

Electronic Supplementary Information for

Tuning the surface structure of Cu₂O@Pt for enhanced ethanol electrooxidation

Xiang Li^{a}, Junjun Zhang^b, Bo Xi^a, Yaming Liu,^c Changqing Jin,^a Xiaohua Feng,^a Ge Liu^a*

^aShaanxi Key Laboratory of Optoelectronic Functional Materials and Devices, School of Materials and Chemical Engineering, Xi'an Technological University, Xi'an, Shaanxi 710021, China.

^bState Key Laboratory of High-Efficiency Utilization of Coal and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan, Ningxia, 750021, China.

^cSchool of Textile Science and Engineering, Xi'an Polytechnic University, Xi'an, Shanxi 710048, China.

*To whom correspondence should be addressed. E-mail: lixiang@xatu.edu.cn

Experimental

Materials

Copper(II) acetate ($C_4H_6CuO_4$, 98%), Sodium dihydrogen phosphate anhydrous (NaH_2PO_4 , 99%), Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, 99%), Sodium hydroxide ($NaOH$, 98%), and Ethanol (C_2H_6O , 99.5%). All chemicals were purchased from Innochem.

Synthesis of the Cu/C nanoparticles

The sodium dihydrogen phosphate (700 mg), copper acetate (340 mg), and Carbon (Ketjen Black, EC-300J, 20 mg) were mixed into deionized water (10 mL). And then, the $NaOH$ (2 mL, 20 mg/mL) solution was dropped into the above mixed solution while stirring. Thirdly, the solution was transferred into teflon-lined stainless steel autoclave, which was placed in an oven maintained at 120 °C for 720 min. Finally, the products of Cu/C nanoparticles were collected via centrifugation with deionized water, and finally dispersed in deionized water (10 mL).

Synthesis of $Cu_2O@Pt/C$ nanoparticles with different contents of Pt atoms.

The above Cu/C nanoparticles dispersed in the deionized water solution (10 mL) were firstly transferred to a stirring platform, and then the different amounts of precursors of chloroplatinic acid (12.5, 25, 50 mg) dispersed in the deionized water solution (5 mL) were added drop by drop at room temperature. After the dripping, the mixture solution was stirred for 12 hours. Finally, the products were collected via centrifugation with deionized water, and dispersed in deionized water (10 mL).

Preparation of the working electrodes and electrochemical measurements

Firstly, the $Cu_2O@Pt/C$ nanocatalysts (12.0 mg) with different compositions of Pt atoms were dispersed in a mixture of 2 mL of deionized water, 2 mL of isopropanol, and 80 μL of 5% Nafion. Then, 20 μL of the suspension was deposited on glassy carbon RDE (0.196 cm^2). And thus, the loading amount of total $Cu_2O@Pt$ nanocatalyst was 6 μg or 30.6 $\mu g\ cm^{-2}$. Secondly, electrochemical experiments were conducted on CHI 660E electrochemical working station (CH Instruments, Inc.) using a three-electrode configuration at 25 °C. A leak-free $Ag/AgCl$ (3M) and a Pt sheet (1 \times 1 cm^2) were used as reference electrode and counter electrode, respectively. All potentials were converted to values with reference to a reversible hydrogen electrode (RHE). The cyclic voltammetry (CV) curves were recorded at 25 °C (0.5 M H_2SO_4 solution, 50

mV s⁻¹). For the electrooxidation of ethanol, the CV curves were recorded at 0.5 M H₂SO₄ + 1 M C₂H₅OH solution (0.05 to 1.2 V, 50 mV s⁻¹). The electrochemical active surface areas (ECSAs) were obtained by the charges associated with the reduction peaks of hydrogen adsorption charge (210 μC cm⁻²).

Characterizations

Transmission electron microscopy characterizations were performed at FEI Talos-F200S. Powder XRD patterns were recorded at D8 DISCOVER A25 Burker. XPS analyses were performed at Kratos Ultra DLD spectrometer. Inductively-coupled plasma mass spectrometry was performed at Agilent 7800.

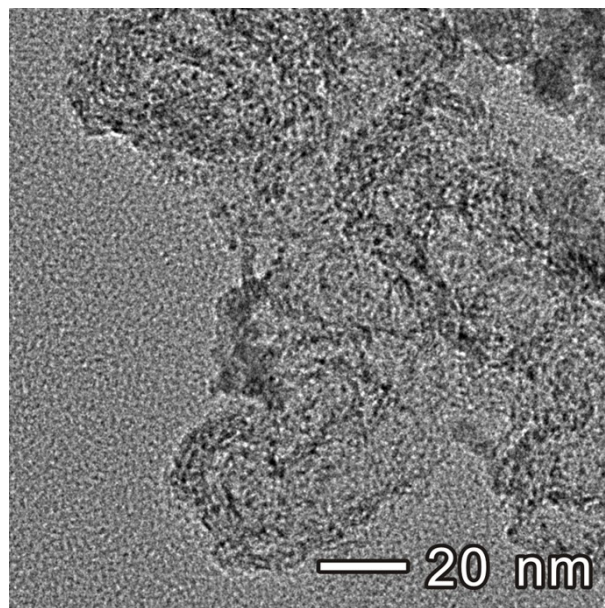


Figure S1. TEM image of the as prepared Cu/C nanoparticles.

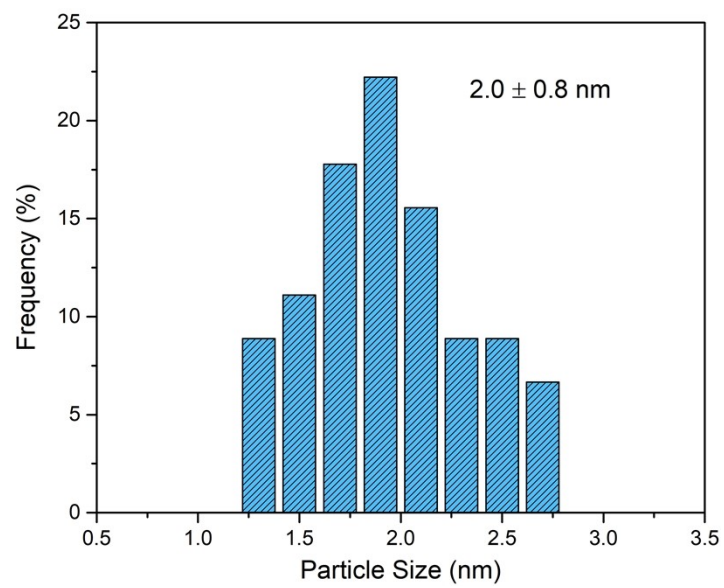


Figure S2. Size distribution of the as prepared Cu/C nanoparticles.

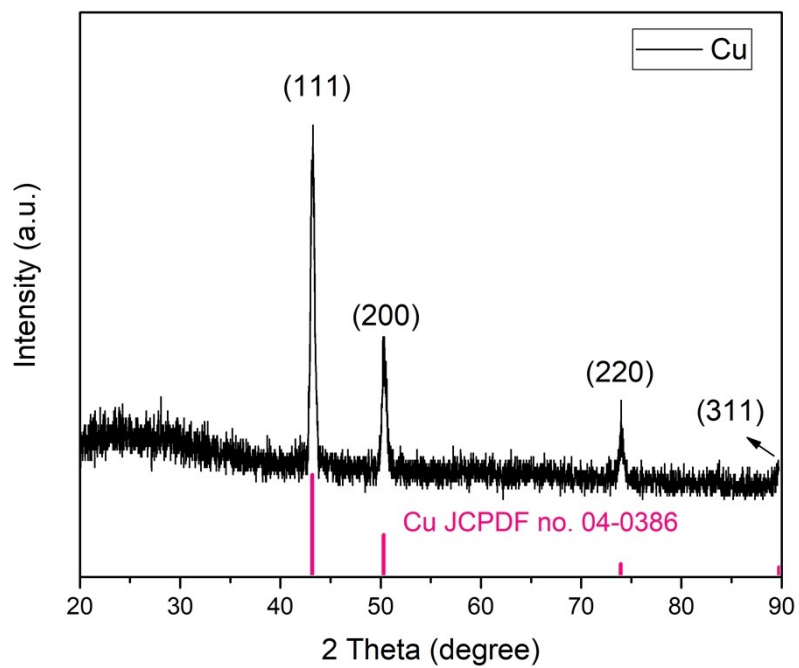


Figure S3. The XRD pattern of the as prepared Cu/C nanoparticles.

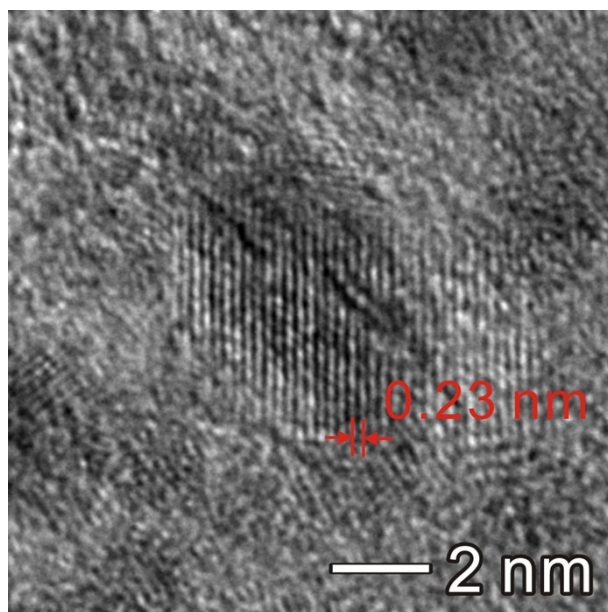


Figure S4. The HRTEM characterizations of Cu₂O@Pt_{0.24}/C nanoparticles.

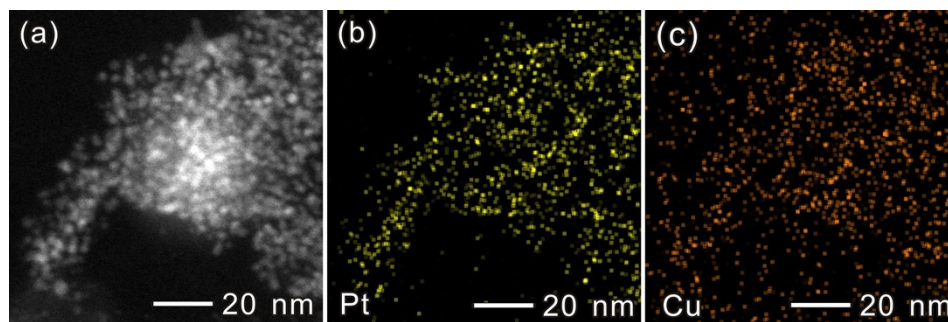


Figure S5. The TEM characterizations of $\text{Cu}_2\text{O}@\text{Pt}_{0.07}/\text{C}$ nanoparticles. (a) HAADF-STEM image. (b,c) EDX-Mapping images of Pt and Cu.

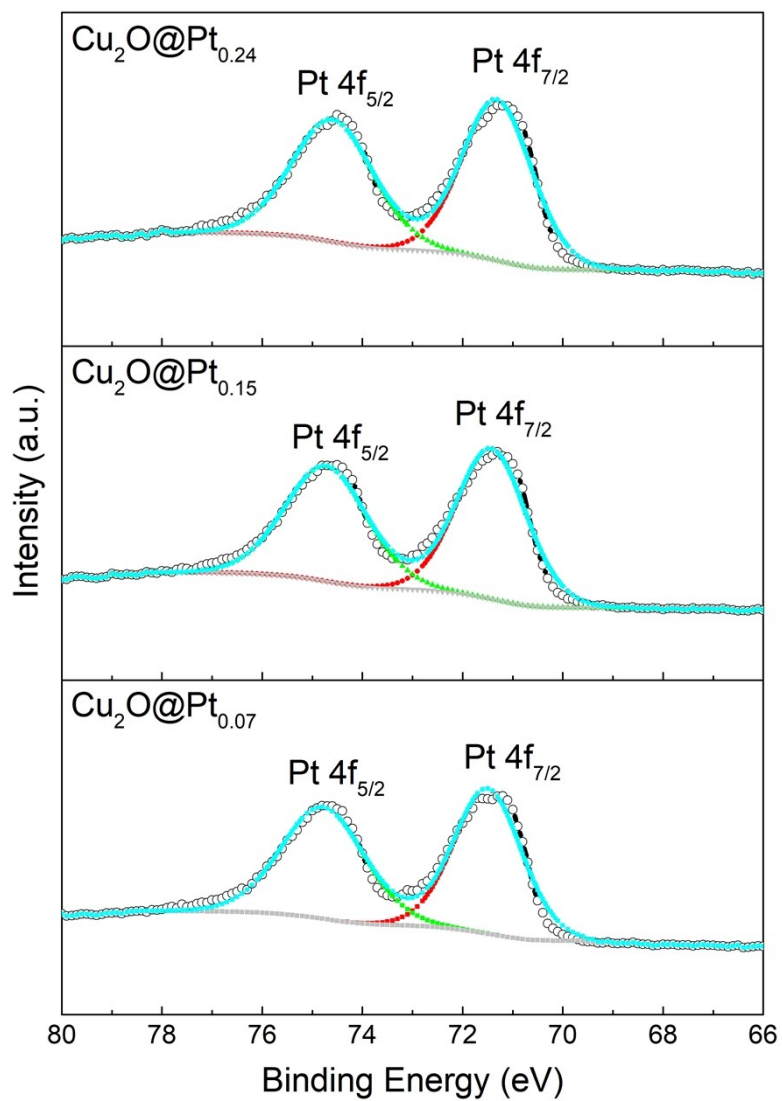


Figure S6. The XPS characterizations of Pt 4f core levels for $\text{Cu}_2\text{O}@Pt/C$ nanoparticles with different contents of Pt atoms.

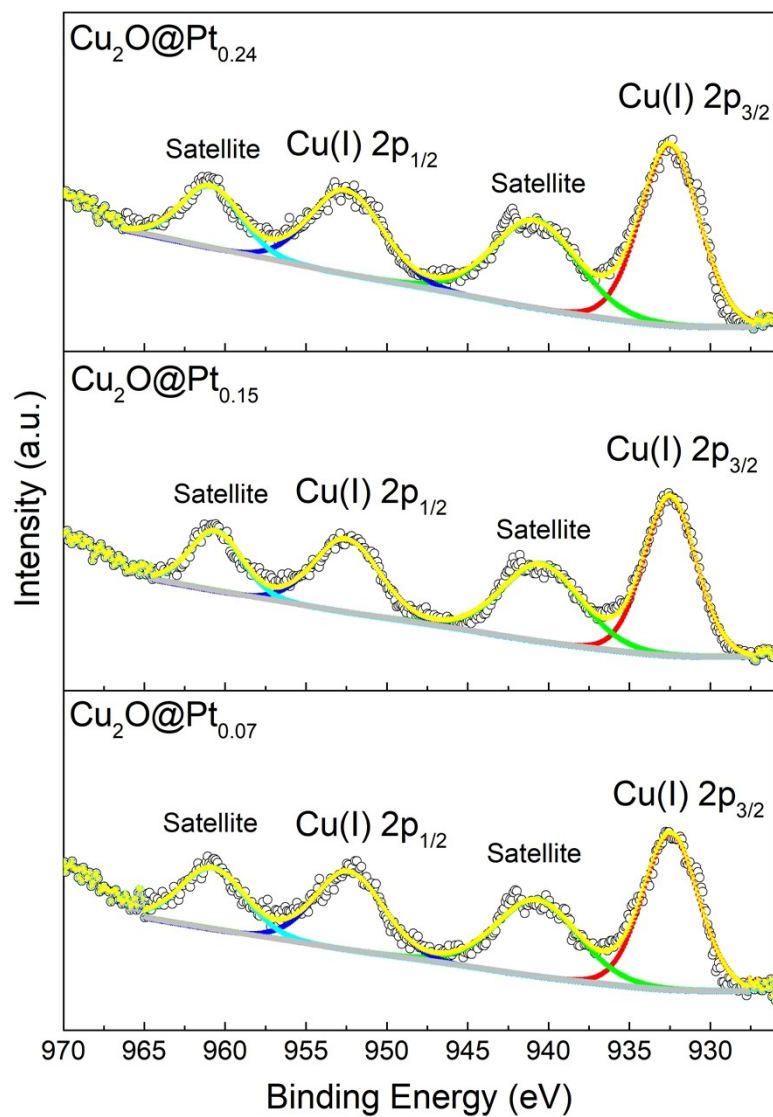


Figure S7. The XPS characterizations of Cu(I) 2p core levels for Cu₂O@Pt/C nanoparticles with different contents of Pt atoms.

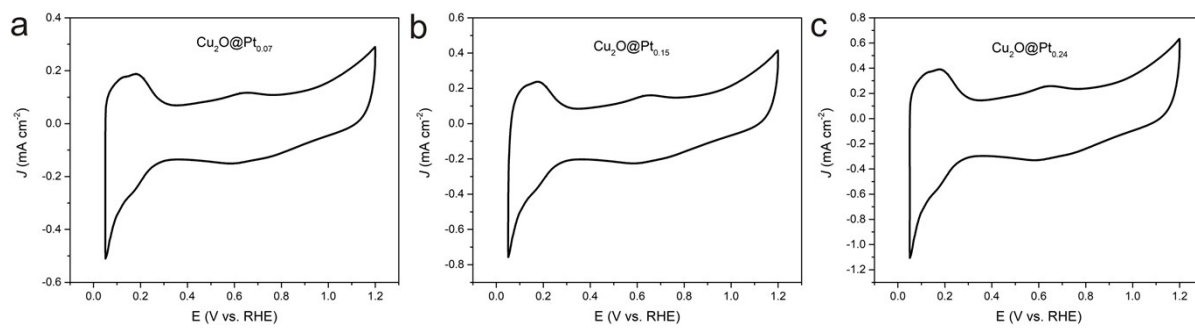


Figure S8. Cyclic voltammetry curves of $\text{Cu}_2\text{O}@Pt/C$ nanoparticles with different contents of Pt atoms in N_2 -saturated H_2SO_4 (0.5 M) solution at a scanning rate of 50 mV s^{-1} .

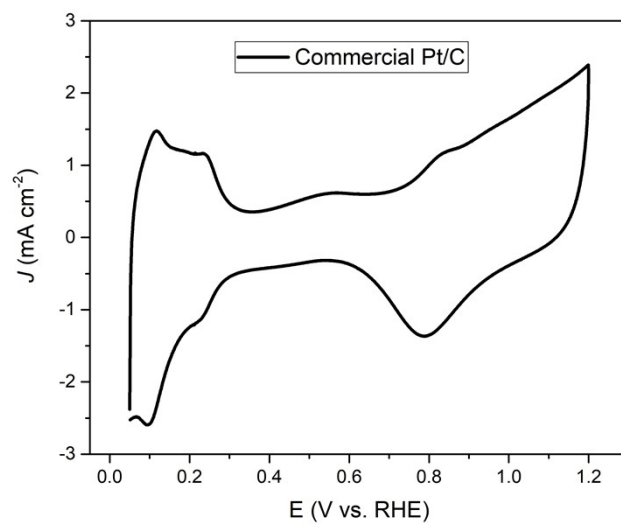


Figure S9. Cyclic voltammety curves of commercial Pt/C catalyst in N_2 -saturated H_2SO_4 (0.5 M) solution at a scanning rate of 50 mV s^{-1} .

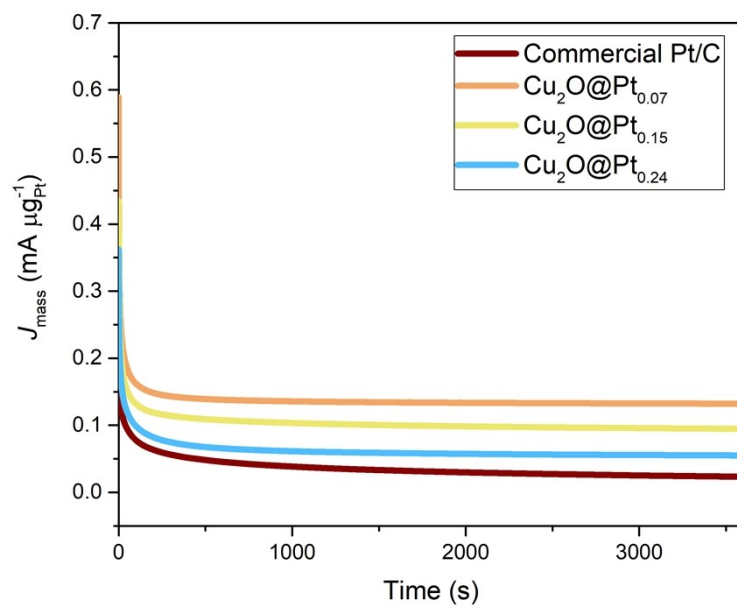


Figure S10. Chronoamperometry curves of $\text{Cu}_2\text{O}@Pt/C$ nanoparticles and commercial Pt/C catalyst at the highest current (vs. RHE) in N_2 -saturated $\text{CH}_3\text{CH}_2\text{OH}$ (1 M) + H_2SO_4 (0.5 M) solution.

Table S1. The metal ratios (Cu/Pt) of Cu₂O@Pt/C nanoparticles with different contents of Pt atoms which are determined by ICP-MS.

Sample	M(Pt)	M(Cu)	n(Cu)/n(Pt)
1	6.3 mg	30.6 mg	1:0.07
2	32.7 mg	70.3 mg	1:0.15
3	46.7 mg	64.8 mg	1:0.24

Table S2. The metal loadings of the Cu₂O@Pt/C nanoparticles with different contents of Pt atoms and commercial Pt/C catalyst on electrode which are determined by ICP-MS.

Sample	Cu ₂ O@Pt _{0.07}	Cu ₂ O@Pt _{0.15}	Cu ₂ O@Pt _{0.24}	Commercial Pt/C
Pt (ug)	1.0	1.9	2.5	6
Cu (ug)	5.0	4.1	3.5	0

Table S3. Specific ECSAs of the Cu₂O@Pt/C nanoparticles with different contents of Pt atoms and the commercial Pt/C catalyst.

Sample	Cu ₂ O@Pt _{0.07}	Cu ₂ O@Pt _{0.15}	Cu ₂ O@Pt _{0.24}	Commercial Pt/C
ECSA (m ² /g)	36.3	32.2	29.8	55.4

Table S4. The EOR performances of the Cu₂O@Pt/C nanoparticles with different contents of Pt atoms and the commercial Pt/C catalyst.

Catalysts	J_{mass} (mA ug _{Pt} ⁻¹)	J_{specific} (mA cm ⁻²)
Commercial Pt/C	0.218	0.39
Cu ₂ O@Pt _{0.07}	0.611	1.68
Cu ₂ O@Pt _{0.15}	0.509	1.58
Cu ₂ O@Pt _{0.24}	0.386	1.30

Table S5. The comparison of EOR performances of the core-shell Pt-based catalysts.

Catalysts	J_{mass} (mA $\mu\text{g}_{\text{Pt}}^{-1}$)	J_{specific} (mA cm^{-2})	References
$\text{Cu}_2\text{O}@Pt_{0.07}$	0.611	1.68	This work
$\text{SnO}_2@Pt$	0.26	-	<i>Appl. Catal. B: Environ.</i> , 2010, 99, 265-271
$\text{Pt}_{46}@(SnO_2)_{54}$	-	0.5	<i>J. Am. Chem. Soc.</i> , 2014, 136, 10862-10865
$\text{FeP}@PtRh$	0.653	0.92	<i>Nanoscale</i> , 2019, 11, 18866-18873.
$\text{Cu}@Pt$	0.75	0.55	<i>Int. J. Hydrogen Energy</i> , 2014, 39, 11547-11556.
$\text{Rh}@Pt$	0.86	2.62	<i>J. Mater. Chem. A</i> , 2019, 7, 17987-17994.
$\text{Ru}@Pt$	1.8	4.21	<i>ACS Sustainable Chem. Eng.</i> , 2019, 7, 9007-9016.
$\text{Pd}@PdPt$	3.225	3.449	<i>ACS Appl. Nano Mater.</i> , 2023, 6, 10213-10222.
$\text{PtPb}@PtIr$	5.91	7.53	<i>Small</i> , 2022, 18, 2202587.

Table S6. The metal ratios (Cu/Pt) of Cu₂O@Pt/C nanoparticles before and after the stability tests which are determined by ICP-MS.

Sample	n(Cu) / n(Pt)	
	Before	After
Cu ₂ O@Pt _{0.07}	1:0.07	1:0.13
Cu ₂ O@Pt _{0.15}	1:0.15	1:0.19
Cu ₂ O@Pt _{0.24}	1:0.24	1:0.28