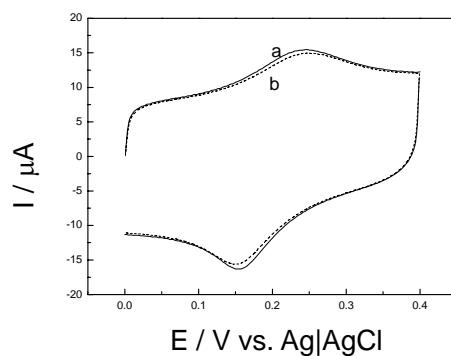


Figure S2. CVs obtained at Au-NS/SOD electrode (a) in 25 mM PBS (pH 7.2), and (b) after potentially scanned for one week. Potential scan rate: 100 mV s^{-1} .

The direct immobilization of SOD molecules at the nanostructured gold electrodes is further verified by the measurement of the open-circuit potential (E_{oc}) of gold nanostructures-immobilized electrodes in N_2 -saturated 25 mM PBS. A 370 mV negative shift of E_{oc} (from +270 mV to -100 mV vs. Ag|AgCl) was observed when the Au-NS/SOD electrode was applied at a potential of -250 mV for 180 s. This negative shift of E_{oc} indicates that an electron is transferred to the redox center of the SOD (i.e., the Cu^{2+} moiety is converted into Cu^+). Whereas, the E_{oc} was returned back to +270 mV when it was measured after holding the electrode at +600 mV for 180 s, indicating the oxidation of the Cu^+ to Cu^{2+} again. Similar result was also obtained at the Au-NR/SOD and Au-NP/SOD gold electrodes. A controlled experiment was performed at the bare nanostructured gold electrodes by holding the electrode potential at -250 mV for 180 s and no obvious negative shift of the E_{oc} was observed. This behavior provides another evidence for the successful immobilization of the SOD at the three kinds of nanostructured gold surfaces.

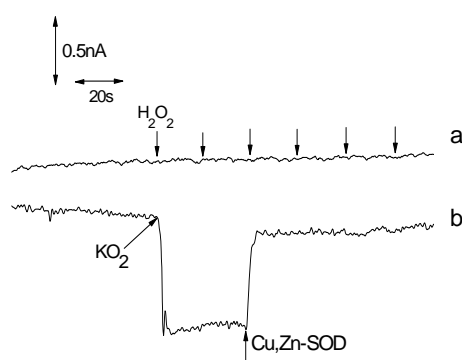


Figure S3. Typical current-time responses of Au-NS/SOD electrode toward 50 μM H_2O_2 (curve a), and in the presence of 3 μM $O_2^{\bullet-}$ (curve b) in 25 mM PBS at -300 mV. The arrows represent the addition of KO_2 and 10 μM Cu, Zn-SOD to the solution.