Combinatorial Biomimetics. Optimization of Composition of Copper(II) Poly-L-Histidine Complex as an Electrocatalyst for O_2 Reduction by Scanning Electrochemical Microscopy

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Supporting Information

Solution phase electrochemical studies: Cyclic voltammograms (CVs) at a glassy carbon (GC) electrode in 0.5 M Na_2SO_4 at pH 5.8 with or without 1 mM Cu^{2+} and O_2 are shown in Fig. S1. The background current of the GC electrode in the absence of Cu^{2+} and O_2 was relatively small (curve 1). In oxygen-saturated solution at a bare GC electrode, the O_2 reduction peak appeared at ~ -0.30 V vs. Ag/AgCl (curve 2). In deaerated 1 mM Cu^{2+} solution, CV at a scan rate of 50 mV/s, showed the reduction of Cu^{2+} to Cu^0 with a cathodic peak potential, E_{pc}, of -0.1 V vs. Ag/AgCl (curve 3). Cu^0 deposited on the electrode surface could be stripped off in the reverse scan with an anodic peak potential, E_{pa}, of 0.07 V. In oxygen-saturated solution, the reduction current increased and E_{pc} shifted slightly to a more positive value. The oxidation peak in the reverse scan was not observed until $E_{pa} \sim 0.3$ V. Cu electrode has been reported to show a high catalytic activity for oxygen reduction in the neutral and alkaline media upon formation of surface $Cu(OH)_{ads}$ or Cu_2O submonolayer.[1,2] It has been suggested that in the presence of oxygen, the interfacial pH increased due to oxygen reduction to OH^- and a catalytic surface of $Cu(OH)_{ads}$ or Cu_2O submonolayer formed, resulting in an increase in the rate of catalytic oxygen reduction.

In a deaerated 0.5 M Na_2SO_4 solution containing 1 mM Cu^{2+}, the cyclic voltammetric behavior at a GC electrode depended on the concentration of poly-L-histidine present in the solution (see Fig. S2). The magnitude of the current decreased with respect to that observed with only Cu^{2+} present in the solution. In the potential range ($-0.3 \leq E \leq 0.3$ V) studied, when the mole fraction of Cu^{2+} was low, e.g., 0.33 for curve 1 of Fig. S2(a), the reduction current increased gradually to reach a plateau and a small stripping peak near the peak potential (~ 0.08 V vs. Ag/AgCl) for Cu^0 stripping was obtained in the reverse scan (see curve 1 of Fig. S2(a)). When the concentration of histidine residues was increased, the reduction current decreased and the re-oxidation peak disappeared in the reverse scan. Extending the potential window from 0.6 to -0.6 V vs. Ag/AgCl and using a Cu^{2+} mole fraction of 0.09, we observed that the reduction plateau exhibited from -0.1 to -0.5 V vs. Ag/AgCl and a re-oxidation peak was obtained at 0.41 V vs. Ag/AgCl (see Fig. S2(b)). These results suggest that Cu^{2+} ion complexes well with poly-L-histidine at a Cu^{2+} mole fraction of 0.09 at pH 4.5. The current decrease was attributed to the

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lower diffusion coefficients of the Cu^{2+}-poly-L-histidine complexes formed and the increase of the complexation with increasing molar ratio of histidine residues to Cu^{2+}. CVs on a GC electrode in a solution containing 1 mM Cu^{2+} and 10 mM histidine residues in 0.5 M Na_2SO_4 at pH 4.5 in the absence or presence of O_2 are shown in Fig. S2(c). In a deaerated solution, the Cu^{2+}-poly-L-histidine complex started to reduce at 0.2 V vs. Ag/AgCl. In oxygen-saturated solution, the oxygen reduction commenced at -0.05 V vs. Ag/AgCl in the solution containing Cu^{2+}-poly-L-histidine complex, that is slightly more anodic than that in the absence of complex (~ -0.13 V vs. Ag/AgCl) (compare curve 2 of Fig. S2(c) with curve 2 of Fig. 1). Thus, Cu^{2+}-poly-L-histidine complex in the solution also shows some electrocatalytic effect for oxygen reduction.

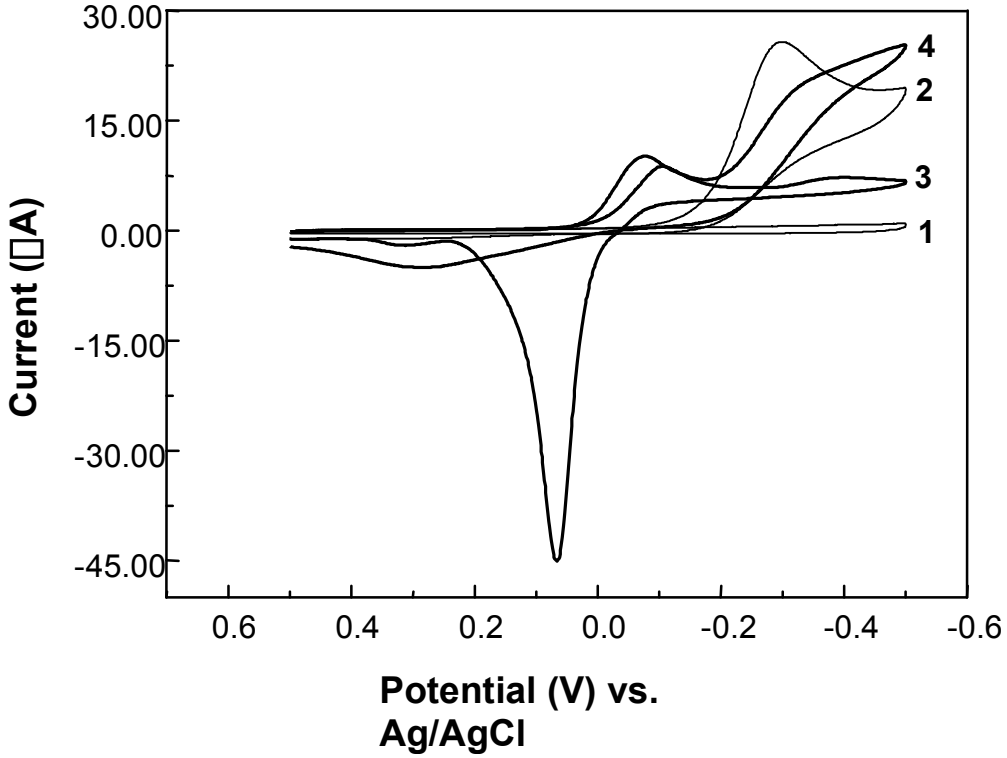

Figure S1. Cyclic voltammograms in the absence or presence of 1 mM Cu^{2+} in 0.5 M Na_2SO_4 at GC electrode (3 mm in diameter) in the absence or presence of O_2. Potential scan rate, ν = 50 mV/s. *Curve 1*: no Cu^{2+}, no O_2; *Curve 2*: no Cu^{2+}, with O_2; *Curve 3*: 1 mM Cu^{2+}, no O_2; *Curve 4*: 1 mM Cu^{2+}, with O_2.

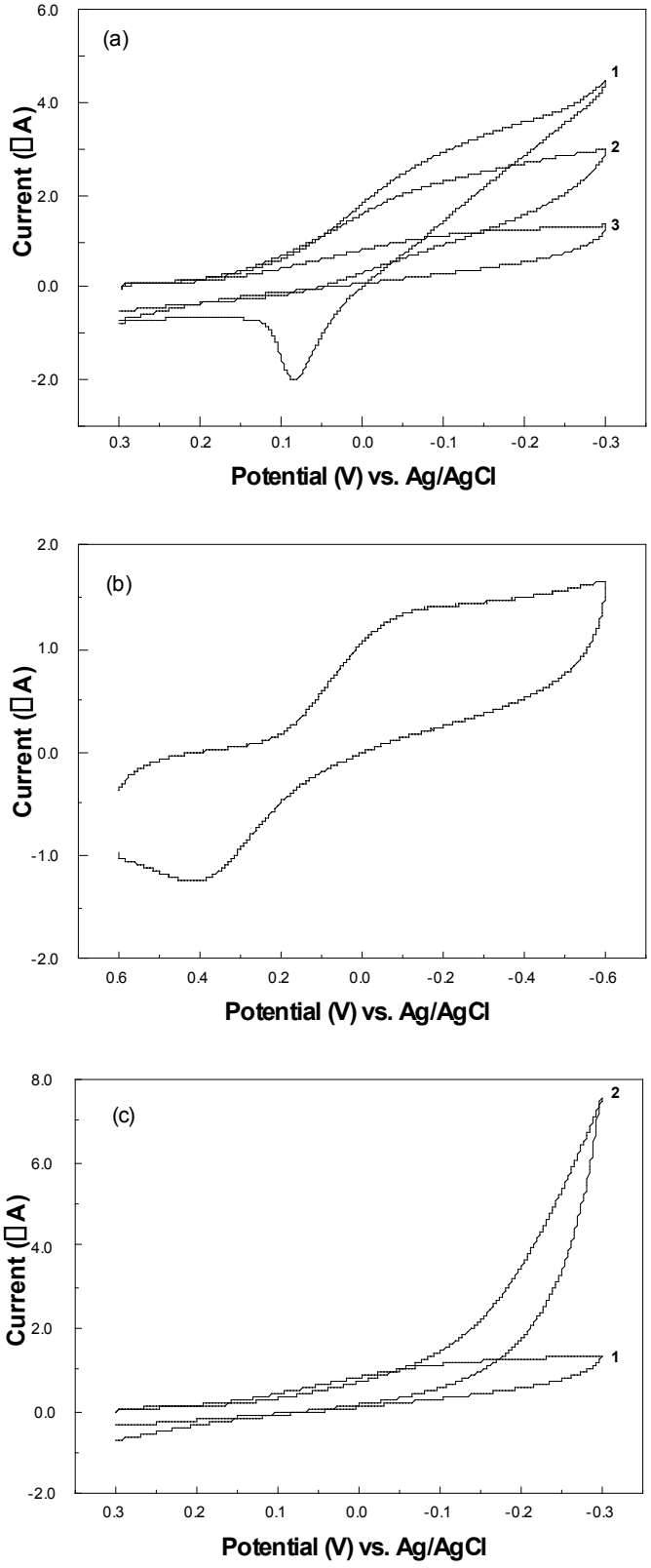

Figure S2 (a). Cyclic voltammograms in the presence of various concentrations of poly-L-histidine with 1 mM Cu^{2+} in 0.5 M Na_2SO_4 at GC electrode (3 mm in diameter) in the absence of O_2 at pH 4.5. Potential scan rate, □ = 50 mV/s. *Curve 1*: 2 mM histidine residues; *Curve 2*: 4 mM histidine residues; *Curve 3*: 10 mM histidine residues. (b) Expansion of potential widow of curve 3 in (a). (c) Cyclic voltammograms in the absence and presence of O_2 in 0.5 M Na_2SO_4 containing 1 mM Cu^{2+} and 10 mM histidine residues.

The procedure for the preparation of the Cu-poly-his modified glassy carbon electrodes: The desired amount of poly-L-histidine (MW: 5000~15000) was added into 2 ml Milli-Q water. Sulfuric acid was continuously dropped into this solution until poly-L-histidine was totally soluble. The desired amount of $Cu(NO_3)_2.3H_2O$ was then added into the solution. After the solution was sufficiently mixed, the solution pH was adjusted to the desired value by NaOH. Ten □L of this mixed solution was pipetted onto the surface of GC electrodes. The Cu^{2+}-poly-L-histidine modified electrode was then dried in a container full of nitrogen. After the modified membrane was dried, the electrode was gently rinsed with Milli-Q water.

Array preparation: In the preparation of arrays of Cu^{2+}-poly-his complex spots of various compositions, two different solutions containing 10 mM poly-L-histidine and 10 mM $Cu(NO_3)_2.3H_2O$, respectively, were first prepared. 5% v/v glycerol was added to each solution to avoid premature evaporation of the spots. The dispenser was filled with poly-L-histidine solution (3 □L), which was dispensed in a programmed number of drops at each site. Each composition was prepared repeatedly to test the reproducibility. Thus, the arrays contained 5 rows and 5 columns of spots. After dispensing the poly-L-histidine spots, the dispenser was emptied, thoroughly rinsed first with ethanol and then with Milli-Q water, and refilled with 3 □L of Cu^{2+} solution. The plotter positioned the dispenser exactly over the previously prepared poly-L-histidine spots and a number of drops of Cu^{2+} solution dispensed to make the total amount of drops always equal to 12. The spots of the array were then agitated for 5 min in a Vortex Genie 2 agitator (Fisher). To remove the glycerol of the spots, the array was heated in the oven at 100°C over night.

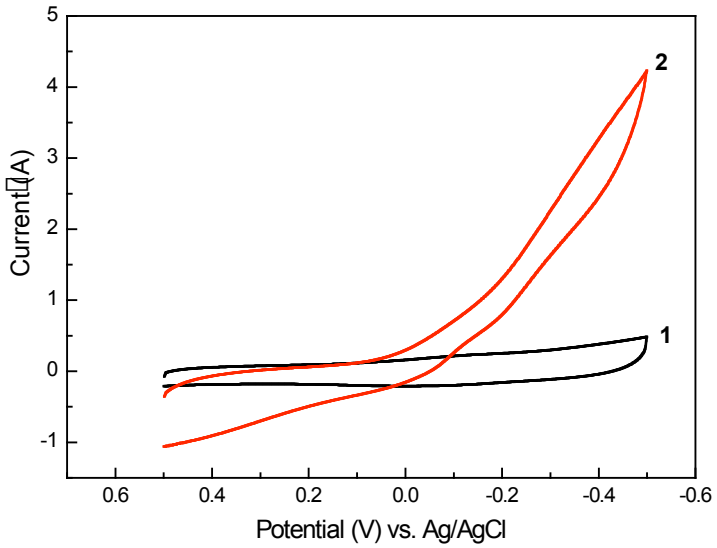

Figure S3. Cyclic voltammograms (CVs) of Cu^{2+}-poly-his modified GC electrode in 0.2 M PBS (pH 7) compared with bare GC electrode in the absence of O_2. The condition of modified films: 8 mM histidine residues, 2 mM Cu^{2+} at pH 5. Potential scan rate, v = 50 mV/s. Curve 1: bare GC; Curve 2: modified GC.

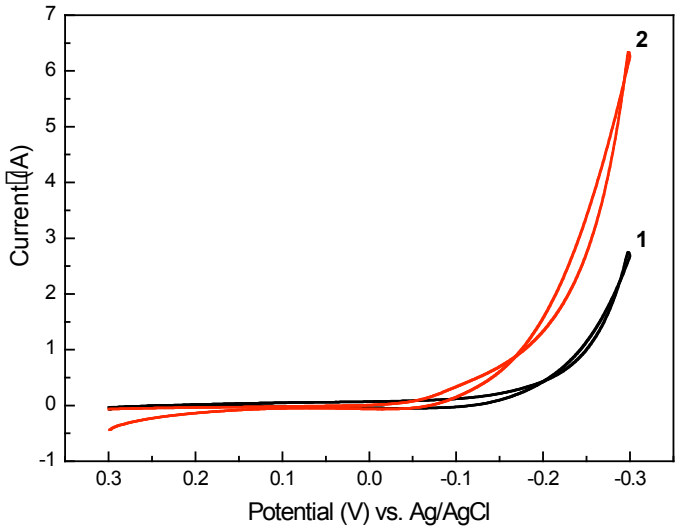

Figure S4. CVs of Cu^{2+}-poly-his modified GC electrode in 0.2 M PBS (pH 7) compared with bare GC electrode in the presence of O_2 after subtracting the background current. The condition of modified films: 8 mM histidine residues, 2 mM Cu^{2+} at pH 5. Potential scan rate, □ = 50 mV/s. Curve 1: bare GC; Curve 2: modified GC.

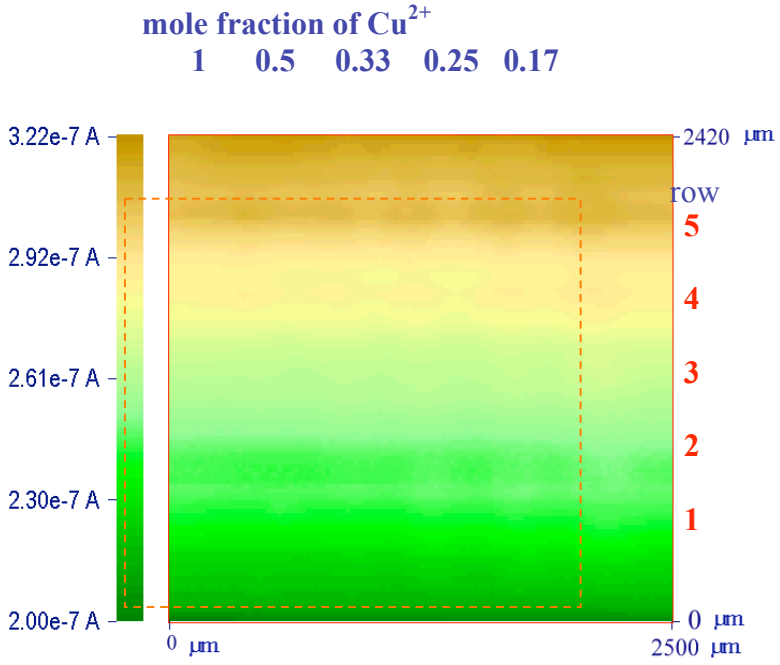

Figure S5. SECM image of the array containing 5 rows and 5 columns of spots with different mole fraction of Cu^{2+} at pH 7 phosphate buffer, i_T = 73 nA (i_T: tip current), E_s = -0.3V vs. Ag/AgCl, tip raster rate: 20 □m each 0.2 s.

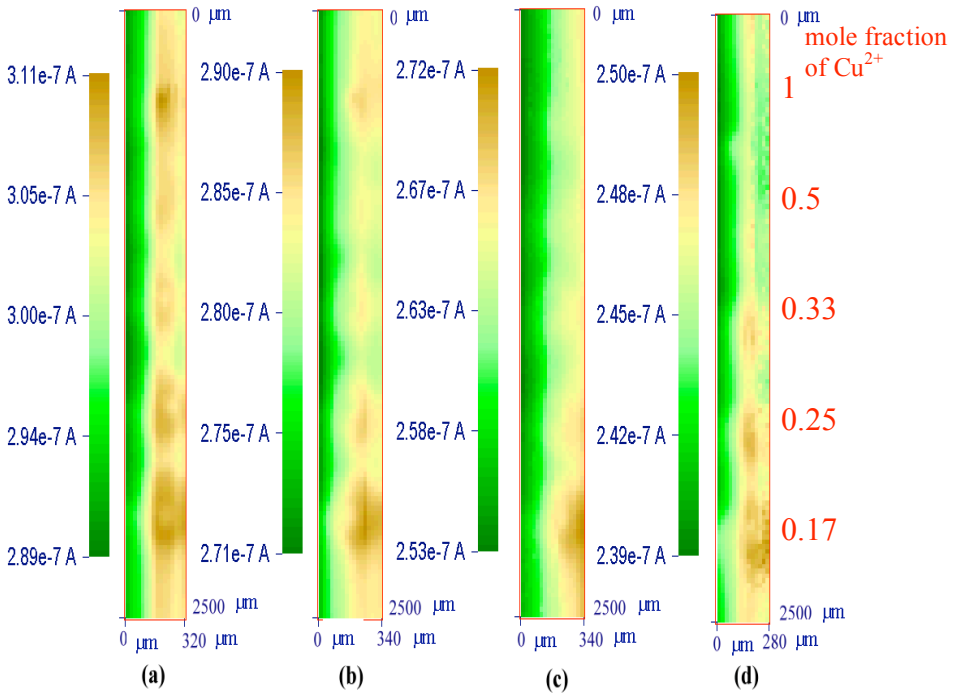

Figure S6. SECM images of Cu^{2+}-poly-his arrays containing spots with different mole fraction of Cu^{2+} at pH 7 phosphate buffer, i_T = 73 nA (i_T: tip current), E_s = -0.3 V vs. Ag/AgCl, tip raster rate: 20 μm each 0.2 s (a) the fifth row (b) the fourth row (c) the third row (d) the second row.

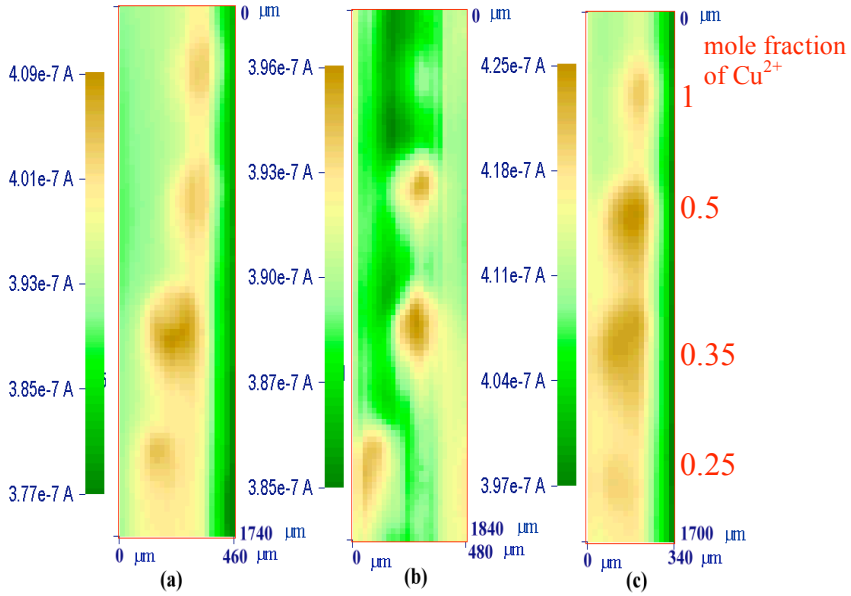

Figure S7. SECM images of Cu^{2+}-poly-his arrays containing spots with different mole fraction of Cu^{2+} at pH 7 phosphate buffer, i_T = 80.6 nA (i_T: tip current), E_s = -0.2 V vs. Ag/AgCl, tip raster rate: 20 μm each 0.2 s (a) the third row (b) the second row (c) the first row for the first scan. Tip and substrate distance: 30 μm.

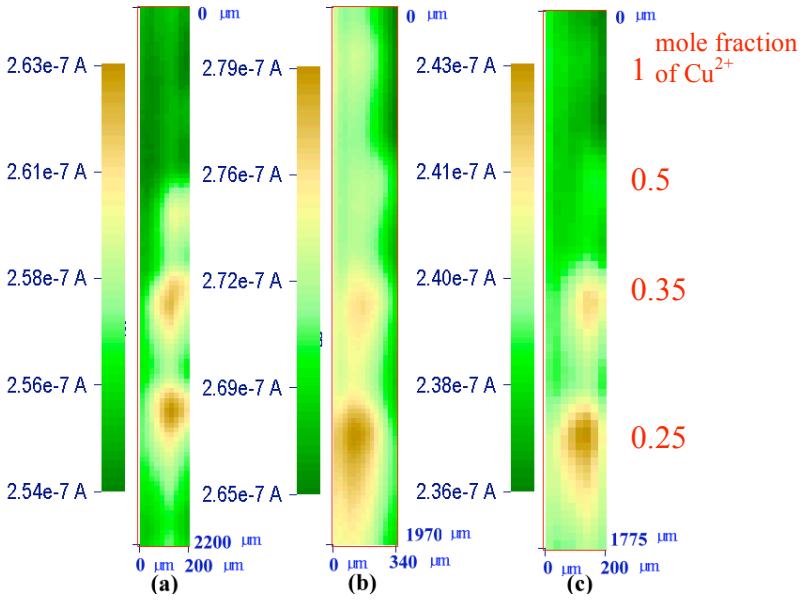

Figure S8. SECM images of Cu^{2+}-poly-his arrays containing spots with different mole fraction of Cu^{2+} at pH 7 phosphate buffer, i_T = 80.6 nA (i_T: tip current), E_s = -0.2 V vs. Ag/AgCl, (a) the second scan (b) the third scan (c) the fourth scan; scan rate: 20 μm each 0.2 s for (a), (b) and 40 μm each 0.2 s for (c). Tip and substrate distance: 30 μm.

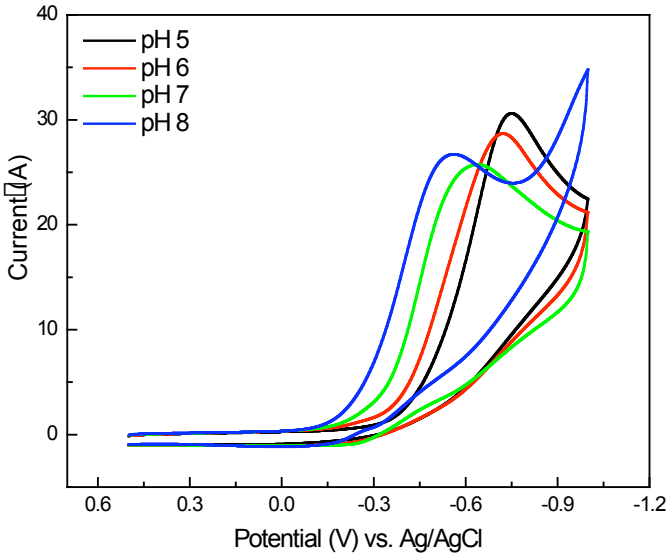

Figure S9. Cyclic voltammograms of GC electrode in 0.2 M PBS at various pH values in the present of O_2, Potential scan rate, = 50 mV/s.

[1] Vazquez, M. V.; Sanchez, S. R.; Calco, E. J.; Schiffrin, D. J. *J. Electroanal. Chem*. **1994**, 374, 189-197.
[2] King, F.; Litke, C. D.; Tang, Y. *J. Electroanal. Chem*. **1995**, 384, 105-113.