Electrical Supporting information

An efficient difunctional photocatalyst prepared in situ from Prussian blue analogues for catalytic water oxidation and visible light absorption

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Synthesis of CuO and $Co(OH)_2$

The synthesis of CuO was according to the reported literature.[34] 1.20 g of $Cu(CH_3COO)_2 \cdot H_2O$ was dissolved in 300 mL of distilled water in a round-bottomed flask equipped with a refluxing device. 1.00 mL glacial acetic acid was added by providing continuous magnetic stirring; a blue solution was appeared. This blue solution was then heated to 40 °C, 0.80 g of NaOH (s) was quickly added into the solution and then again heated to 100 °C for 30 min, where a large amount of brownish black precipitate was produced. After cooling it to the room temperature, the precipitate was centrifuged, washed once with distilled water and dried in a vacuum oven at 80°C during whole night. The method of synthesis $Co(OH)_2$ was similar to CuO expect that the reaction time was 1 h.

Characterization

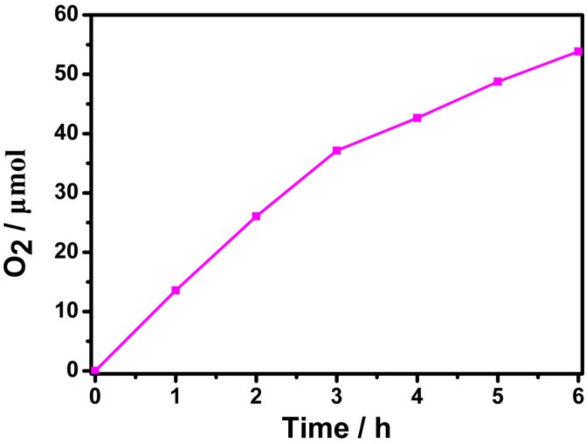
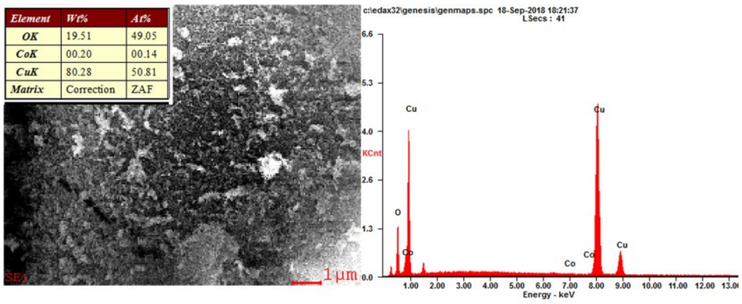


Fig. S1 Kinetics of O_2 evolution of the chemical system using CuO as catalyst. Reaction condition: NaOH solution: 0.10 M, 10 mL; CuO: 5 mg; $Na_2S_2O_8$: 20 mM; vigorous stirring at RT.



Element	Wt%	At%
OK	19.51	49.05
CoK	00.20	00.14
CuK	80.28	50.81
Matrix	Correction	ZAF

Fig. S2 EDS of catalyst 1.

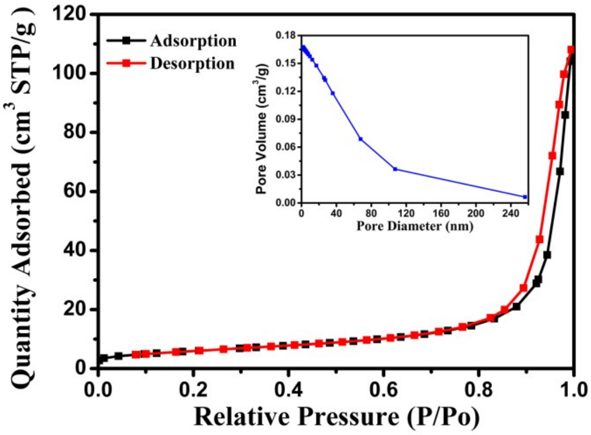


Fig. S3 Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curve (inset) of catalyst 1

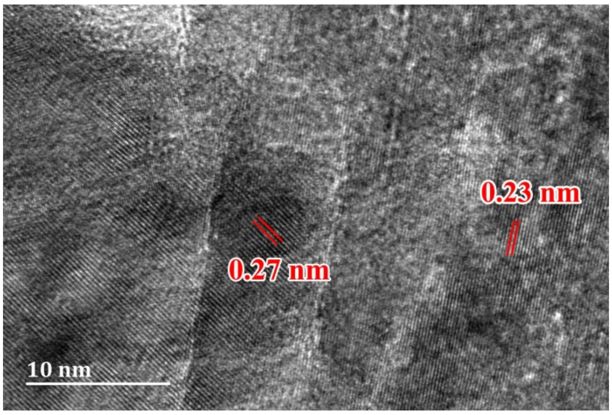


Fig. S4 High-resolution TEM images of catalyst 1.

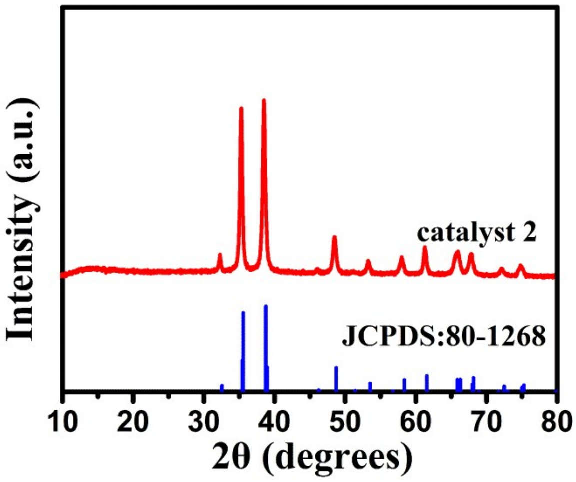


Fig. S5 XRD pattern of catalyst 2

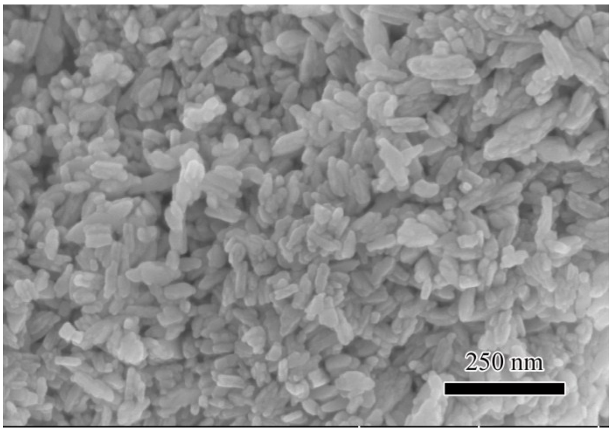
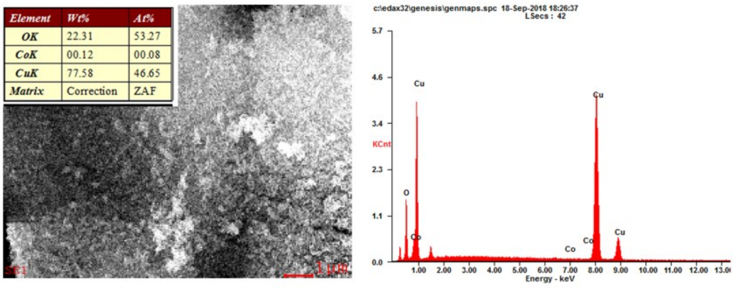


Fig. S6 FESEM image of catalyst 2



Element	Wt%	At%
OK	22.31	53.27
CoK	00.12	00.08
CuK	77.58	46.65
Matrix	Correction	ZAF

Fig. S7 EDS of catalyst 2.

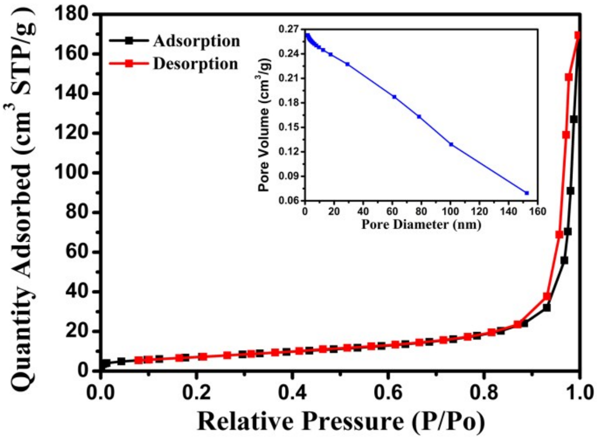


Fig. S8 Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curve (inset) of catalyst 2.

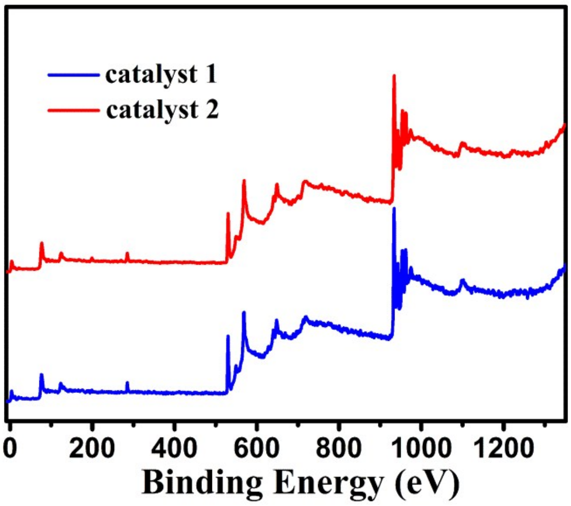


Fig. S9 XPS of catalyst 1 and 2 in the energy regions.

Fig. 10 FESEM mapping images of catalyst 2.

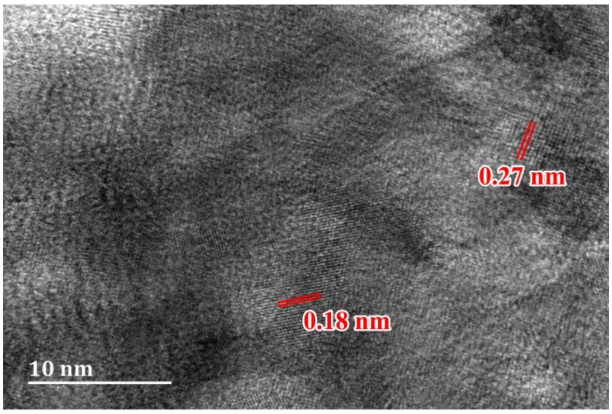


Fig. S11 High-resolution TEM images of catalyst 2.

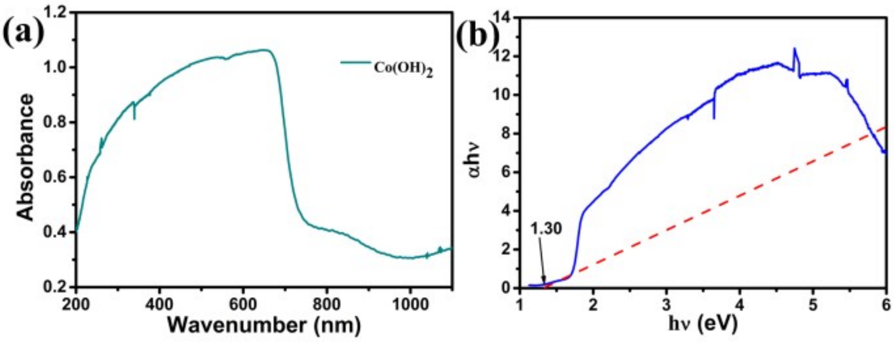


Fig. S12 (a) UV-vis absorption spectra of $Co(OH)_2$. (b) (αhν) r versus hν curve of $Co(OH)_2$.

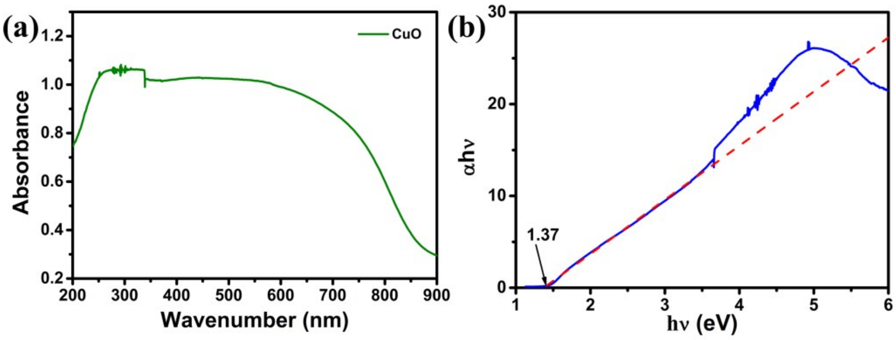


Fig. S13 (a) UV-vis absorption spectra of CuO. (b) (αhν) r versus hν curve of CuO.

Table S1 data of samples.

sample	Cu (ppm)	Co (ppm)	$n_{Cu} : n_{Co}$	loading weight (mg/mg catalyst)	S_{BET} (m^2·g^{-1})
Cu-Co PBA	6237.5	2549.7	2.3		-
Catalyst 1	21802.5	271.5	74.5	0.01546	21.3575
Catalyst 2	21798.7	272.7	74.1	0.01554	26.9158

Water oxidation by $Co(OH)_2$/ CuO

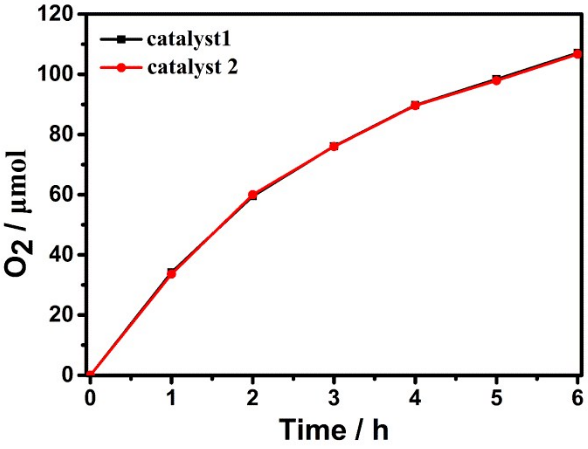


Fig. S14 Kinetics of O_2 evolution of the photocatalytic system using different catalysts. Reaction condition: NaOH solution: 0.10 M, 10 mL; catalyst: 2.05mg; $Na_2S_2O_8$: 40 mM; vigorous stirring at RT.

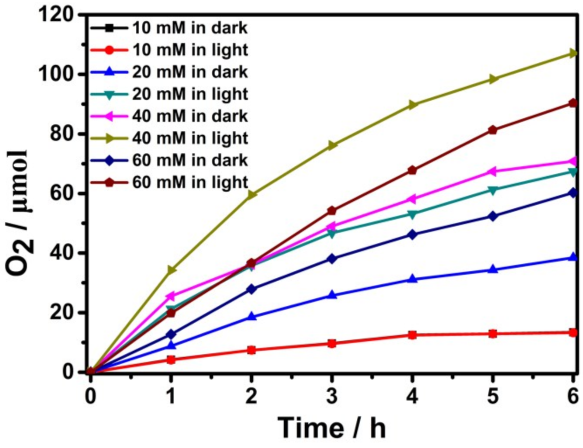


Fig. S15 Kinetics of O_2 evolution of the photocatalytic system using catalyst 1with different concentration of $Na_2S_2O_8$. Reaction condition: NaOH solution: 0.10 M, 10 mL; Cu-Co PBA: 5 mg; vigorous stirring at RT.

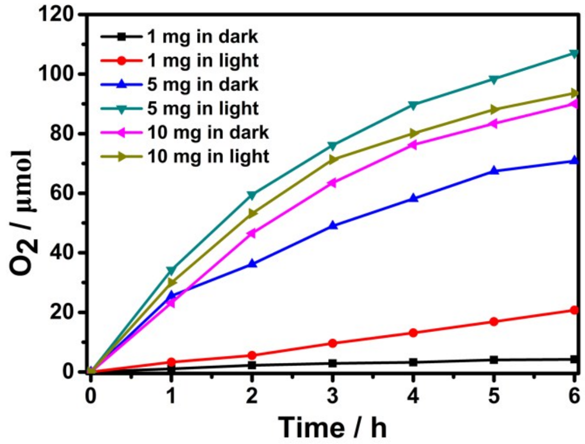


Fig. S16 Kinetics of O_2 evolution of the photocatalytic system using different amount of catalyst 1. Reaction condition: NaOH solution: 0.10 M, 10 mL; $Na_2S_2O_8$: 40 mM; vigorous stirring at RT.

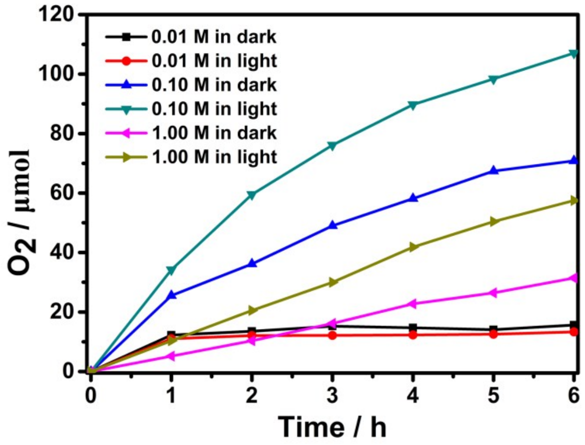


Fig. S17 Kinetics of O_2 evolution of the photocatalytic system using different concentration of NaOH solution. Reaction condition: NaOH solution: 10 mL; Cu-Co PBA: 5 mg; $Na_2S_2O_8$: 40 mM; vigorous stirring at RT.

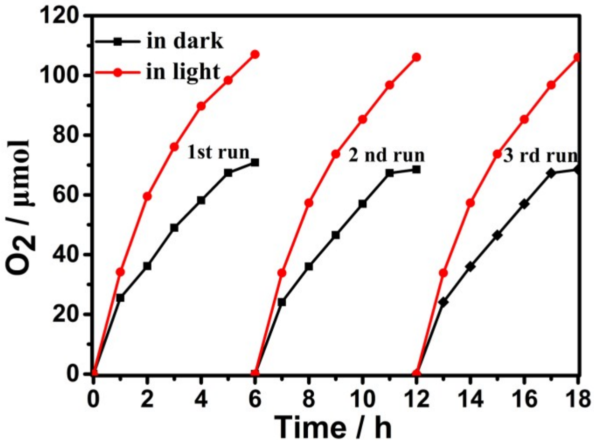


Fig. S18 The reuse of catalyst 1of water oxidation reaction. Reaction condition: NaOH solution: 0.10 M, 10 mL; Cu-Co PBA: 5 mg; $Na_2S_2O_8$: 40 mM; vigorous stirring at RT.

Calculation

According to the data of XRF, the average molecular weight of $Co(OH)_2/CuO$ was 79.4 g/mol.

AR (the photic area of reactor) = d·h = 2×3.5 cm^2 = 7.0 cm^2

E = 52.8 $mW·cm^{-2}$

The number of incident photos (N)

$$N = \frac{E\lambda}{hc} = \frac{52.8 \times 10^{-3} \times 7 \times 3600 \times 6 \times 420 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 1.69 \times 10^{22}$$

Optimal reaction condition:

NaOH solution: 0.10 M; Cu-Co PBA: 5 mg; $Na_2S_2O_8$: 40 mM.

The total TON:

$$TON = \frac{Number\ of\ reacted\ electrons}{Number\ of\ reacted\ electrons}$$

$$= \frac{4 \times 107.07 \times 10^{-6} \times 6.02 \times 10^{23}}{\left(2.05 \times 10^{-3} / 79.4\right) \times 6.02 \times 10^{23}}$$

$$= 16.6$$

Deduction of the effect of chemocatalytic activities:

$$\mathrm{TON} = \frac{Number\ of\ reacted\ electrons}{Number\ of\ reacted\ electrons}$$

$$= \frac{4 \times (107.07 - 70.84) \times 10^{-6} \times 6.02 \times 10^{23}}{\left(2.05 \times 10^{-3}/_{79.4}\right) \times 6.02 \times 10^{23}}$$

$$= 5.6$$

$$\mathrm{QY}\ \% = \frac{4 \times Number\ of\ evolved\ O2\ molecules}{Number\ of\ incident\ photons} \times 100$$

$$= \frac{4 \times (107.07 - 70.84) \times 10^{-6} \times 6.02 \times 10^{23}}{1.69 \times 10^{22}} \times 100$$

$$= 0.52\%$$

NaOH solution: 0.10 M; Cu-Co PBA: 5 mg; $Na_2S_2O_8$: 20 mM.

The number of incident photos (N)

λ = 420 nm

$$N = \frac{E\lambda}{hc} = \frac{52.8 \times 10^{-3} \times 7 \times 3600 \times 6 \times 420 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 1.69 \times 10^{22}$$

$$\mathrm{QY}\ \% = \frac{4 \times Number\ of\ evolved\ O2\ molecules}{Number\ of\ incident\ photons} \times 100\%$$

$$= \frac{4 \times (46.03 - 38.44) \times 10^{-6} \times 6.02 \times 10^{23}}{1.69 \times 10^{22}} \times 100\%$$

$$= 0.108\%$$

λ = 500 nm

$$N = \frac{E\lambda}{hc} = \frac{52.8 \times 10^{-3} \times 7 \times 3600 \times 6 \times 500 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 2.01 \times 10^{22}$$

$$\mathrm{QY}\ \% = \frac{4 \times Number\ of\ evolved\ O2\ molecules}{Number\ of\ incident\ photons} \times 100\%$$

$$= \frac{4 \times (47.53 - 38.44) \times 10^{-6} \times 6.02 \times 10^{23}}{2.01 \times 10^{22}} \times 100\%$$

$$= 0.109\%$$

λ = 765 nm

$$N = \frac{E\lambda}{hc} = \frac{52.8 \times 10^{-3} \times 7 \times 3600 \times 6 \times 765 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 3.08 \times 10^{22}$$

$$QY\ \% = \frac{4 \times Number\ of\ evolved\ O2\ molecules}{Number\ of\ incident\ photons} \times 100\%$$

$$= \frac{4 \times (43.36 - 38.44) \times 10^{-6} \times 6.02 \times 10^{23}}{3.08 \times 10^{22}} \times 100\%$$

$$= 0.038\%$$

Photon flux (I_0)

$$I_0 = \frac{E\lambda}{hc} = \frac{52.8 \times 10^{-3} \times 420 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 1.1156 \times 10^{17}\ \mathrm{mol \cdot s^{-1} \cdot cm^{-2}}$$

$$= 4.016 \times 10^{20}\ \mathrm{mol \cdot h^{-1} \cdot cm^{-2}}$$

$$= \frac{4.016 \times 10^{20}}{6.022 \times 10^{23}} \times 10^{6}\ \mu\mathrm{einstein \cdot h^{-1}}$$

$$= 6.6689 \times 10^{2}\ \mu\mathrm{einstein \cdot h^{-1}}$$

Deduction of the effect of chemocatalytic activities:

$$rate = \frac{46.03 - 38.44}{6}\ \mu\mathrm{mol \cdot h^{-1}} = 1.265\ \mu\mathrm{mol \cdot h^{-1}}$$

$$\zeta p = \frac{rate}{I_0} = \frac{1.265}{6.6689 \times 10^{2}} \times 100\% = 0.21\%$$

To prove the authenticity of the data, we used two different models of GC to obtain working curve using external standard and detect oxygen in the air. The air sample was 100 μL .The basic parameters of the two GC are shown in Table S2. Table S3 was showed the working curve and peak area of oxygen from the two GC.

Table S2 Main parameters of gas chromatography.

Instrument model	Chromatographic column	Carrier gas	Carrier gas flow rate	Column temperature	Bridge current
Shimadzu GC-14B	5Å molecular sieve column (2 m × 4 mm)	Ar	20 mL/min	30 °C	85 mA
Shimadzu GC-2014C	5Å molecular sieve column (2 m × 4 mm)	Ar	20 mL/min	50 °C	70 mA

Table S3 oxygen detected by different two GC.

Instrument model	Working curve	Peak area of O_2	O_2 (μmol)
Shimadzu GC-14B	Y=979.89X+529.18 (R^2=0.9972)	110628.9	113.36
Shimadzu GC-2014C	Y=385.62X+2495.71 (R^2=0.9961)	46211.0	112.36