Electronic Supporting Information

Microwave-assisted polyol synthesis of copper nanocrystals without additional protective agents

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Experimental details

Materials. Copper (II) chloride ($CuCl_2$), ethylene glycol, diethyl ether, 1M HCl and 1M NaOH were obtained from Wako Chemical Co. All other solvents and other chemicals were reagent grade from Wako Chemical Co, and were used without further purification. Ultra pure water used throughout all experiments was purified with an Advantec RFD 250 NB system.

Preparation of CuNCs. In a typical synthesis, 2mL ethylene glycol (EG) solution of 38mM $CuCl_2$ was mixed with 2mL EG solution of 0.5M NaOH in a glass tube by magnetic stirring for 10 min. The mixture solution was placed in the microwave oven (IDX green motif Ib, Japan) and reacted under medium power for 30 min at the reaction temperature of 185°C with vigorous stirring under N_2 atmosphere. The color of mixture turned rapidly from light blue to light brown within a few minutes. The schematic diagram to illustrate the process of the preparation of the Cu NCs is shown in Figure S1.

After the reaction, 1mL HCl aqueous solution (1 M) was mixed with the resultant solution of 4mL. After further adding 4mL diethyl ether to this solution, the synthesized Cu NCs were transferred from the original solution to diethyl ether using a separating funnel. The diethyl ether solution turned slowly from transparent to light yellow. Thus, the Cu NCs could be extracted into diethyl ether phase, and the extract of Cu NCs was dried with a rotary evaporator at a low temperature of 30 °C. It should be noted that the attitude of the disposal of Cu NCs was about 40% when the synthesized Cu NCs were transferred from the original solution to diethyl ether, even repeat manipulations of extraction with 30 times for a single sample. Thus, the problem of the extraction efficiency should be improved in the future. The re-dispersion of the dried Cu NCs was possible in various solvents (e.g. ethylene glycol, *N,N*-dimethylformamide, ethanol, and water). Normally, we stored the obtained Cu NCs as the re-dispersion of the dried Cu NCs in ethanol or ethylene glycol.

Photophysical properties of Cu NCs. UV–visible absorption spectra were measured using a JASCO V-670 spectrometer. Fluorescence excitation and emission spectra were obtained on a JASCO FP-6200 fluorimeter. Absolute quantum yield of Cu NCs in solutions were measured by using a Systems Engineering Inc QEMS-2000-PL with an integrating sphere.

Fourier Transform Infrared spectroscopy (FT-IR). FT-IR spectroscopy was performed on a Jasco FT-IR 4200 spectrometer. Approximately 1 mg of dried Cu NCs was put onto the KBr disks.

X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectra were recorded with a Quantera SXM spectrometer (Physical Electronics, Inc.) using the monochromatic Al Kα line at 1486.7 eV. The base pressure was approximately 2×10^{-8} Torr. To compensate for charging effect, binding energies were referenced to C 1s at 284.7 eV of hydrocarbon.

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). MALDI-MS was conducted with an AXIMA CFR MALDI-TOF mass spectrometer. After vacuum evaporation of excess diethyl ether solvent, Cu NCs were dispersed in ethanol. Cu NCs in 1 μL of ethanol were deposited on a MALDI target plate and air-dried. In the MALDI-MS of PEGs adsorbed on the surface of Cu NCs, α-Cyano-4-hydroxycinnamic acid (CHCA) as a matrix was further added on the MALDI target plate. The sample was irradiated by a 337 nm N_2 pulse laser. Results from 100 laser pulses were averaged to obtain the spectra.

Transmission electron microscopy (TEM). A drop of NCs dispersed in methanol was placed on a carbon-coated Cu grid, and TEM images were recorded with a JEOL JEM-2010F at an acceleration voltage of 200 kV. HR-TEM (high resolution TEM) image was obtained with a Hitachi H-9500 at an acceleration voltage of 300 kV. The raw magnification of the image was × 1,000,000.

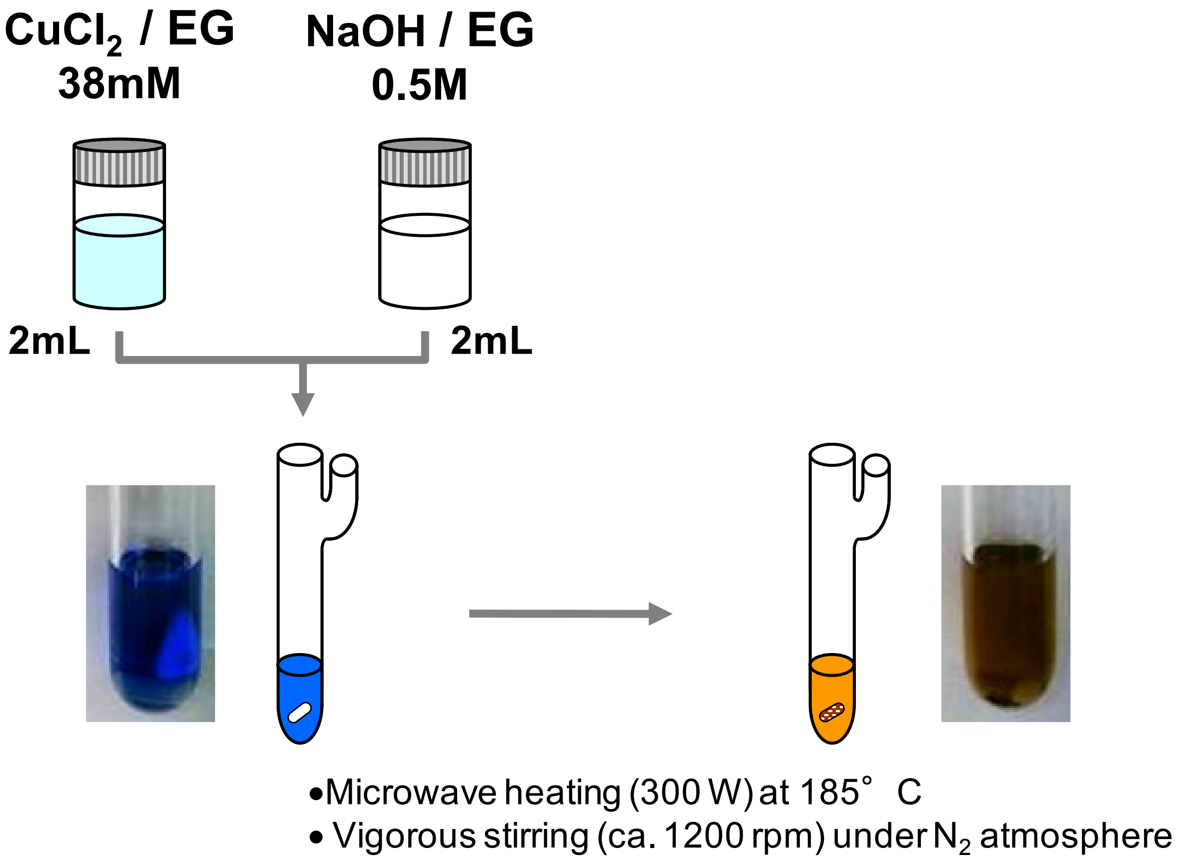

Figure S1. The schematic diagram to illustrate the process of the preparation of the Cu NCs.

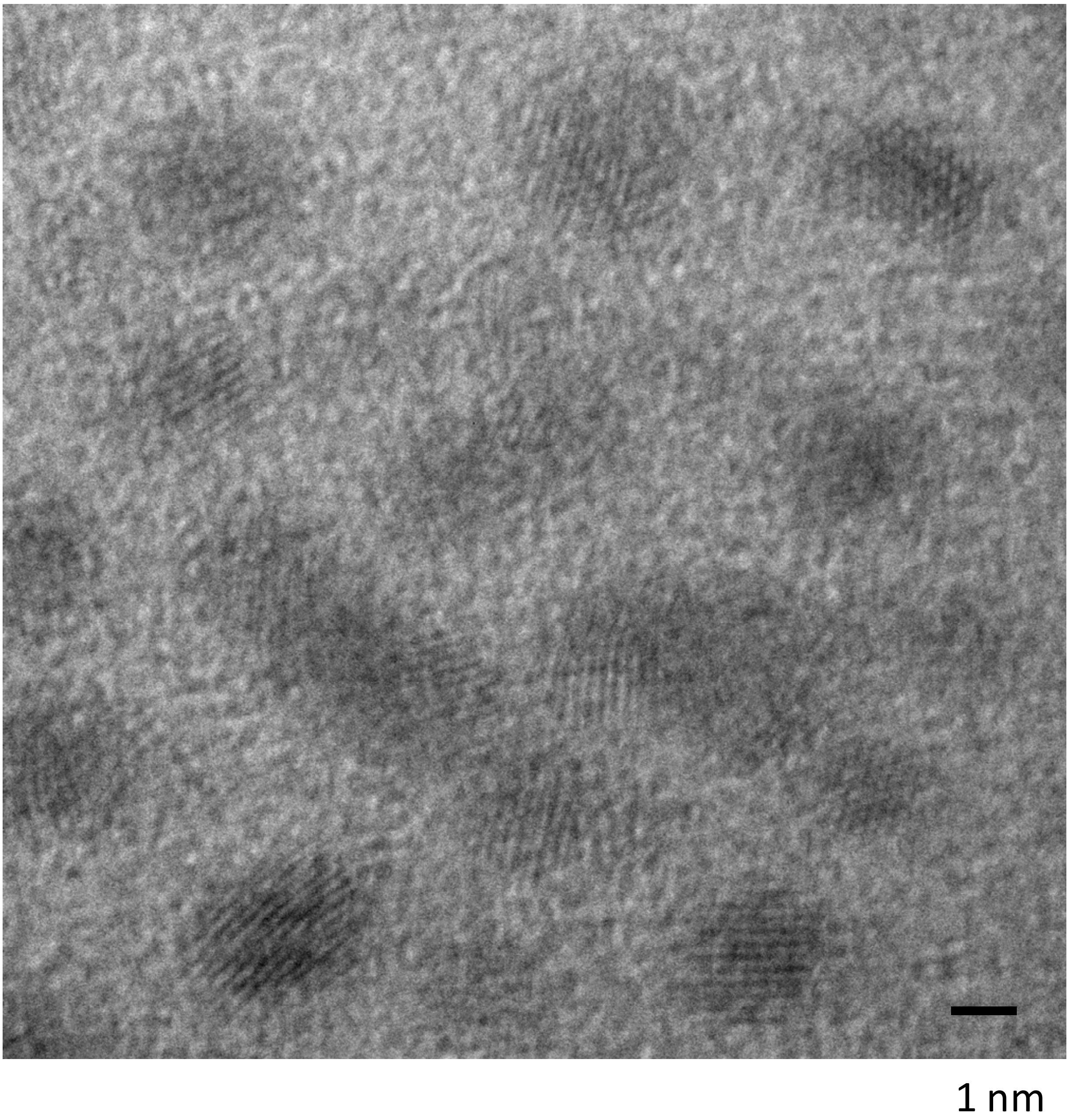

Figure S2. The high resolution TEM images of Cu NCs, showing that the crystal lattice fringes are 0.2 nm apart, which agrees with the d value of the (111) planes of the metallic Cu crystal.

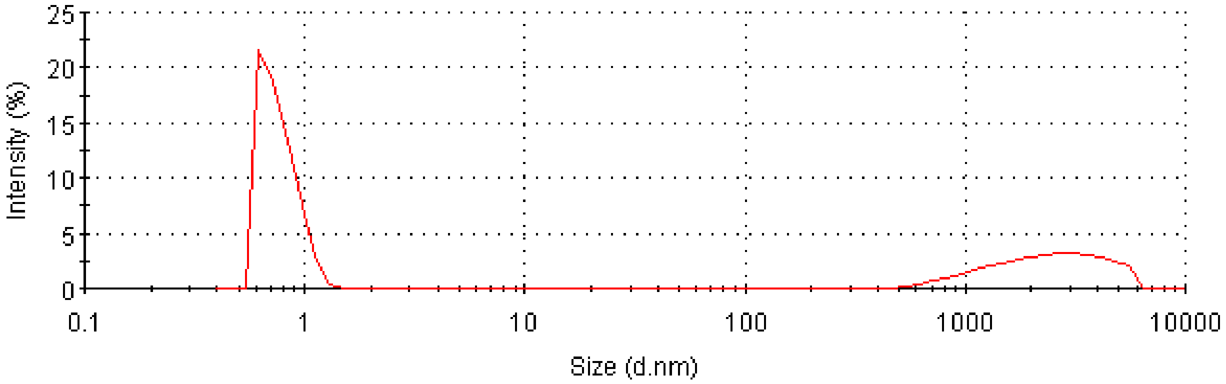

Figure S3. The dynamic light scattering (DLS) measurements (Malvern Instruments - Zetasizer) of Cu NCs showing non-aggregated and extremely tiny Cu NCs with the sizes of about 1 nm.

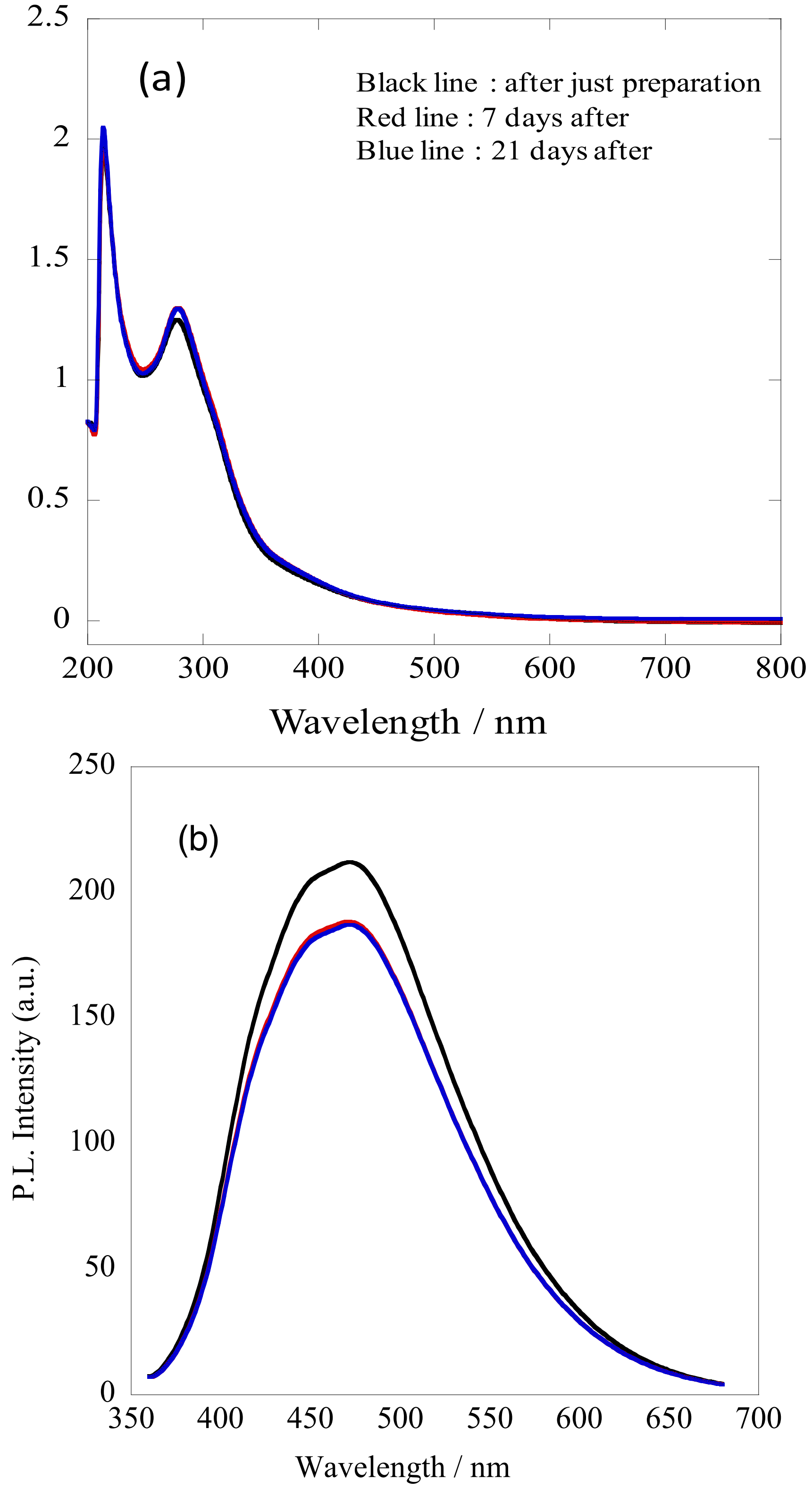

Figure S4 (a) UV-vis and (b) photoluminescence emission spectra at an excitation wavelength of 350 nm.of Cu NCs in ethylene glycol. The CuNCs extracted into diethyl ether phase were re-dispersed in ethylene glycol. The Spectra were recorded after the just preparation (black line), 7 (red line) and 21 days (blue line).

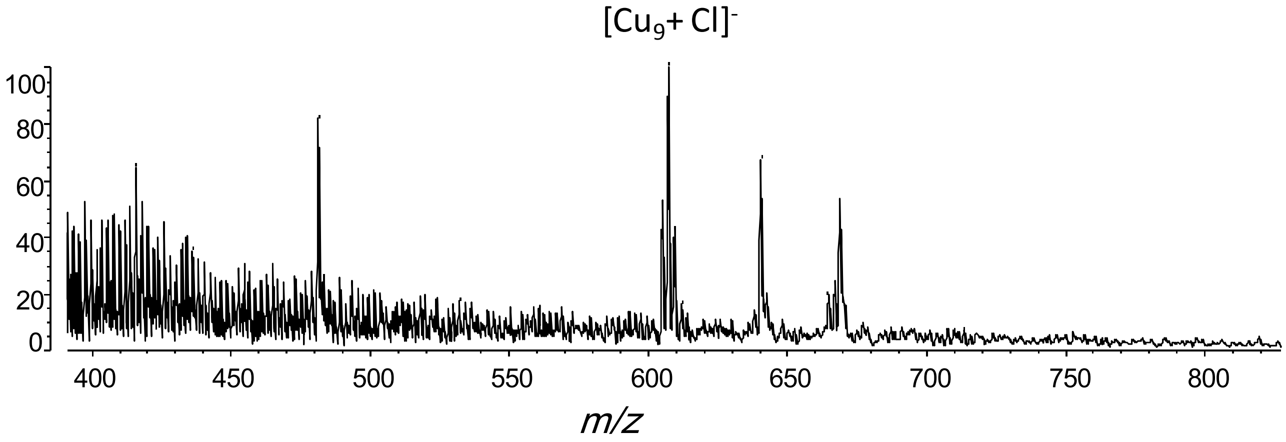

Figure S5 Laser/desorption mass spectrometry (LDI-MS) without the use of organic matrixes for the Cu NCs extracted into diethyl ether phase.

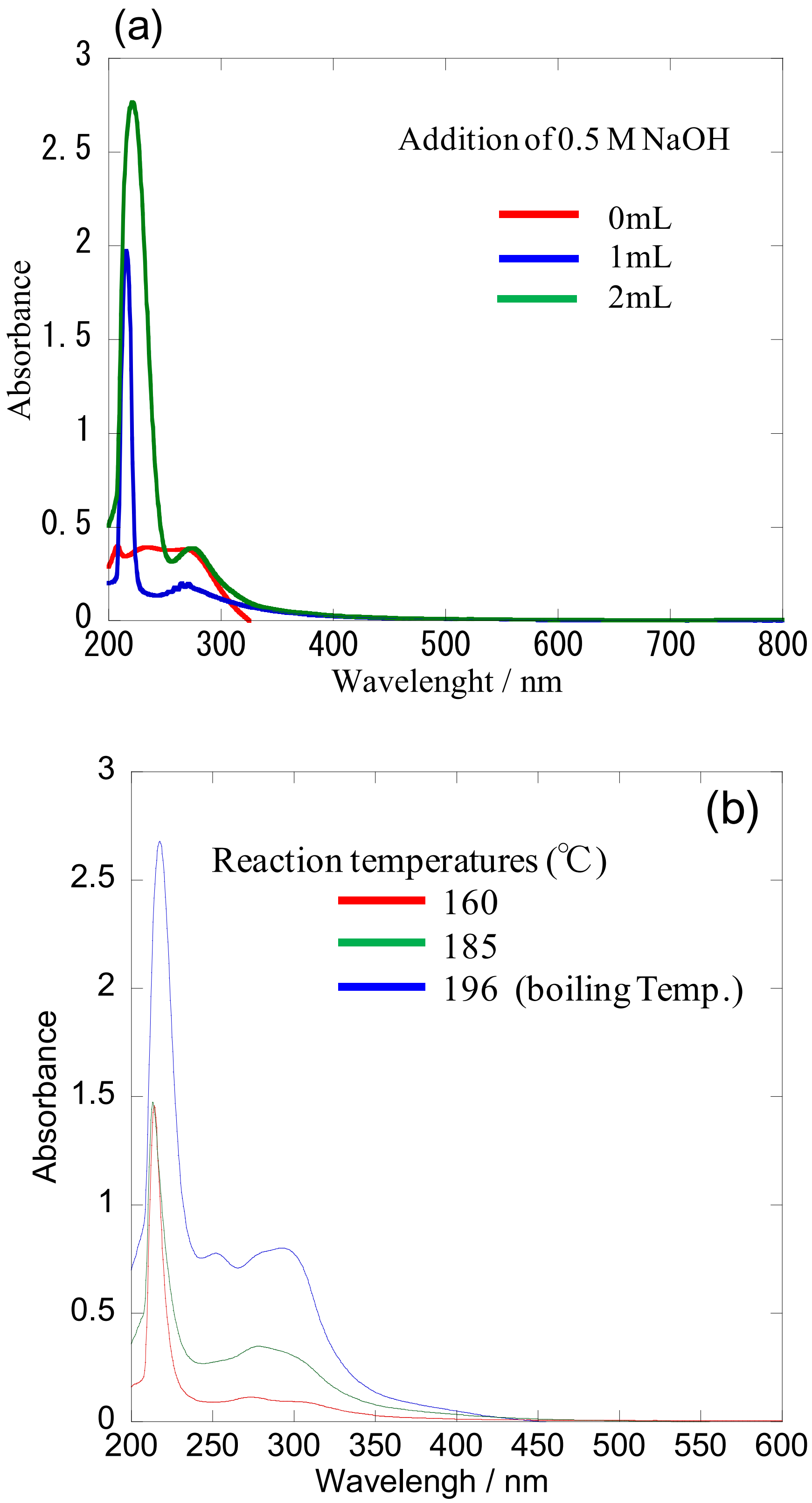

Figure S6 (a) UV-vis spectra of as prepared Cu NCs in ethylene glycol (a) at the different amount of addition of NaOH and (b) at different reaction temperatures with an excitation wavelength of 350 nm of Cu NCs in ethylene glycol.