Supporting Information

for

Highly Stable and Blue-emitting Copper Nanocluster Dispersion Prepared by Magnetron Sputtering over Liquid Polymer Matrix

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Materials. Polyethylene glycol (PEG, an average molecular weight of 600 g/mol), was purchased from Wako (Japan). 11-mercaptoundecanoic acid (MUA, 95 %, an average molecular weight of 218.36 g/mol and a melting point of 50 °C) was purchased from Sigma Aldrich. PEG and MUA were vacuum dried at 100 °C for 2 h to remove eventual volatile substances right before the synthesis. Copper 99.5% pure sputtering target (ϕ 50 mm, 3 mm thickness) was purchased from Nilaco, Japan and used as received. Acetone, methanol, and chloroform were used as received.

Sputtering Apparatus. A modified magnetron sputtering device (Figure 1) was used for preparation of nanoclusters in low vapor pressure liquids. A mechanical stirrer was installed for breaking the surface tension of the liquid, therefore avoiding the formation of a thin metal film, and for mixing the liquid to form a uniform sample. An oil rotary pump and a turbo molecular pump were used to evacuate the sputtering chamber. A temperature control system was installed, to keep both the sputtering copper target and the liquid substrate at controlled temperatures. The atmosphere in the chamber was controlled by evacuating multiple times (8 times) the chamber up to 10^{-3} Pa, then injecting Ar gas up to 10^{1} Pa. During the sputtering experiment the Ar gas flux was controlled to have a constant pressure of 2.0 Pa in the sputtering chamber.

Synthesis of Cu nanoclusters in PEG and MUA. MUA of various amount (0, 0.07, 0.10, 0.21, 0.70, and 1.00 g) was pre-heated to melt at 50 °C then mixed with 7.0 g of PEG to form the liquid substrate that was contained into a petri dish of 26 cm^2 surface area. A metallic Cu target was placed 6 cm above the surface of liquid. The target was pre-sputtered for 10 min to clean its surface. Then, the sputtering onto the liquid substrate was performed for 60 minutes at sputtering current of 20 mA. The substrate temperature was maintained at 40 °C.

Characterization. UV-Visible spectra were taken using a Shimadzu UV-1800 spectrophotometer on liquid using a fused quartz cuvette with 1 cm optical path. Photoluminescence (PL) measurements were performed on the same samples using a Jasco FP-6600 spectrofluorometer. TEM measurements were performed using a JEOL 2000 FX (200kV). TEM samples were prepared by adding methanol to dilute the nanocluster dispersions before dropping them onto carbon-coated copper grids. XPS measurements were performed using a JEOL JPS-9200. As for XPS measurements, nanoclusters were separated from the liquid matrix by microfiltration using acetone as solvent (sample : solvent = 1 : 15, vol/vol) and PTFE membrane (pore size of 0.2 μm, Advantec, Japan). The obtained yellowish powder was placed on a pre-treated Si wafer for XPS measurement[30]. The surface treatment for Si wafers was performed by dipping Si wafers in aqueous solution of hydrofluoric acid (5%) to remove the oxide layers and smoothen the surface. After that the wafers were rinsed with water and ethanol, then dried and underwent Ultraviolet-ozone cleaning to remove residual organic contamination on Si surface. The binding energy of Si (2p) was used as the reference for correcting the charging effect.

$$N = \left(\frac{E_{Fermi}}{E_{emission}}\right)^3$$

Equation SE1. Estimation of the number of copper atoms in a cluster according to the Jellium model approximation.[1] For emission at 437 nm, the number of copper metal atoms in a cluster is $N = 15$.

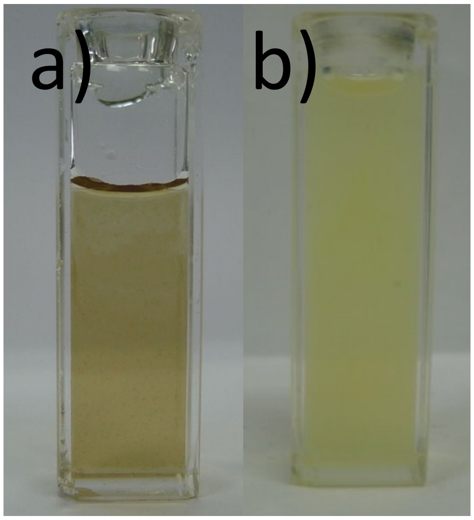

Figure S1. Photograph of as-synthesized sample sputtered onto PEG (a), and mixture of PEG with 1.0 g of MUA (b).

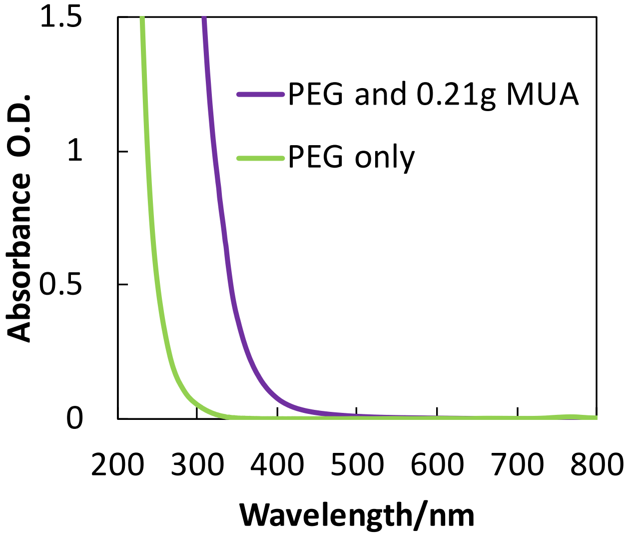

Figure S2. UV-Visible absorbance of PEG, and mixture of MUA and PEG.

XPS spectra and analysis

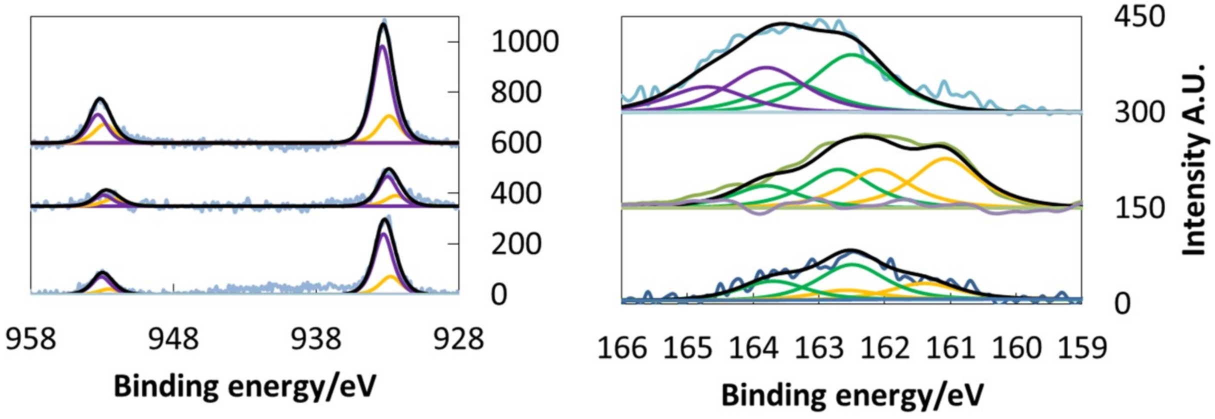

Figure S3. Narrow scan XPS spectra of Cu 2p (a) and S 2p (b) for nanoclusters prepared using 1.00, 0.21 and 0.10 g of MUA in PEG from top to bottom, respectively. The light blue and black curve are the raw and sum spectra, respectively. Cu 2p spectra were deconvoluted respecting the two components Cu(0), and Cu(I) corresponding to purple and orange curves. S 2p spectra were deconvoluted into two components labelled using a purple curve for free thiol, whereas a green and an orange one for the bound states of S.

Table. S1 XPS data results for the Cu and S 2p3/2 binding energy for the various samples, and comparison to some references.

Samples and references (Ref.)	XPS binding energy of Cu(0) 2p3/2, purple curve (eV)	XPS binding energy of Cu(I) 2p3/2, orange curve (eV)	XPS binding energy of S 2p3/2, purple curve (eV)	XPS binding energy of S 2p3/2, orange curve (eV)	XPS binding energy of S 2p3/2, green curve (eV)
1.00 g MUA	932.9	932.4	163.9	162.4	
0.21 g MUA	932.8	932.2		162.5	160.9
0.10 g MUA	932.8	932.3		162.4	161.2
Ref. Cu(0)^{x}	932.6 ± 0.2				
Ref. Cu(I) oxide^{x}	932.4 ± 0.2				
Ref. C-S-H^{y}				163.8 ± 0.4	
Ref. Cu_2S^{z}	932.5 ± 0.2			161.9 ± 0.4	
Ref. CuS^{xx}	932.0 ± 0.2			162.1 ± 0.6	

x: M. C. Biesinger, L. W. M. Lau and A. R. Gerson, R. S. C. Smart. *Appl. Surf. Sci.*, 2010, **257**, 887.
y: D. G. Castner, K. Hinds and D. W. Grainger. *Langmuir*, 1996, **12**, 5083.
z: C. D. Wagner. *Discuss. Faraday Soc.*, 1975, **60**, 291.

xx: R. Scheer and H. J. Lewerenz. *J. Vac. Sci. Technol.*, 1994, **12**, 56.

We confirmed the composition of the obtained nanoclusters in the solution using XPS. The results, showed in Figure S3 and summaried in Table S1, indicate the formation of Cu(0) at 932.9-932.8 eV in binding energy as the main component (purple curves).[2,3] The absence of peaks between 936 and 945 eV in binding energy indicates the absence of copper (II) oxide. The presence of Cu(I) or Cu_xS ($1<x\leq 2$) in sulfide compounds or Cu(I) oxide is possible (orange curve, 932.2-932.4 eV in binding energy), owing to the fact that the surface of the nanoclusters was partially oxidized or cordinated with thiol in MUA (to form Cu-thiol complex). The XPS spectrum for S 2p showed the presence of S in different binding states with metal element for samples prepared using MUA of 0.10 g to 0.21 g. The S in free thiol molecules (unbound state) was found for sample prepared with maximum amount of MUA (1.00 g) owing to some excess MUA molecules that could not be removed with filtration. Therefore our samples are composed of metallic copper nanoclusters capped with MUA on their surface.

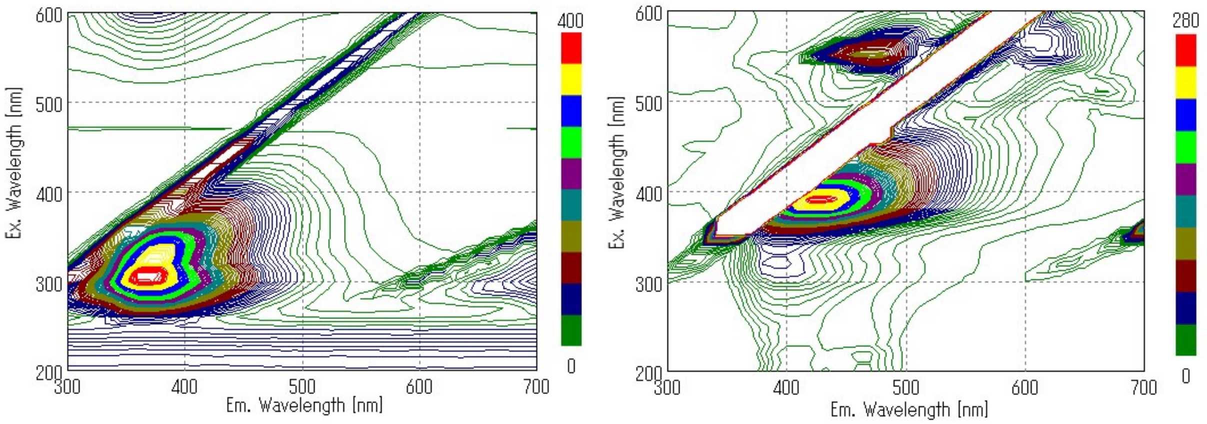

Figure S4. 3D photoluminescence mapping images of a mixture of 0.21 g MUA in 7.00 g PEG (left) and of copper nanoclusters sputtered into this mixture (right). The liquid without copper nanoclusters showed an emission peak at 382 nm (excitation at 313 nm) which is distinguished from the emission spectrum from copper nanoclusters (emission peak at 437 nm and excitation peak at 393 nm).

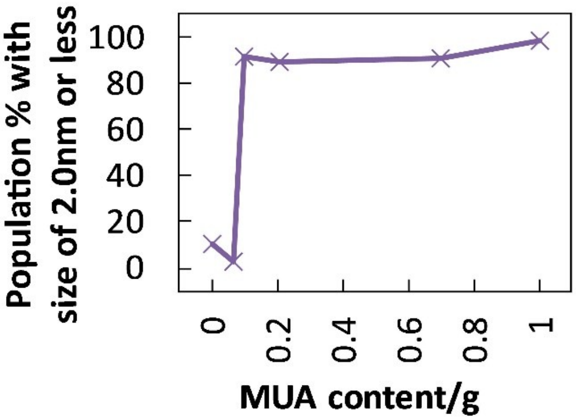

Figure S5. Fraction of nanoclusters with size of 2.0 nm or less, obtained using differerent amount of MUA.

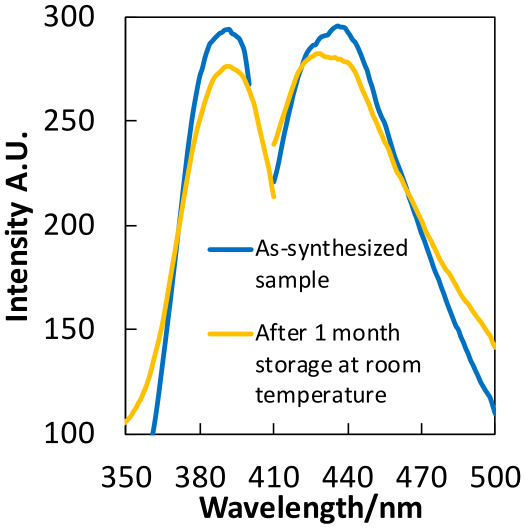

Figure S6. Photoluminescence intensity over time. A sample containing 1 g of MUA was stored at room temperature for one month, and PL was measured again. The intensity decreased only slightly.

References

[1] N. K. Das, S. Ghosh, A. Priya, S. Datta and S. Mukherjee. *J. Phys. Chem. C*, 2015, **119**, 24657-24664.

[2] D. Mott, J. Yin, M. Engelhard, R. Loukrakpam, P. Chang, G. Miller, I-T. Bae, N. C. Das, C. Wang, J. Luo and C-J. Zhong. *Chem. Mater.*, 2010, **22**, 261-271.

[3] M. Fantauzzi, D. Atzei, B. Elsner, P. Lattanzi and A. Rossi. Surf. Interface Anal., 2006, **38**,922.