One-Pot Synthesis, Photoluminescence, and Electrocatalytic Properties of Subnanometer-Sized Copper Clusters

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0.025 g $CuNO_3$ + 0.136 g TOABr in 25 mL Absolute alcohol stirred at 80 ^{o}C for 30 min.

↓ Cooled + 0.0766g 2- mercapto -5-n- propylpyrimidine (MPP) Ar stream for 6 h.

↓ 0.047 g $NaBH_4$

Cluster product

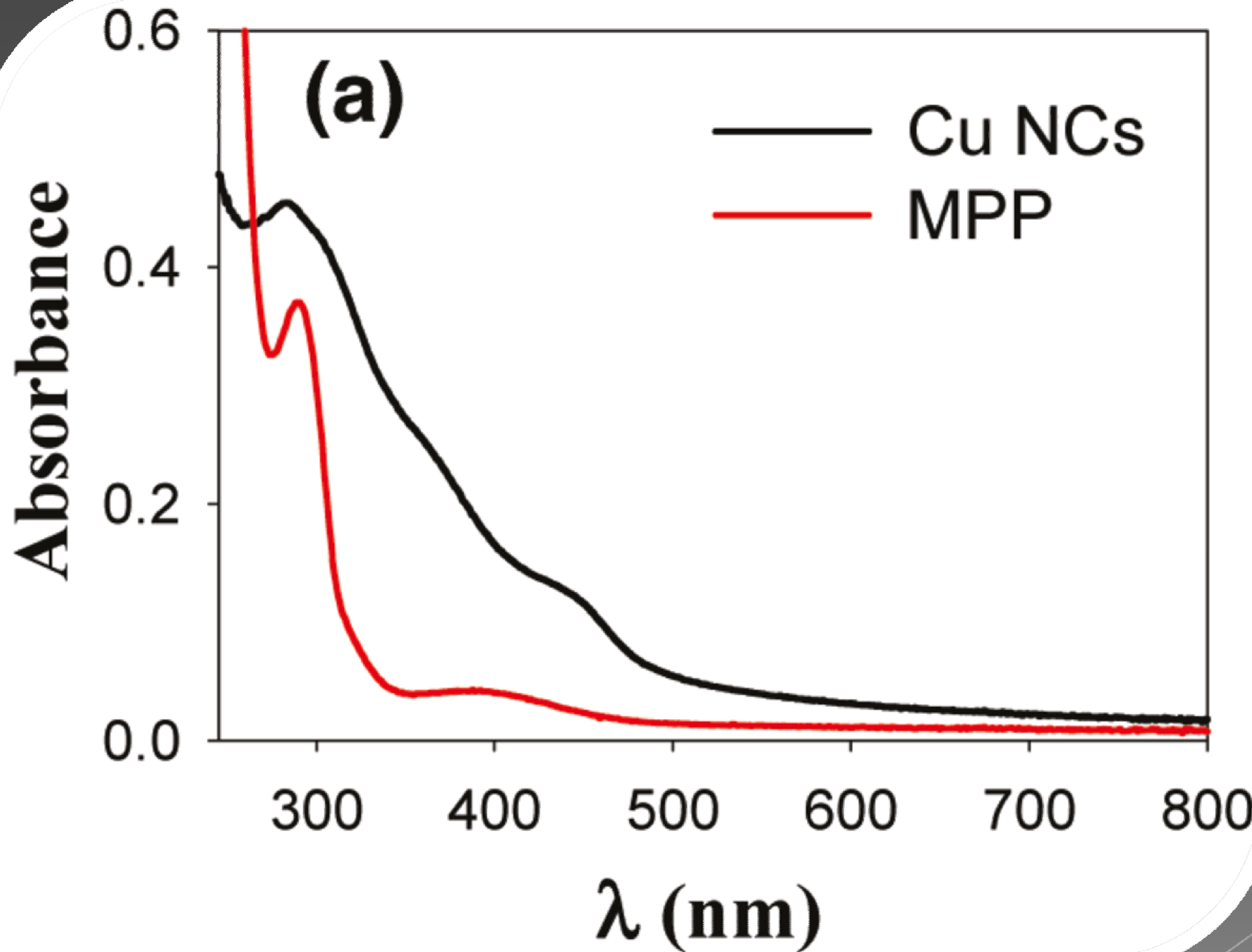


Figure 1. (a) UV-vis absorption spectra of the Cu nanoclusters and monomeric MPP in CHCl3.

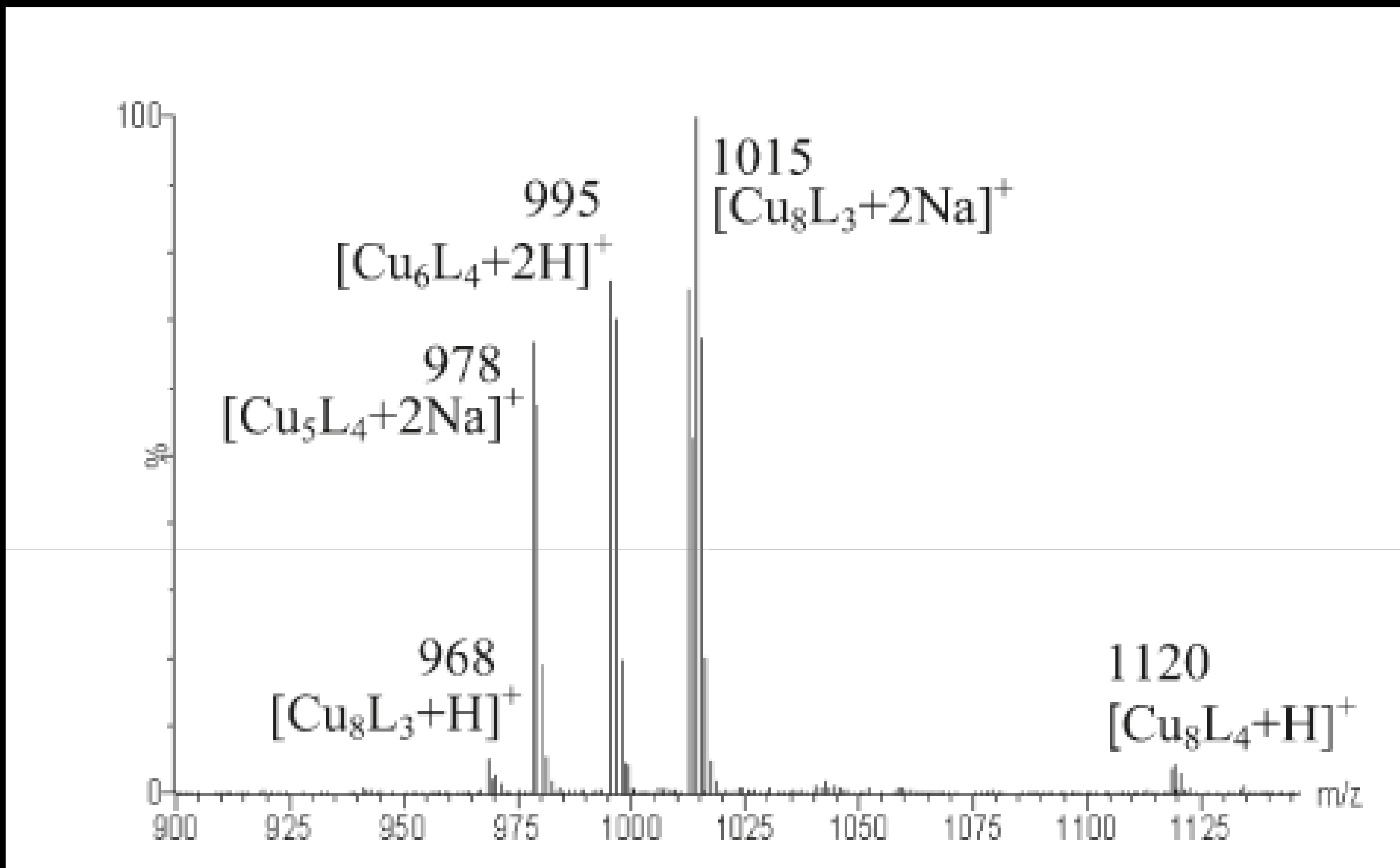


Figure 2. Representative ESI mass spectrum of a copper cluster sample detected in the positive-ion mode.

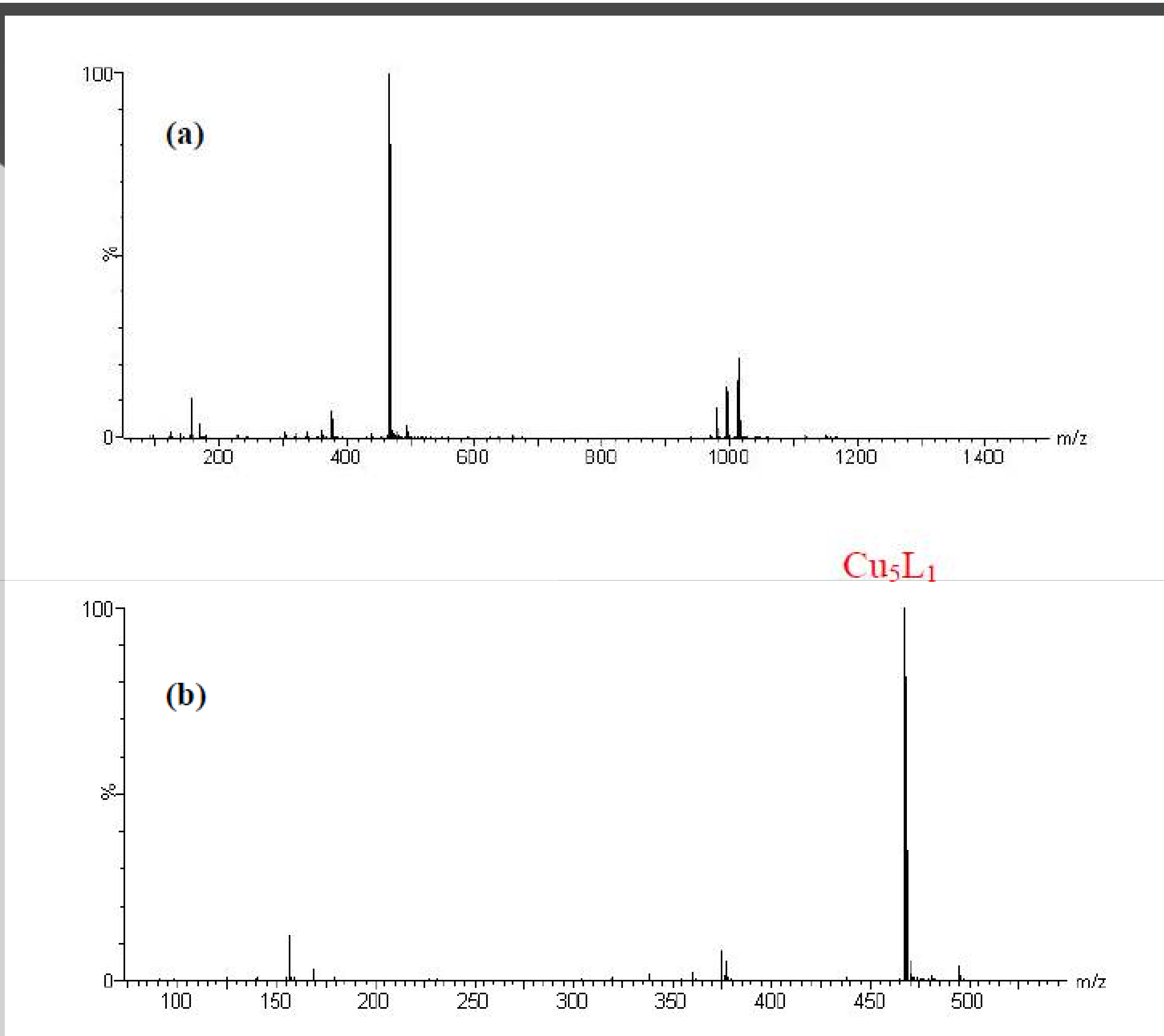
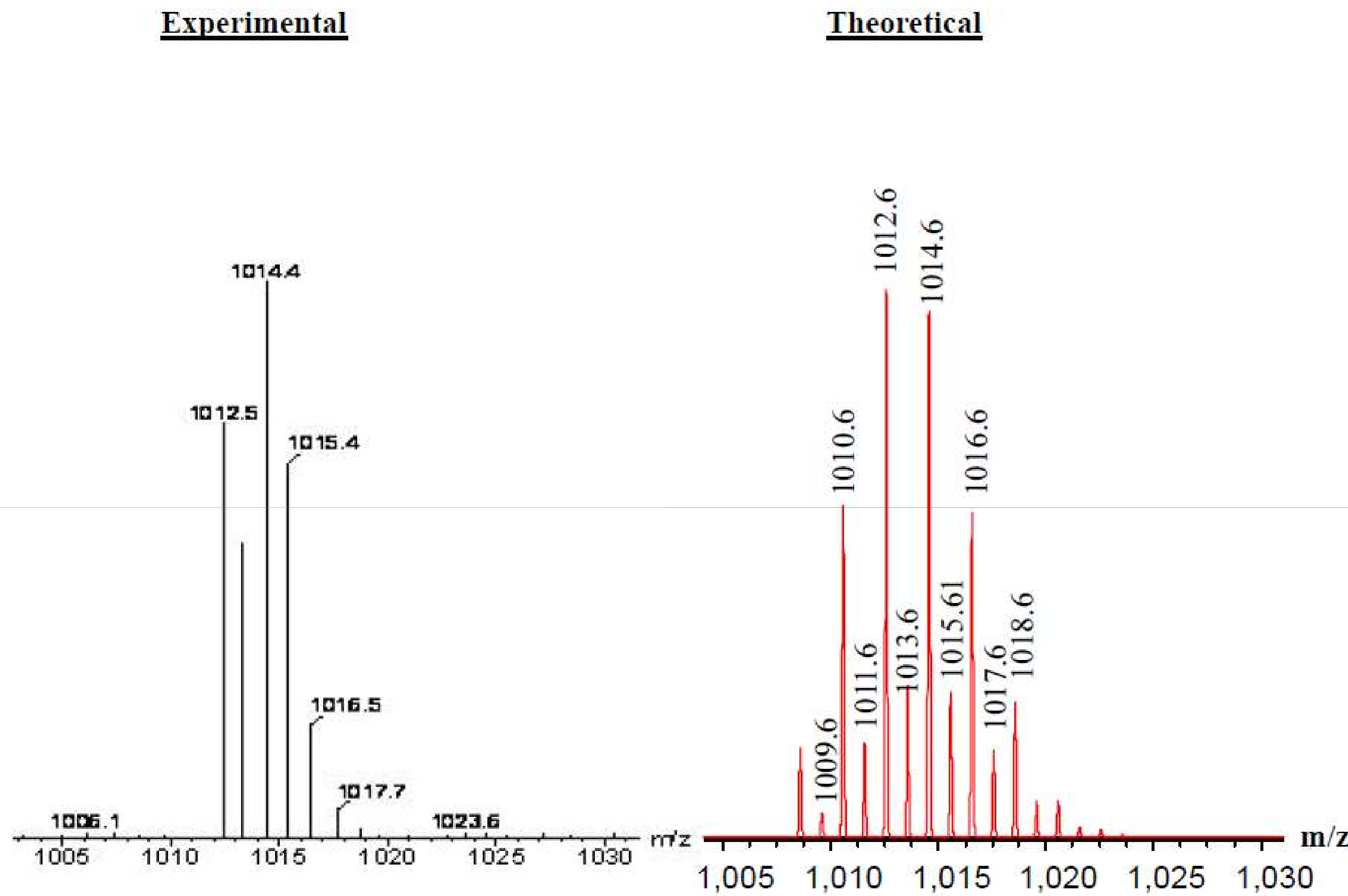
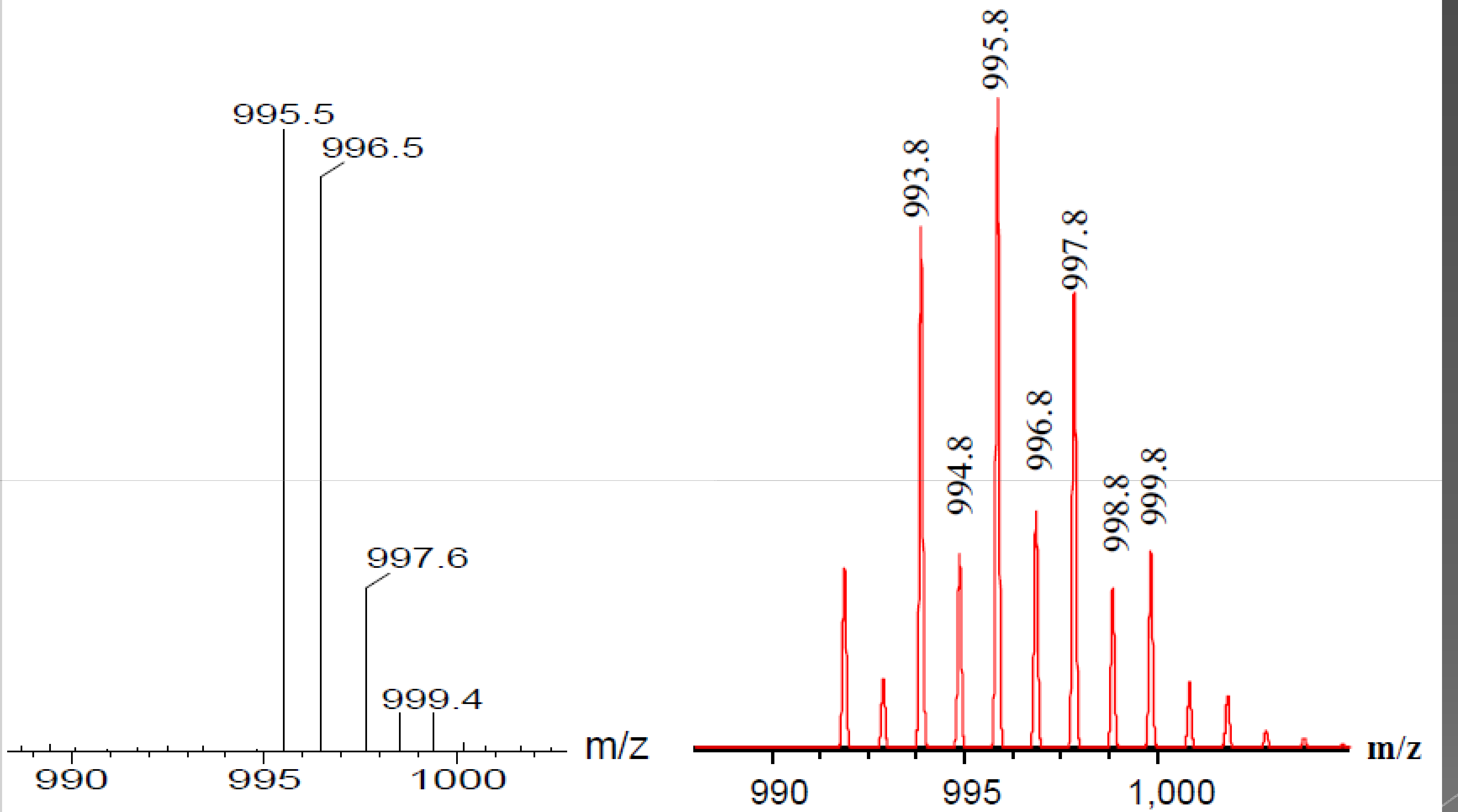


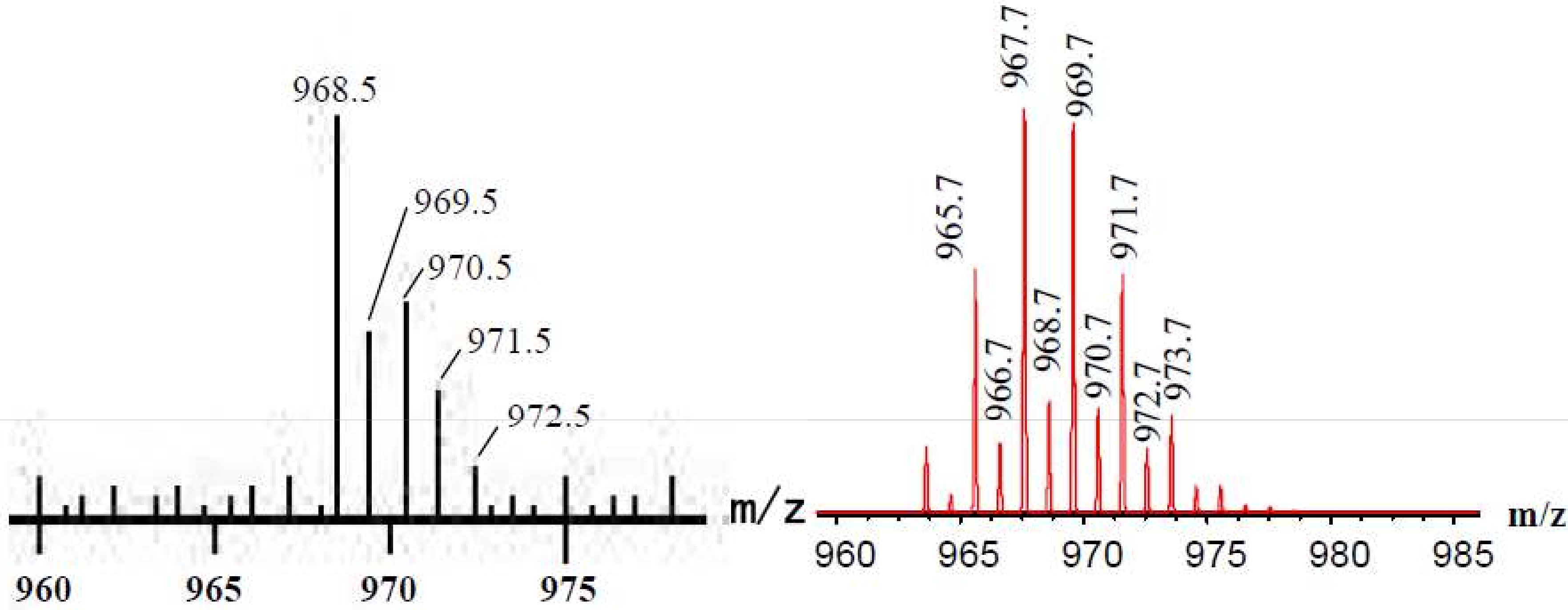
Figure 3. ESI mass spectra of the Cu nanoclusters: (a) full range; and (b) low m/z range.



$[Cu_8L_3+2Na]^+$ ($L= C_7H_9N_2S$)



$[Cu_6L_4+2H]^+$ (L= $C_7H_9N_2S$)



[Cu_8L_3+H]$^+$ (L= $C_7H_9N_2S$)

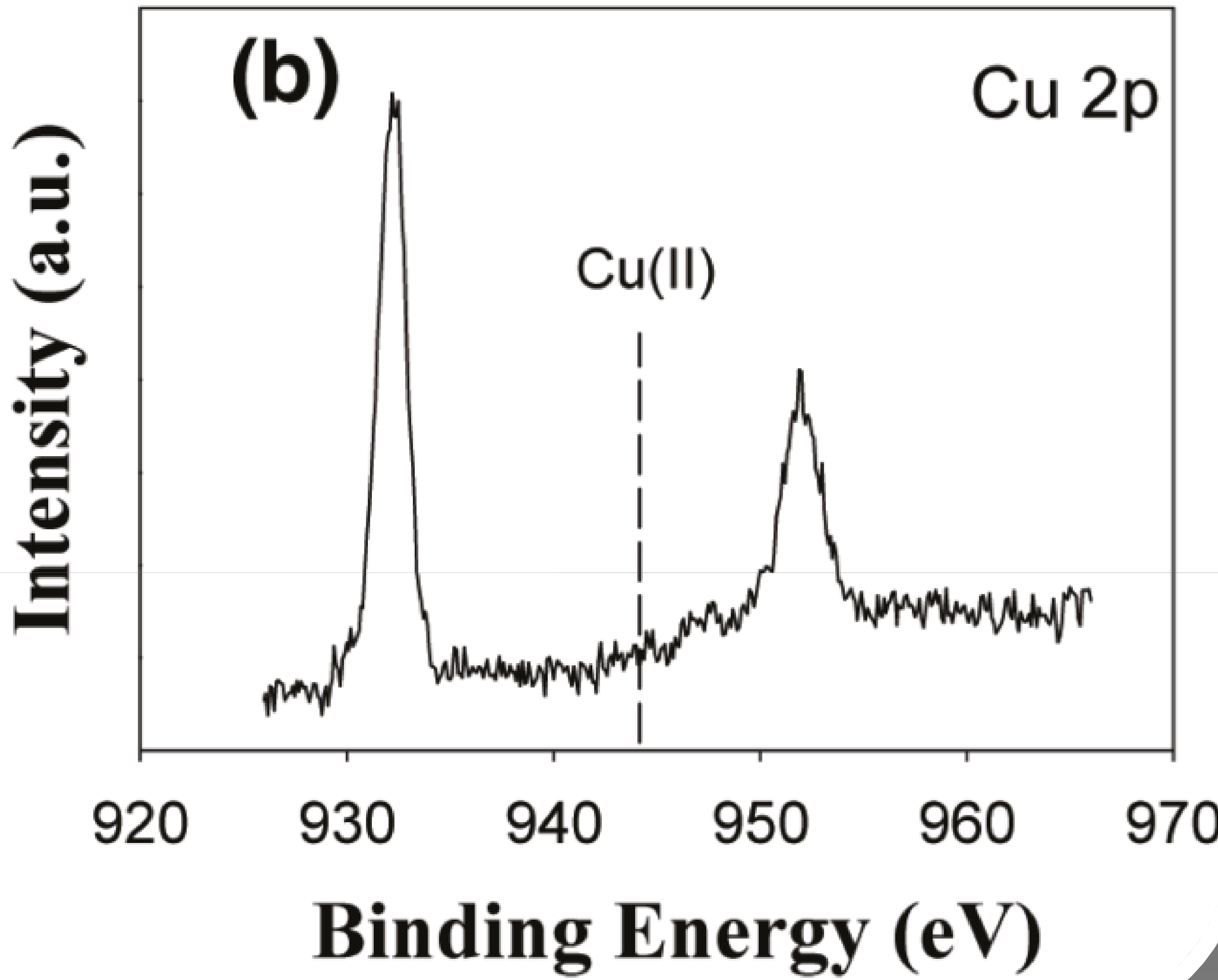
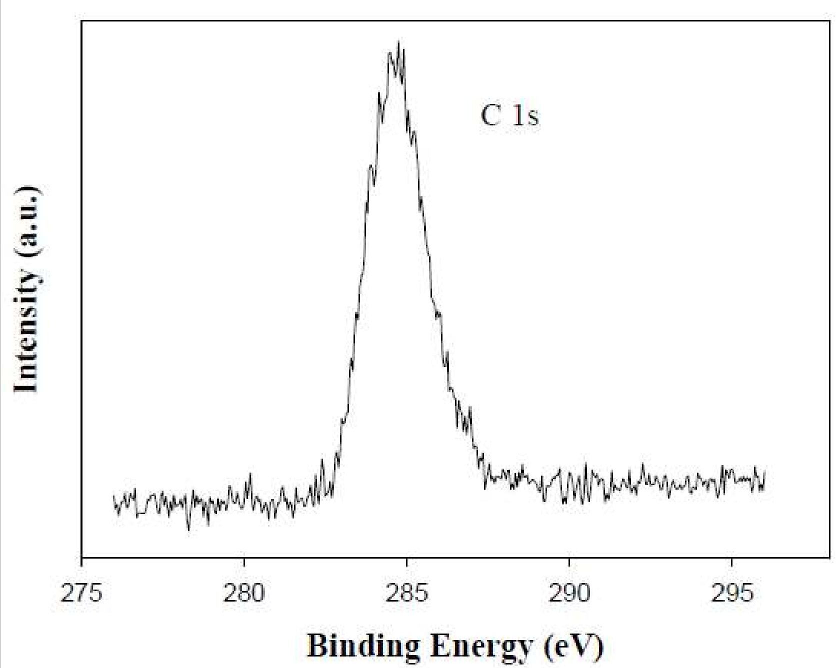
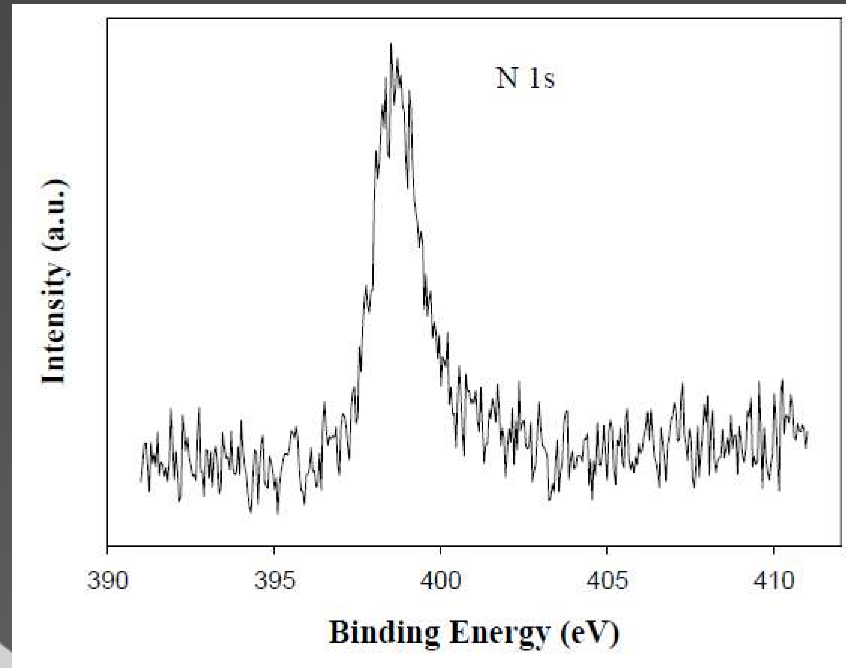
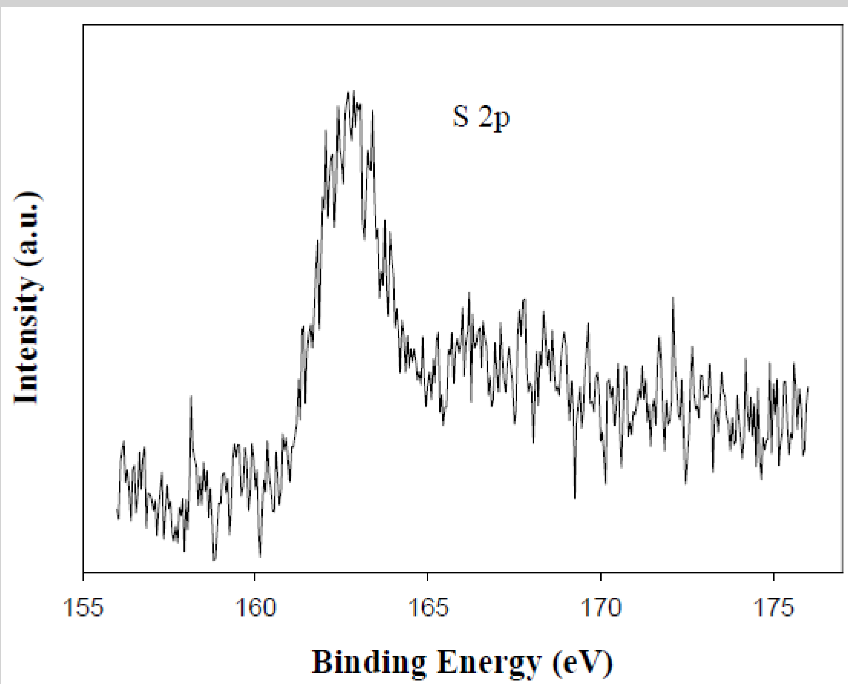


Figure 3. XPS of Cu 2p electrons in Cu nanoclusters; the dashed line shows the binding energy of Cu(II) 2p electrons.







Typical XPS spectra of C 1s, N 1s and S 2p involved in Cu nanoclusters

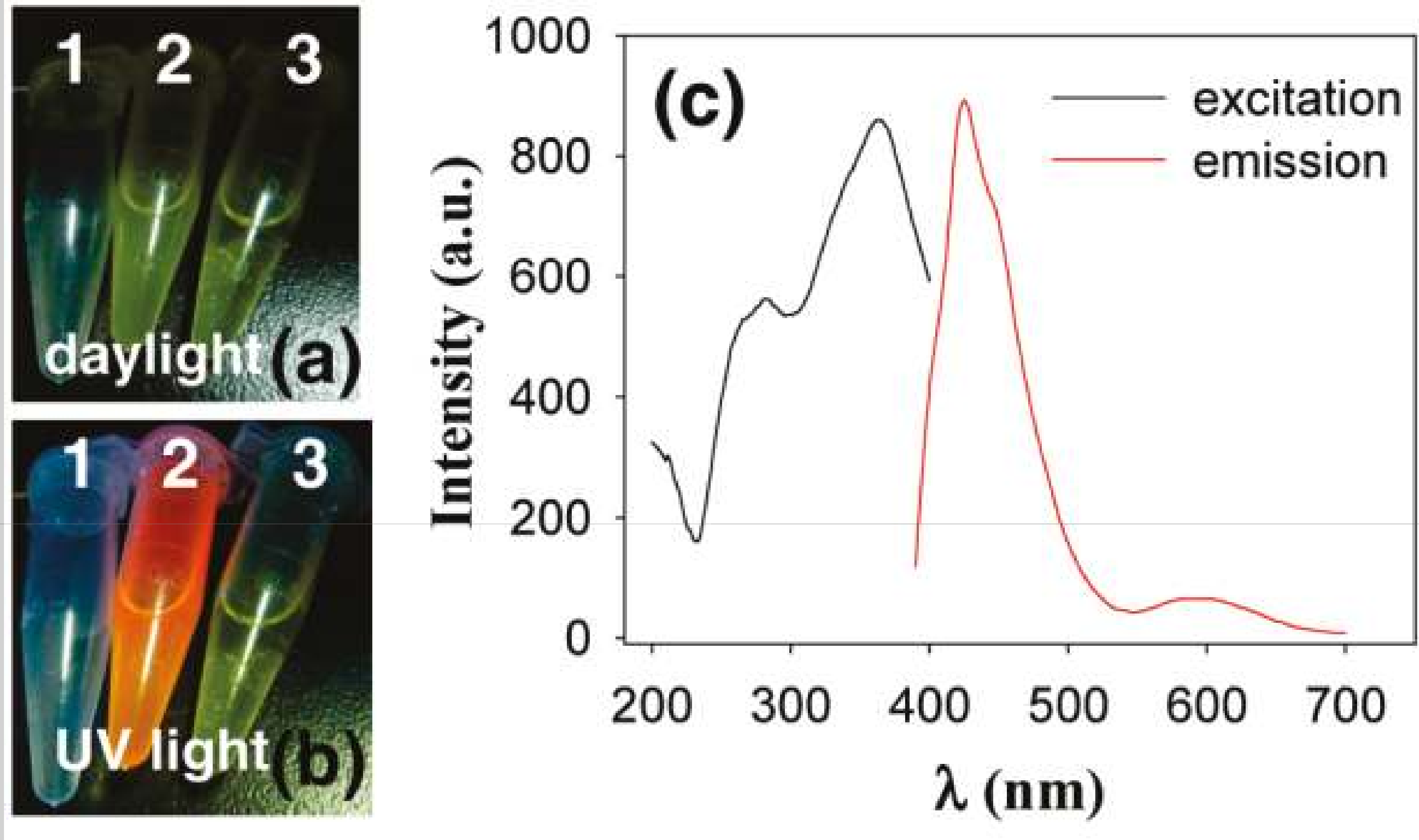


Figure 4. Photographs of the samples under (a) daylight (b) UV light: (1) empty tube; (2) Cu clusters in CHCl3; (3) MPP in CHCl3. (c) Excitation (black curve, λem = 425 nm) and emission (red curve, λ_{ex} = 364 nm) spectra of the copper nanoclusters in CHCl3.

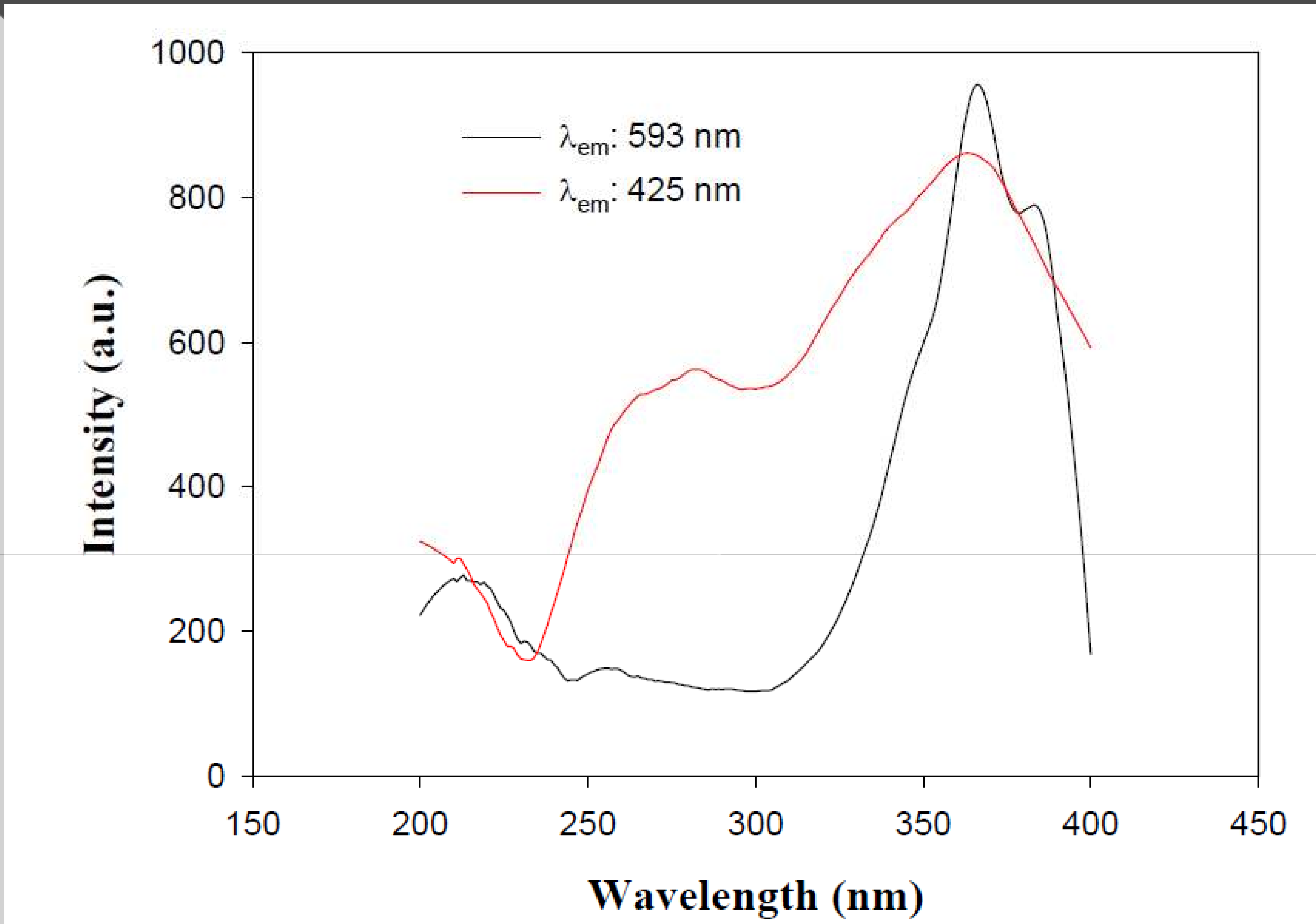
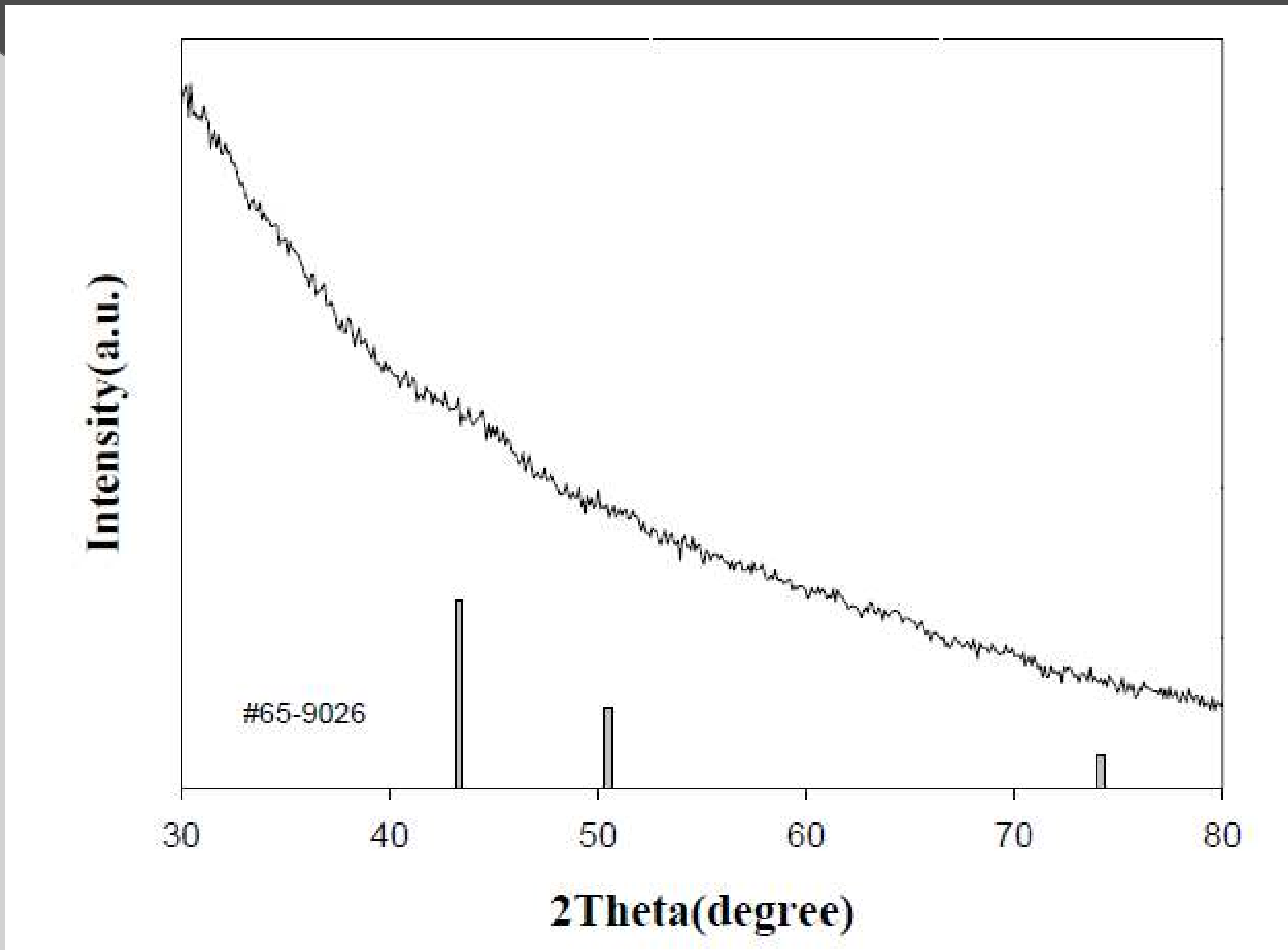
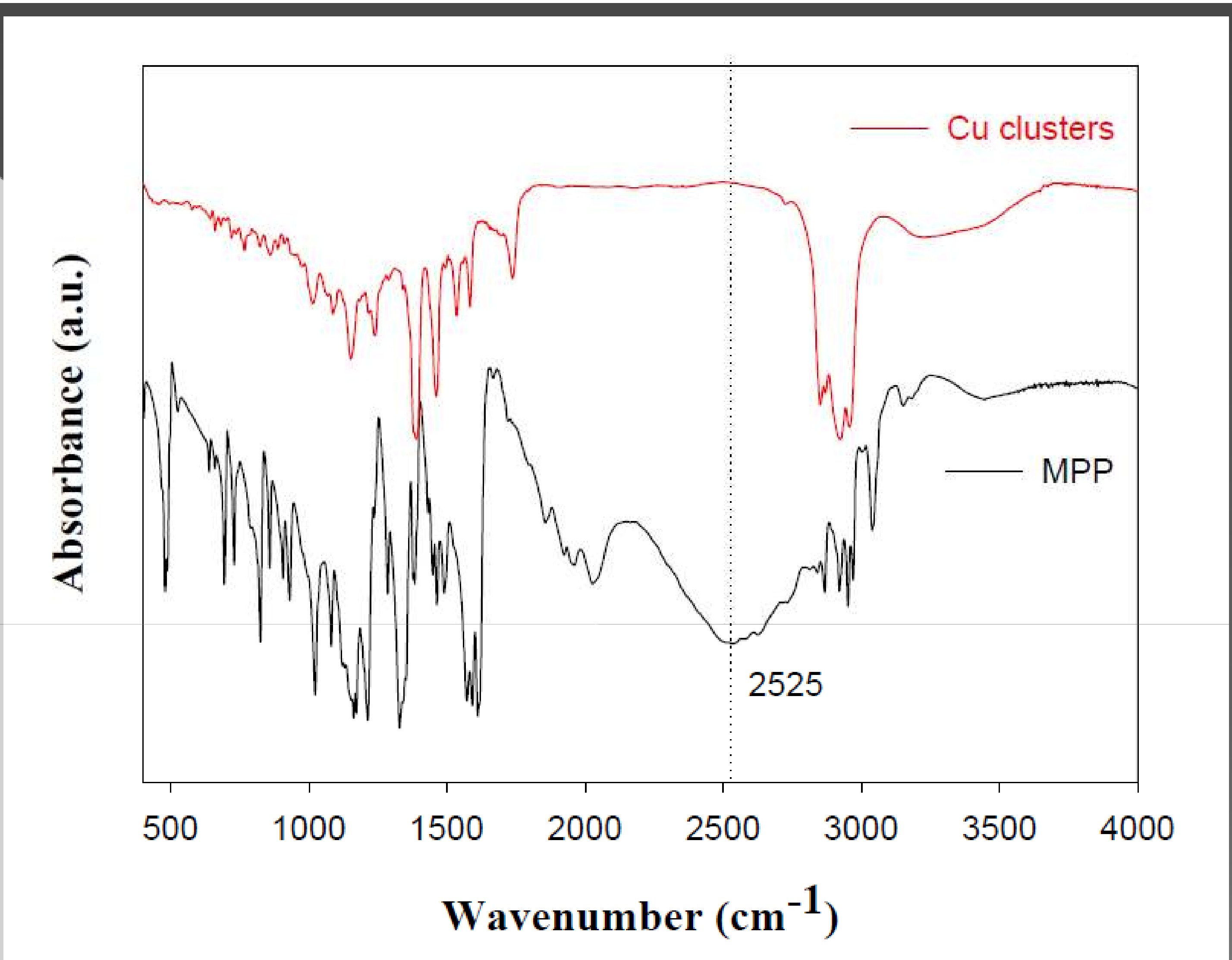


Figure 6. Excitation spectra of the copper nanoclusters with λ_{em} = 425 and 593 nm in $CHCl_3$.



XRD patterns of the synthesized Cu nanoclusters. For comparison, bulk Cu from the joint Committee Powder Diffraction Standard was also included.



FTIR spectra of the MPP-protected Cu nanoclusters and monomeric MPP

Recently, copper complexes have been found to exhibit significant electrocatalytic activity for oxygen reduction reactions

Here, the electrocatalytic activity of Cu nanoclusters as cathode catalysts for ORR was examined by electrochemical measurements, with the Cu clusters deposited onto a glassy carbon electrode (referred to as Cu-NCs/GC).

It can be seen that, in the N2-saturated solution, only a featureless voltammetric profile was observed within the potential range of -1.2 to þ0.4 V. By contrast, when the electrolyte solution was saturated with O2, obvious reduction currents emerged, suggesting the electrocatalytic activity of the Cu nanoclusters for oxygen reduction.

The onset potential of O2 reduction (-0.07 V) was found to be highly comparable to those observed with Au11 clusters (-0.08 V) and some commercial Pt catalysts, suggesting that copper nanoclusters might serve as effective non-platinum electrocatalysts for fuel cell electrochemistry.

In addition, repeated cycling of potentials yielded almost identical voltammograms, indicative of the structural stability of the Cu nanoclusters during electrocatalysis.

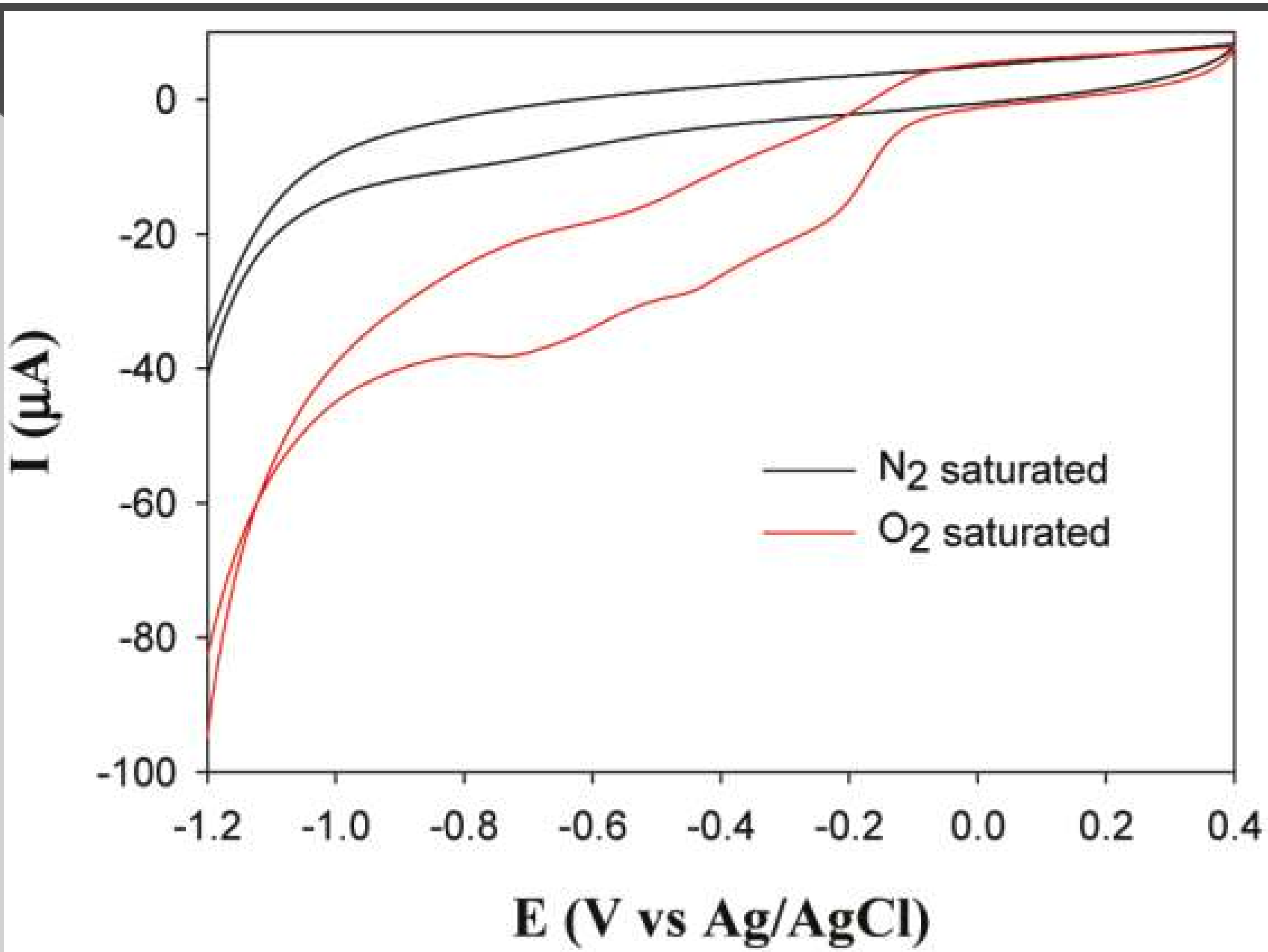


Figure 4. Cyclic voltammograms of Cu-NCs/GC electrode in 0.1 M KOH saturated with N2 (black curve) or O2 (red curve). Potential scan rate, 0.1 V/s.

Summary

MPP-protected copper nanoclusters, Cu_n with n~ 8, could be successfully synthesized with a simple method based on one-pot wet chemical reduction.

The cluster composition was characterized by electrospray ionization mass spectrometry.

This is the first time that stable copper nanoclusters with less than eight atoms in the core were synthesized.

The clusters exhibited interesting dual luminescence, with emission maxima at 425 and 593 nm, and thus might be exploited as a novel fluorophore.

The synthesized Cu nanoclusters also showed a high catalytic activity for oxygen reduction.