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Pt-Cu Bimetallic Electrocatalysts with Enhanced Catalytic Properties for Oxygen Reduction

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1. Experimental details

1.1 Materials and characterization

Carbon black VXC-72R was purchased from Cabot Corporation and treated with nitric acid (65.0 ~ 68.0 wt%) at 70 °C for 1h before using as a support. The following commercial chemicals including Nafion® solution (5 wt%, purchased from Aldrich), a carbon supported Pt catalyst (Pt/C-JM, Pt: 9.4 wt %, supplied by Johnson Matthey Company), melamine (purity: 99%, supplied by Alfa Aesar), H₂PtCl₆·6H₂O (Sinopharm Chemical Reagent Beijing Co.ltd), Cu(CH₃COO)₂·H₂O (Beijing Yili Chemical Corp), ethylene glycol (Xilong Chemical Corp) and HClO₄ (GR grade, Tianjin Xinyuan Chemical Corp) were used as received.

TEM photographs were taken on a FEI Tecnai G²F20 instrument. XRD patterns were recorded by a Rigaku-2500Pc diffractometer with monochromatic Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$) at an accelerating voltage of 40 kV and a tube current of 300 mA. Inductively coupled plasma atomic emission spectrometry (ICP-AES, Leeman Corp.) was used to analyze the metal contents of PtCu/MMC and PtCu/C. The content of N in MMC was analyzed by elemental analysis (Elementar vario MICRO CUBE, vario EL, Elementar Analysensysteme, Germany). The IR absorption spectrum was carried out on FTIR (Vector 22, Bruke Corp.). XPS measurements were carried out

with an Axis Ultra photoelectron spectrometer with a monochromatic AlK_{α} X-ray (1486.7 eV) source. The binding energies of MMC were referenced to the C 1s (graphite) binding energy at 284.5 eV and melem prepared in this work was referenced to the C 1s binding energy of contamination carbon at 284.8 eV. Electrochemical tests of the prepared electrodes were conducted using a Model CHI 660C workstation.

1.2 Synthesis of MMC and Melem

Melamine (100 mg) was dissolved in ultrapure water (100 mL). VXC-72R (400 mg) was dispersed in the aqueous solution of melamine by ultrasonication for 30 minutes. Then, water in the mixture was removed at 130 °C and the obtained solid was heated at 340 °C for 1 h in a muffle furnace. The obtained product was washed with ultra pure water and acetonitrile and then dried at 70 °C for 1 h in a vacuum oven to obtain MMC. The content of nitrogen in MMC was 4.4 wt%. Melem was prepared with the similar method by heating melamine in the absence of VXC-72R.

1.3 PtCu/MMC Synthesis

The ethylene glycol (EG) solution (40 ml) of $Cu(CH_3COO)_2 \cdot H_2O$ (26.5 mg) was mixed with an EG solution (1.4 mL) of $H_2PtCl_6 \cdot 6H_2O$ (31.1 mg), followed by adjusting the pH to 10 by adding an EG solution of NaOH (0.25 M). The mixture was dropped into the suspension of MMC (86.5 mg) which had been dispersed in EG (80 mL). The mixture was then heated to 198 °C and maintained for 4 h under N_2 atmosphere. After cooling to room temperature, the mixture was filtered and the solid product was washed by water and ethanol. Then the product was dried at 70 °C for 1 h in a vacuum oven to obtain PtCu/MMC. PtCu/C was prepared by the same method with VXC-72R as support.

1.4 Electrochemical Measurements

1.4.1 Preparation of working electrodes: The working electrodes were prepared as follows: PtCu/MMC or PtCu/C catalysts (10 mg), a Nafion® solution (100 μ L, 5 wt%) and C_2H_5OH (5 mL) were mixed ultrasonically for 20 minutes. The obtained suspension (20 μ L) was transferred onto a freshly polished glassy carbon disk electrode (0.196 cm^2) and dried at room temperature, the platinum loading in de-PtCu/MMC, de-PtCu/C, and Pt/C-JM electrode were 3.57, 3.68, and 3.68 μ g, respectively.

1.4.2 Electrochemical dissolution process: Rotating disk electrode (RDE)

measurements were performed in a conventional three-compartment electrochemical cell containing an aqueous solution of HClO₄ (0.1 M), in which a Ag/AgCl electrode was used as the reference electrode and a platinum foil was used as the counter electrode. All potentials in this work were relative to hydrogen electrode (RHE). The prepared catalysts were electrochemically etched to leach out Cu by cycling the potential between 0.05 and 1.2 V at a sweep rate of 100 mV s⁻¹ for 100 cycles in N₂-saturated HClO₄ solutions. The final CV profile reached a temporarily stable shape. The specific electrochemical surface area of catalyst (SESA, m² g⁻¹_{Pt}) was calculated from cyclic voltammograms by integrating the area in the hydrogen underpotential deposition (H_{UPD}) region.

1.4.3 Activity tests for catalysts: Oxygen reduction activities were measured at 1600 rpm and 30 °C in an aqueous solution of HClO₄ (0.1 M) by positive-going potential sweeps from 0.05 to 1.2 V versus RHE at a scan rate of 5 mV s⁻¹. ORR polarization curves were obtained from the difference of current densities between O₂ and N₂ atmosphere, ($i_{O_2-N_2} = i_{O_2} - i_{N_2}$).

The kinetic current density (i_k) was calculated based on the Koutecky-Levich equation:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \quad (1)$$

where i is the measured current and i_d is the diffusion-limiting current. i_k calculated from Eq. (1) was normalized to Pt loading on electrode and SESA to obtain mass and specific activity, respectively.

1.4.4 Accelerated aging tests (AAT) for catalysts: Potential scans were carried out between 0.6 and 1.1 V at 30 °C in an O₂-saturated aqueous solution of HClO₄ (0.1 M) under stirring. The electrochemical catalytic activities of the electrodes before and after AAT were evaluated by positive-going potential sweeps from 0.05 to 1.20 V versus RHE at a scan rate of 5 mV s⁻¹. The electrochemical surface areas of de-PtCu/MMC catalyst before and after AAT were measured as aforementioned method.

2 Characterization of melem, MMC and Pt-Cu catalysts

Elemental analysis of melem prepared by heating melamine in the absence of VXC-72R at 340 °C for 1 h in a muffle oven: found: C 32.96; N 63.87, H 2.75; calc. for C₆N₁₀H₆: C 33.03, N 64.22, H 2.75%. The differences between the calculated and measured data are reasonable.

Fig. S1 shows the IR absorption spectrum of melem prepared in this work, which is well coincident with the previously reported IR absorption spectrum of melem.¹ The absorption bands at 3111, 3356 and 3410 cm^{-1} are assigned to the stretching vibrations of NH_2 .^{1,2} The sharp peaks at 1616, 1483, and 802 cm^{-1} are the feature of cyameluric ring (melem ring).³ All of the results demonstrate that the main condensate of melamine under our experiment condition is melem.

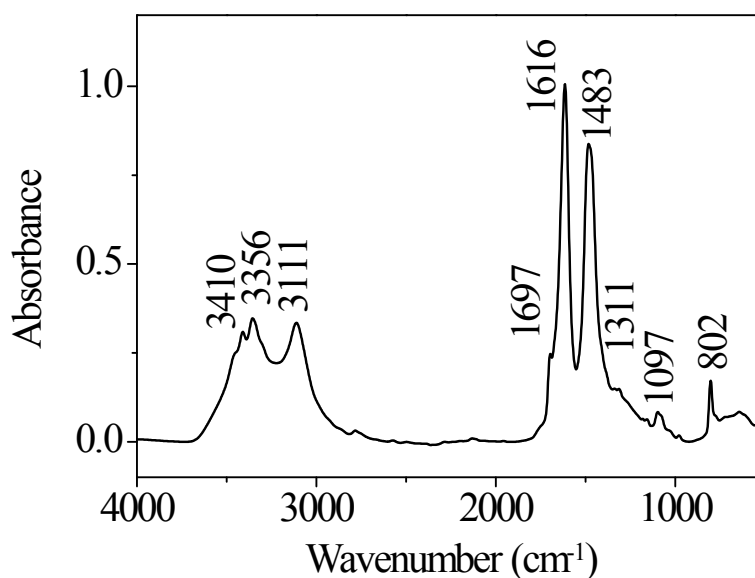


Fig. S1 The IR absorption spectrum of melem prepared in this work

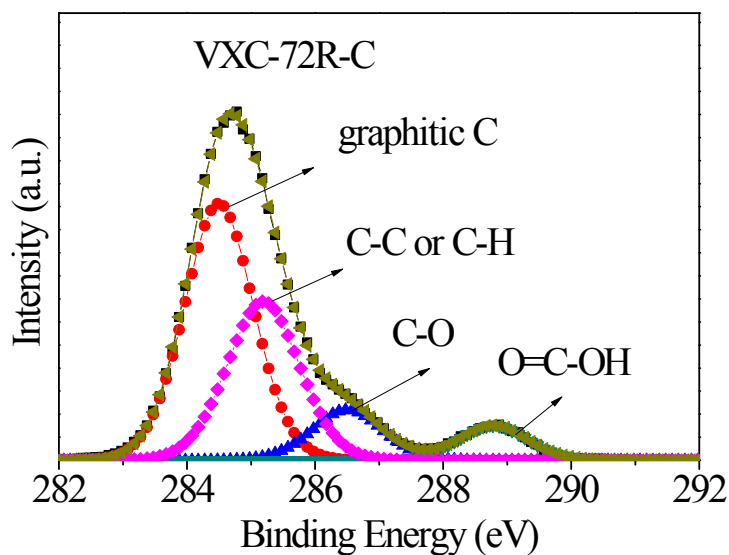


Fig. S2 The C 1s XPS spectrum of VXC-72R.

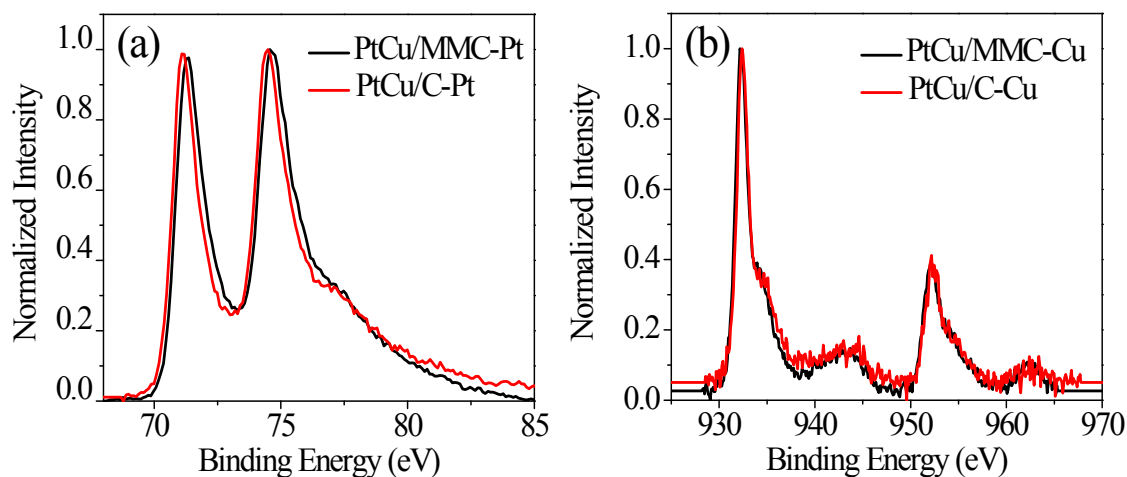


Fig. S3 XPS spectra of Pt 4f (a) and Cu 2p (b) in PtCu/MMC and PtCu/C.

The binding energies of Pt 4f_{7/2} and Cu 2p_{3/2} of 71.3 and 932.2 eV, respectively, indicated that Pt and Cu in the catalysts are present in a metallic state. Signals locating at 933.7 eV, originated from a small amount of oxidized copper species⁴ at the NPs' surfaces, were also observed because the samples were exposed to air before XPS measurements.

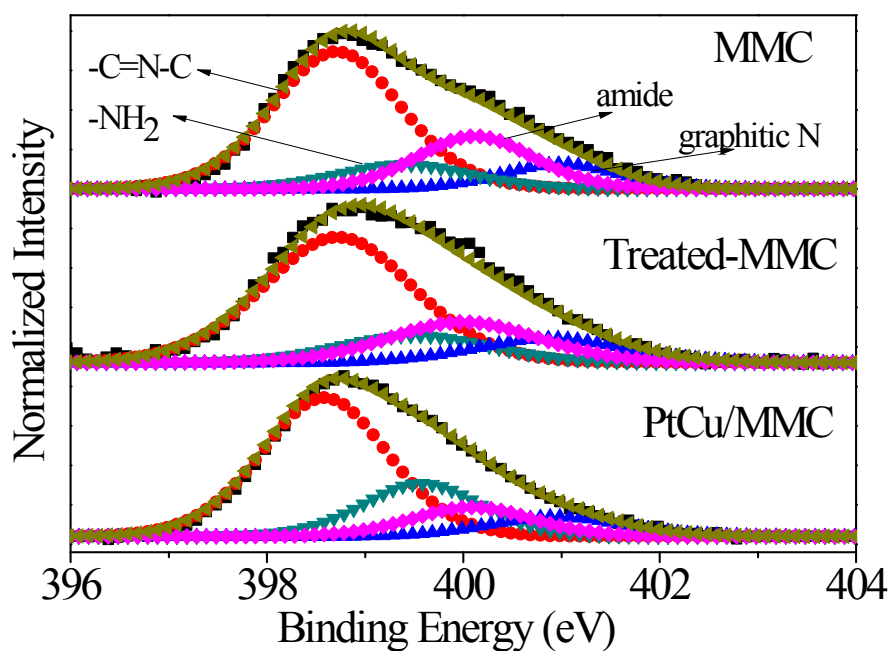


Fig. S4 XPS spectra of N 1s in MMC (Top), Treated-MMC (Middle) and PtCu/MMC (Bottom).

Fig. S4 shows the XPS spectra of N 1s in MMC, MMC treated with the same conditions as in the preparation of PtCu/MMC (Treated-MMC) and PtCu/MMC. The binding energies and relative ratios of the four fitting peaks (corresponding to -C=N-

C, -NH₂, amide and graphitic N species) are summarized in Table S1. The ratio of amino/amide in MMC is 11:21. Compared to the N 1s XPS spectrum of MMC, Treated-MMC shows a small decrease in the ratio of amide groups to amino groups, due to the alcoholysis of about 10% the amide groups of MMC with ethylene glycol (Table S1). As shown in Figure 2d, the peak shape of the N 1s XPS spectrum of PtCu/MMC is different from that of MMC or Treated-MMC, which were derived from the alcoholysis of about 50% of the amide groups of MMC with ethylene glycol as indicated by the curve fitting results shown in the Figure S4 and Table S1. It is obvious that the presence of Pt-Cu alloy NPs increased the ratio of alcoholized amide groups through the coordination interaction between melem or amino groups and the surface atoms of Pt-Cu NPs. Such an interaction would be propitious to produce supported Pt-Cu alloy NPs with small particle sizes and to suppress the aggregation of Pt-Cu alloy NPs during the preparation and catalytic processes.

Table S1 Binding energies and ratios of all kinds of nitrogen species in Fresh MMC, Treated MMC and PtCu/MMC

	-C=N-C		-NH ₂		Amide N		Graphitic N	
	Binding energy /eV	*Ratio %	Binding energy /eV	*Ratio %	Binding energy /eV	*Ratio %	Binding energy /eV	*Ratio %
Fresh MMC	398.7	59	399.4	11	400.1	21	400.9	10
Treated-MMC	398.7	58	399.4	13	400.1	18	400.9	11
PtCu/MMC	398.6	59	399.6	21	400.1	12	400.9	9

*Percentage of nitrogen of the corresponding species.

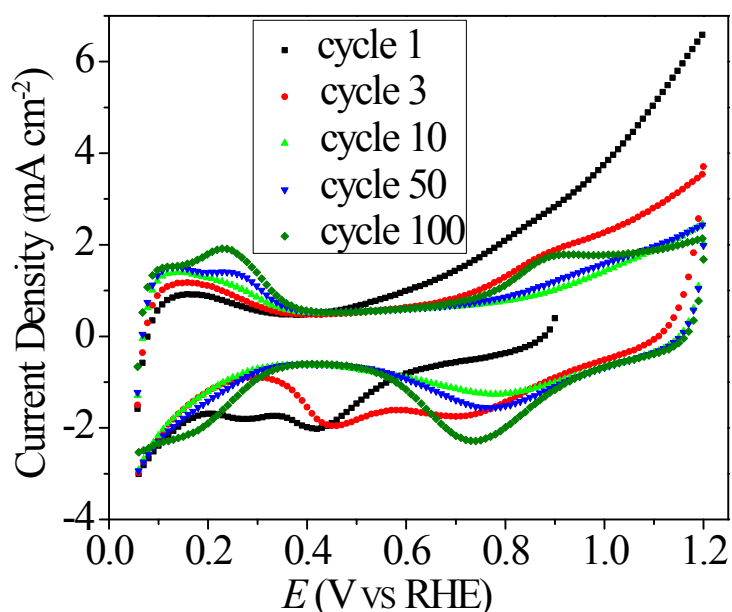


Fig. S5 Etching process for PtCu/MMC

Fig. S5 shows the electrochemical etching process over PtCu/MMC. Cyclic voltammograms were performed between 0.05 V and 1.20 V at a sweep rate of 100 mV s^{-1} . The first cycle does not show the characteristic peaks associated with underpotentially deposited hydrogen on platinum surfaces between 0.05 and 0.4 V, due to a low atomic ratio of Pt to Cu (24:76 as measured by EDX). The oxidation current signal appeared around 0.4 to 1.2 V indicates the dissolution of Cu. With further cycles, the oxidation current intensity of Cu decreased as the surfaces of the bimetallic particles became enriched with Pt, as indicated by the growth of hydrogen adsorption/desorption peaks in the range from 0.05 to 0.4 V. After about 100 cycles, the CV reached a steady state with the characteristic features of a Pt/C catalyst (Fig. 3a), including the familiar hydrogen adsorption/desorption peaks as well as the Pt oxides formation and reduction peaks at 0.88 and 0.74 V on the anodic and cathodic scan, respectively, indicating that Cu dissolution from the NPs surface had either ceased or dropped to undetectable levels and Pt-enriched surfaces formed after the electrochemical etching process of PtCu/MMC.

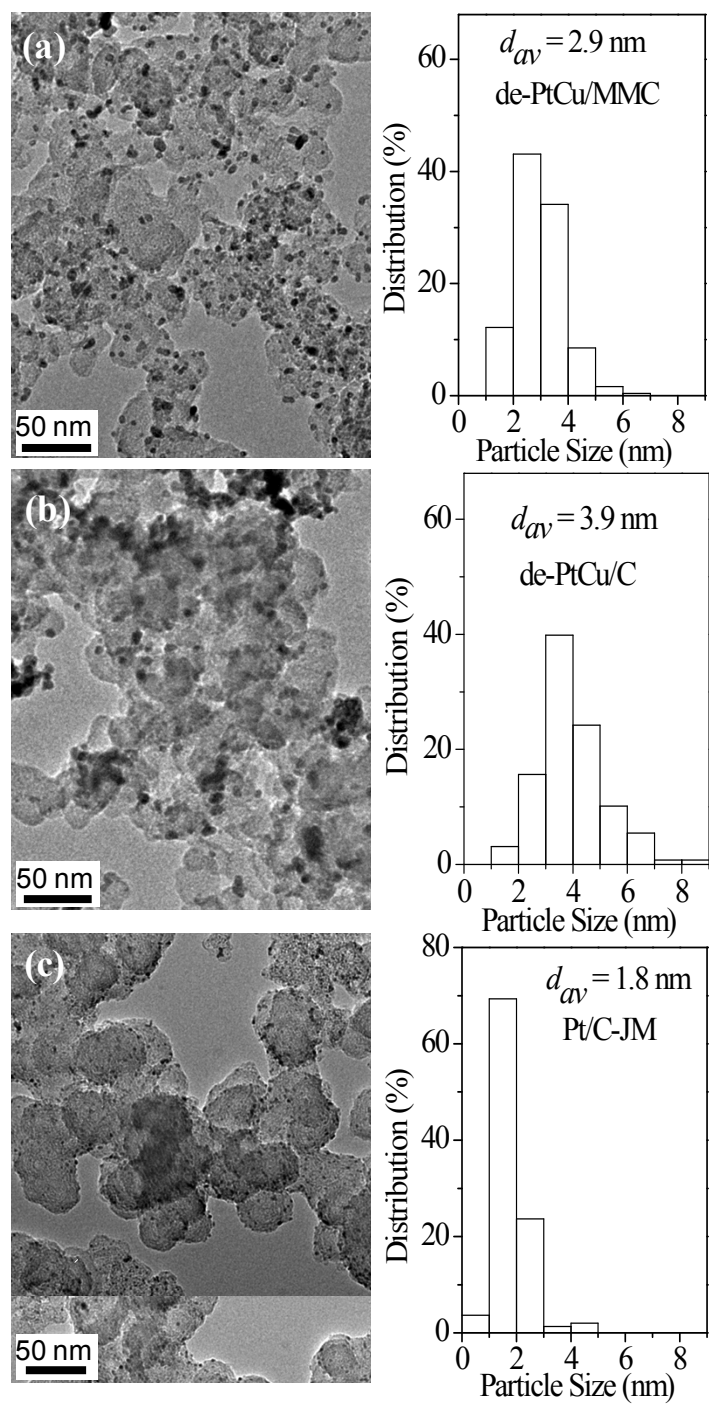


Fig. S6 TEM images and size distributions of de-PtCu/MMC (a), de-PtCu/C (b), and Pt/C-JM(c)

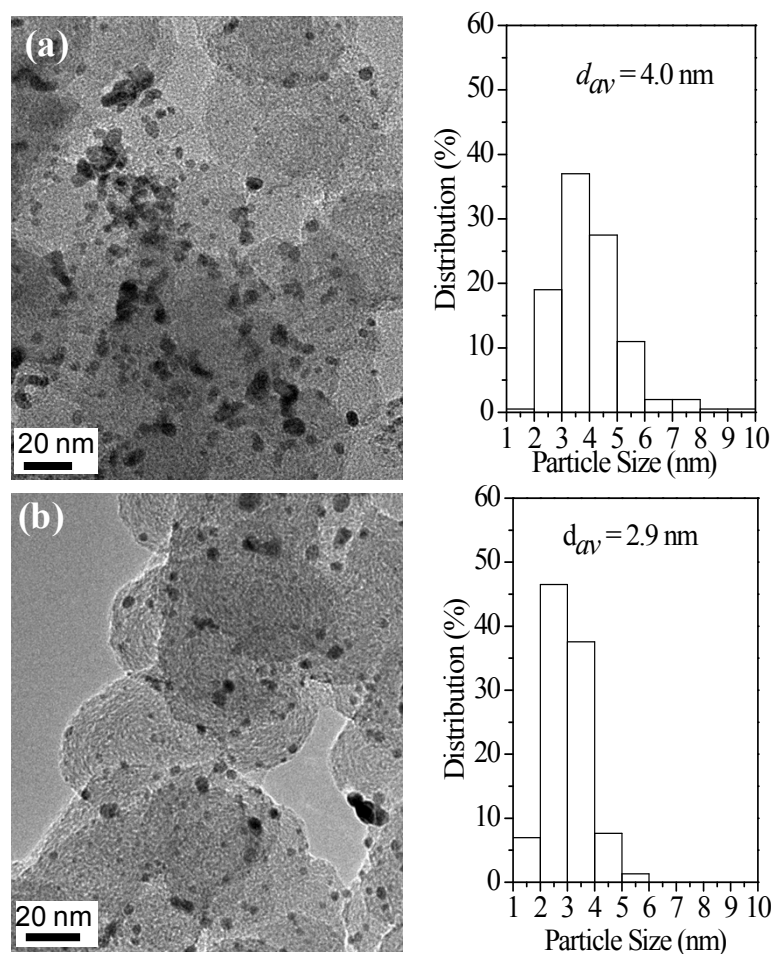


Fig. S7 TEM images and size distributions of Pt-Cu NPs in the de-PtCu/MMC electrode (a) and Pt/C-JM electrode (b) after AAT

Table S2 The atomic ratios of Pt and Cu of Pt-Cu NPs measured by EDX

Catalysts	Cu (at%)	Pt (at%)	Cu/Pt atomic ratio
PtCu/MMC	76	24	3.2
de-PtCu/MMC	23	77	0.30
de-PtCu/MMC after AAT	14	86	0.16

References

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