Title: Facile and sensitive photoelectrochemical detection of kojic acid in food products: a general strategy for immobilization-free analysis of enzyme inhibitors

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The number of pages: total 5 pages including 1 SI Table and 3 SI Figures

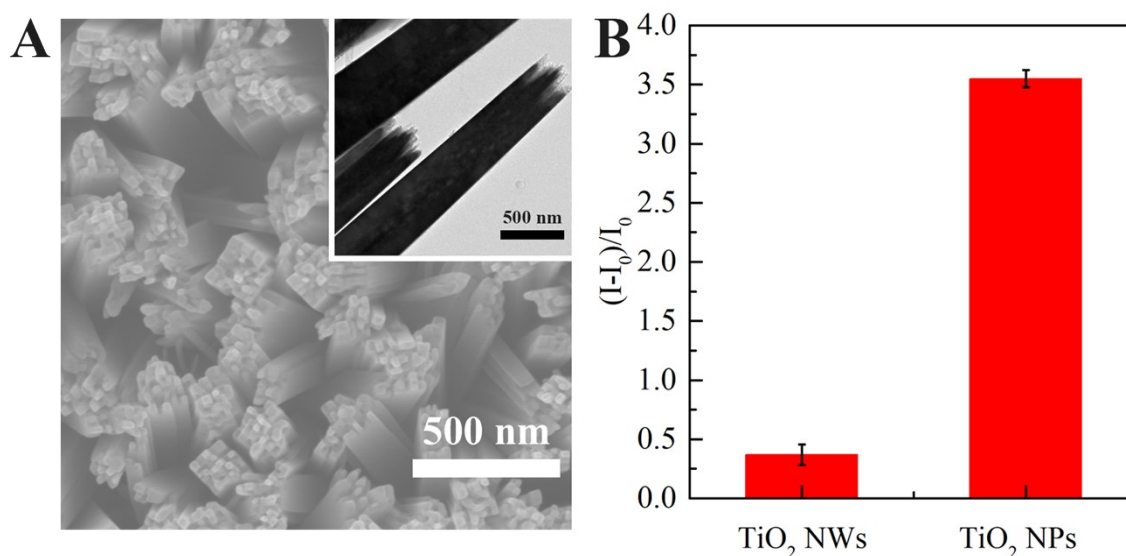**Comparation between TiO$_2$ NWs and TiO$_2$ NPs**

Figure S1. (A) SEM image and (inset of A) TEM image of TiO$_2$ NWs; (B) photocurrent change of TiO$_2$ NWs and TiO$_2$ NPs electrode after incubation with Tyr and L-ty.

As shown in Figure S1A, the diameter of the hydrothermal TiO$_2$ NWs was around 200 nm with small rod-like structures (~20 nm) on the cross section, and the length of TiO$_2$ NWs was at micrometre level. After incubation with 1000 U/mL Tyr and 1.5 mM L-ty, the photocurrent of TiO$_2$ NWs electrode increased 37%, while TiO$_2$ NPs electrode increased 3.5 times (Figure S1B). Hence, TiO$_2$ NPs electrode was selected as the photoactive material for better analytical performance.

XPS survey

Table S1 XPS analysis of elements ratio on the surface of TiO$_2$ NPs before and after incubation

	Ti (%)	O (%)	C (%)	N (%)
before	24.18	52.79	22.15	0.89
after	23.01 ↓	52.78 ↓	22.95 ↑	1.25 ↑

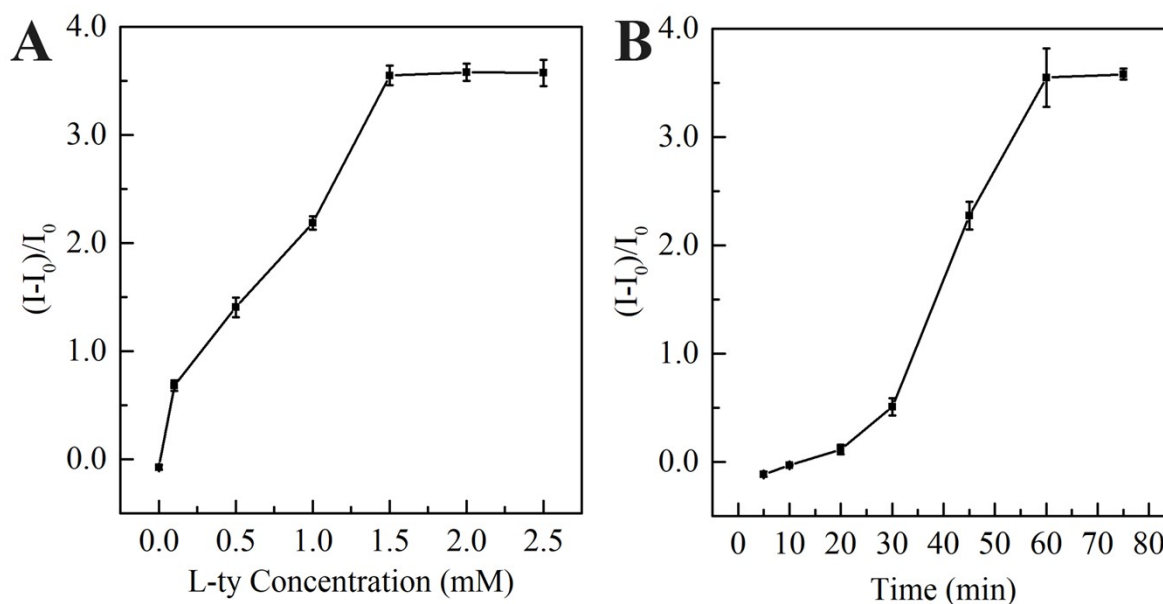**Reaction conditions optimization**

Figure S2. Optimization of (A) L-ty concentration and (B) reaction time.

Figure S2 demonstrated the photocurrent change along with the L-ty concentration and reaction time. After a 60 min incubation of TiO_2 NPs electrodes into the mixed solution of 25 μL 1000 U/mL Tyr and 1mL 0 mM, 0.1 mM, 0.5 mM, 1 mM, 1.5 mM, 2.0 mM, 2.5 mM L-ty respectively, the photocurrent increased dramatically with the L-ty concentration, and reached the maximum change rate of 3.5 times in the presence of 1.5 mM L-ty (Figure S1A), thus 1.5 mM L-ty was chosen as the optimum substrate concentration in the following experiments. Similarly, the reaction time was chosen as 60 min (Figure S1B).

Inherent KA concentration in vinegar

The determination of inherent KA in vinegar was using spectrophotometry according to the national standard method (General Administration of Quality Supervision Inspection and Quarantine of the People's Republic of China, 2021). First, the chromogenic reagent was prepared by dissolving 0.10 g $FeCl_3$ and 0.225 mL concentrated hydrochloric acid with

ultrapure water to 10 mL volume. Then 0.2 mL chromogenic reagent was mixed with standard

KA solution to 10 mL volume where the concentrations KA was 0 mg/L, 10 mg/L, 20 mg/L,

30 mg/L, 40 mg/L, 50 mg/L, 60 mg/L, respectively, and the adsorption value was measured

under irradiation of 500 nm to obtain the standard calibration curve.

0.1 mL vinegar was diluted with ultrapure water to 5 mL (50 folds) and 10 mL (100 folds),

respectively. Then 0.1 mL diluted sample, 0.2 mL chromogenic reagent and different

concentrations of standard KA solution was mixed together and diluted to a 10 mL volume.

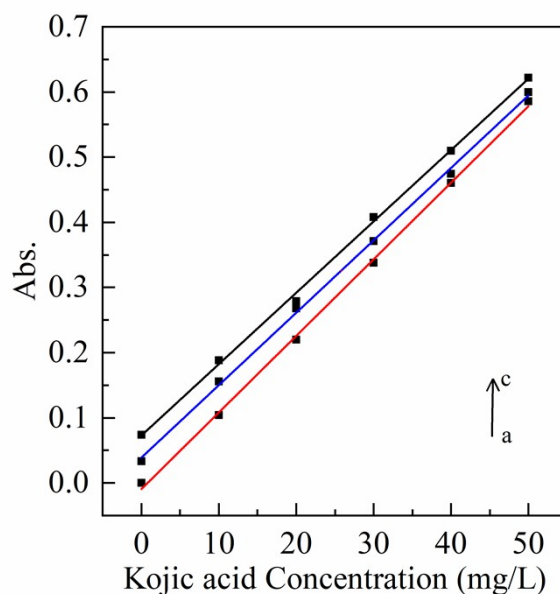The adsorption value was then measured under irradiation of 500 nm.

Figure S3. The calibrated absorption results of standard KA solution (curve a), standard KA

solution adding 100 folds diluted vinegar (curve b) and 50 folds diluted vinegar (curve c).

Figure S3 depicted the calibrated adsorption results of standard KA solution (curve a),

standard KA solution adding 100 folds diluted vinegar (curve b) and 50 folds diluted vinegar

(curve c). The linear equations were (a) $Abs1=0.0118C_{KA}-0.009$, with R^2 of 0.999, (b)

$Abs2=0.0112C_{KA}+0.039$, with R^2 of 0.999 and (c) $Abs3=0.0110C_{KA}+0.073$, with R^2 of 0.998.

The calculated matrix effect for 50 folds diluted and 100 folds diluted vinegar were 6.8% and 4.8%, respectively, which were both below 20%, indicating no obvious interference for KA detection. Then according to the intercept of curve b and curve c, the inherent KA concentration in undiluted vinegar was 0.350 mg/mL, i.e. 2.46×10^{-3} M.

References

General Administration of Quality Supervision Inspection and Quarantine of the People's Republic of China, China National Standardization Management Committee. Kojic acid: GB/T 23534-2009[S]. Beijing: Standards Press of China, 2021 (in Chinese).