Supporting Information

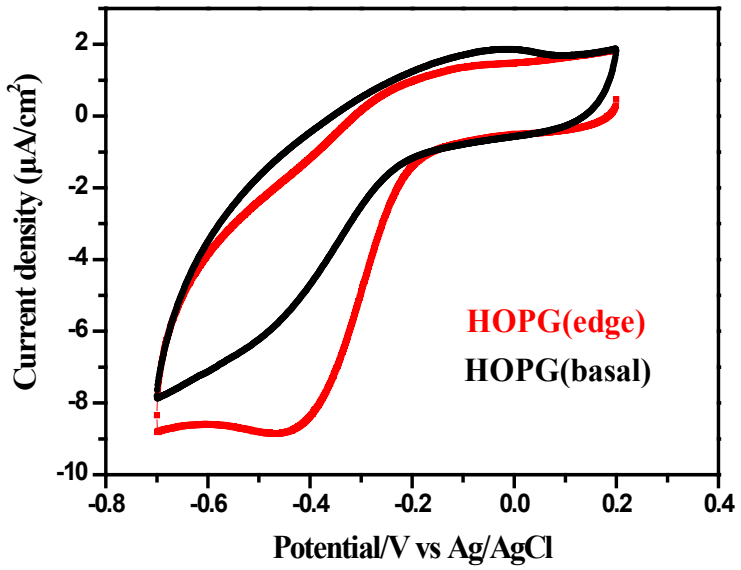

Fig. S1 Electrocatalytic performance of CYP3A4 modified HOPG (basal and edge plane) electrodes. Scan rate: 20 mV/s; PB solution (0.1 M, pH 7.0).

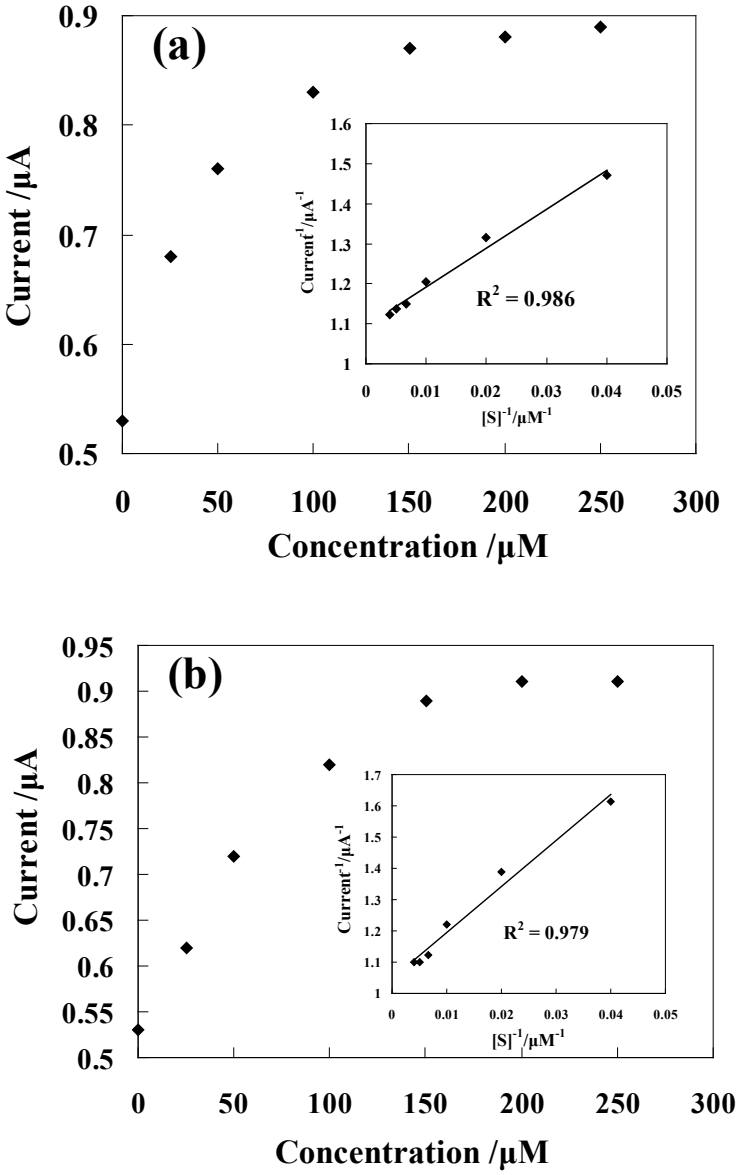

Fig. S2 Calibration plots illustrating the electrode response to testosterone (a) and quinidine (b) addition. Insert: double-reciprocal plot of catalytic current and the concentrations of subtrates. Experimental conditions is same with that in Figure 5.

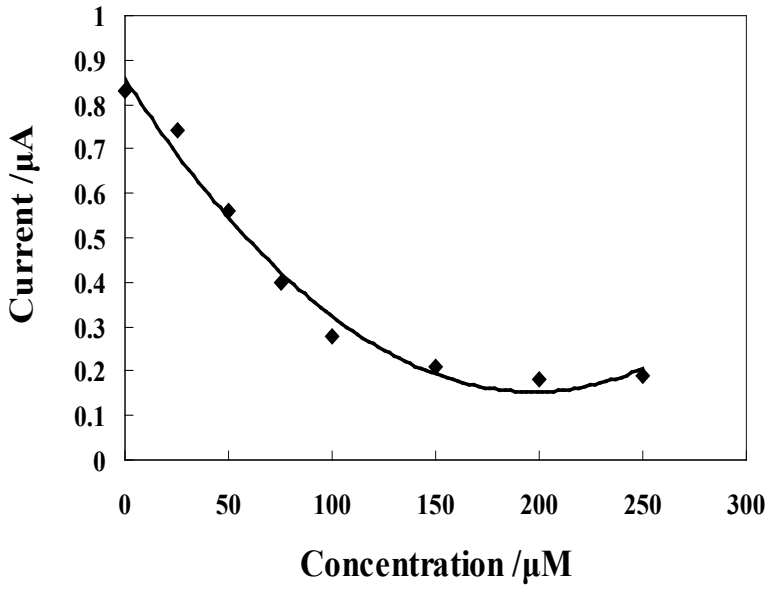

Fig. S3 Bioelectrocatalytic current variation with the addition of increasing concentration of inhibitor ketoconazole. Experimental conditions is same with that in Figure 5.

The IC_{50} value was used to explore the detailed inhibition effects of ketoconazole on testosterone metabolism. Ketoconazole ranged from 0 to 250 μM were gradually added into the PBS solution (pH 7.0) in the presence of constant testosterone concentration. Cyclic voltammetry was performed after each addition. The inhibition data followed a binomial model ($Y= 2E\text{-}05X^2 - 0.0072\ X + 0.8573$), and the IC_{50} value was calculated to be 58.5 μM. The inhibition effect on testosterone metabolism was similar to a previous report (*J. Am. Chem. Soc.*, 2009, **131**, 6646-6647.).