Electronic Supplementary Material (ESI) for Nanoscale

Supporting Information

Photoluminescent AuCu Bimetallic Nanoclusters as pH Sensors and Catalysts

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EXPERIMENTAL SECTION

Chemicals. Copper nitrate ($Cu(NO_3)_2{\cdot}3H_2O$) was obtained from Showa (Meguro-ku, Tokyo, Japan). PA was purchased from Alfa Aesar (Heysham, Lancs). Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4.H_2O$) was obtained from Acros (Geel, Belgium). Ultrapure water (18.25 MΩ cm^{-1}) from a Milli-Q system (Millipore, Billerica, MA, USA) was used in all experiments. All chemicals and solvents were of analytical grade and used without further purification.

Preparation of PA-AuCu NCs. PA solution (30 mM, 900 µL) was mixed with $HAuCl_4$ (10 mM, 50 µL) under vigorous shaking. Nitric acid solution (0.1 M, 50 µL) containing 5 mM $Cu(NO_3)_2$ was then added to the mixture. After vigorous shaking for 1 min, the solution color turned from brown to white milky, indicating the formation of PL PA-AuCu NCs. To obtain reproducible results, the solution was then kept shaking for 2 h at ambient temperature (25 °C) in the dark. To remove excess PA ligands, PA-Cu NCs solution was subjected to centrifugation at relative centrifugal force (RCF) 3000 g. The collected pellet was re-dispersed in water (1 mL). For simplicity, we denote the concentration of the as-prepared PA-AuCu NCs as 1X. The PA-AuCu NCs were stable under ambient temperature for 2 months.

Characterization of PA-AuCu NCs. A Cary Eclipse Varian spectrofluorometer (Walnut Creek, CA, USA) with an excitation wavelength at 280 nm was used to record the PL spectra of PA-AuCu NCs. The absorption spectra of the PA-Cu NCs were recorded using a GBC Cintra 10e double-beam UV–Vis spectrophotometer (Victoria, Australia). A JSM-1200EX II system (JEOL Ltd., Tokyo, Japan) and an FEI Tecnai-G2-F20 instrument (Roanoke, VA, USA) equipped with a Philips Technai G2 dispersive X-ray spectrometer, respectively, were used to take transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images. High angle annular dark-field scanning TEM (HAADF-STEM) images were taken using a Philips Tecnai F20 G2 FEI-TEM. A VG ESCA210 electron spectroscope from VG Scientific (West Sussex, UK) was used for the study of X-ray photoelectron spectroscopy (XPS) of the PA-Cu NCs. The C 1s peak at 284.5 eV was used as a standard to correct the binding energies of Cu and Au in the PA-Cu NCs. The samples for XPS measurements were prepared by depositing drops of the PA-AuCu NCs onto Si substrates, in which the solvent evaporated at ambient temperature and pressure. Thermogravimetric analysis (TGA) of the PA-AuCu NCs was conducted on a TGA/DSC 1-Thermogravimetric Analyzer (Mettler Toledo, Switzerland) under N_2 atmosphere (flow rate of 50 mL min^{-1}). The PL lifetimes of the PA-AuCu NCs were recorded using a photo-counting PicoHarp 300 system (PicoPicoQuant, Berlin, Germany) and a diode laser emitting at 280 nm (FluoTime 300) as the light source.

The molecular masses of the PA-AuCu NCs were determined using matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) MS (Autoflex, Bruker, Germany) that was operated in a reflectron mode. The NCs were all diluted to 0.1X with ultrapure water. Each (0.5 μL) of the as-prepared solutions was mixed with 0.5 uL matrix solution that was prepared by dissolving 10 mg of 2,5-dihydroxybenzoic acid (DHB) in 1 mL of 500:500:1 (v/v/v) acetonitrile/water/trifluoroacetic acid. Aliquots (1.0 μL) of the mixtures were pipetted onto a stainless-steel 384-well MALDI target (Bruker Daltonics, Bremen, Germany) and dried in air at ambient temperature for 30 min prior to analysis. MS experiments were performed in the negative-ion mode. A Nd:YAG laser (355 nm, 6-ns pulses at 20.0 Hz) was used in the MS system. The laser energy was set at 286.7 μJ. The selected experimental parameters were set as follows: an ion source voltage of 19.13 kV for the detection of negative ions, a second ion source voltage of 16.83 kV, a lens voltage of 7.75 kV, reflector voltage of 20.96 kV, and an extraction delay time of 130 ns. MALDI-MS spectra of the samples resulting from 500 laser pulses were collected and averaged for each acquisition.

Catalytic activity of PA-AuCu NCs. Degradation of MB (10 μM) in the presence of PA-AuCu NCs (0.05–0.2X) was monitored by the changes in the absorption of MB and PL of PA-AuCu NCs at the wavelength of 662 and 625 nm, respectively, for different periods of reaction time (0–300 min). The reaction was conducted at ambient temperature. To confirm the degradation mechanism of MB catalyzed by the PA-AuCu NCs, a three-electrode cell system was conducted in a CHI 802A electrochemical workstation (Austin, TX, USA). Cyclic voltammetry (CV) measurements in the presence of 10 uM MB and PA-AuCu NCs at various concentrations (0.05–0.2X) were conducted over a potential range of -1.0 to 0.4 V at a scan rate of 50 mV s^{-1}.

Analysis of acidic rain water samples. Acidic rain water samples collected in Taipei were filtered through 0.2 μm membranes prior to use. The samples were then subjected to the determination of their pH values using the PA-AuCu NCs probe. Aliquots of PA-AuCu NCs solution (1 X, 50 μL) were added to the acidic rain water samples (50 μL), which were then diluted with ultrapure water to 500 μL. After equilibration at ambient temperature for 40 min in the dark, the mixtures were subjected to PL measurement.

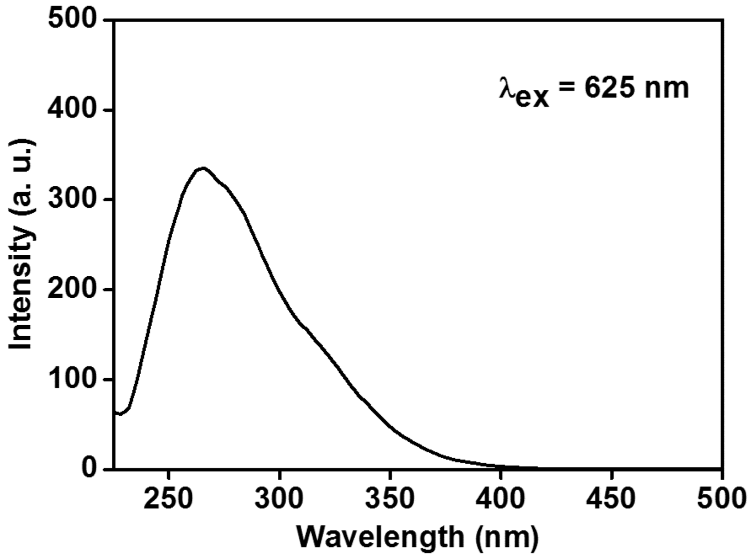

Fig. S1 Excitation spectrum of PA-AuCu NCs. Emission wavelength was at 625 nm.

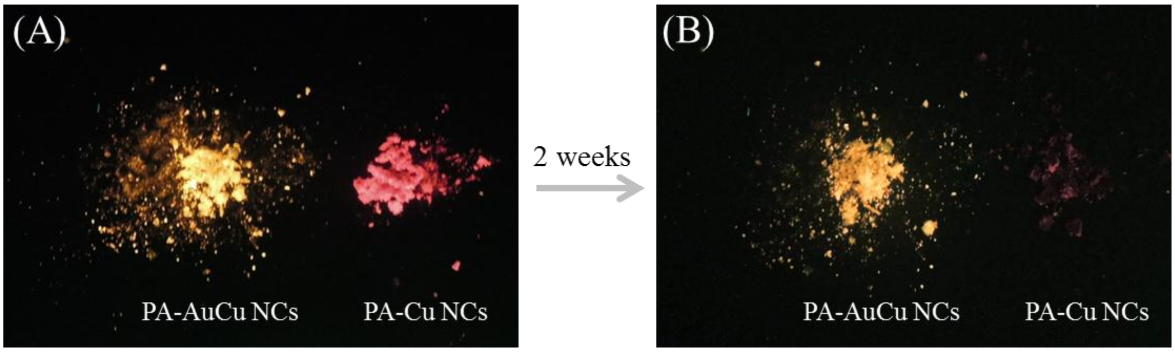

Fig. S2 PL Stability of PA-AuCu and PA-Cu NCs powders before (A) and after (B) storage at ambient temperature and pressure for 2 weeks.

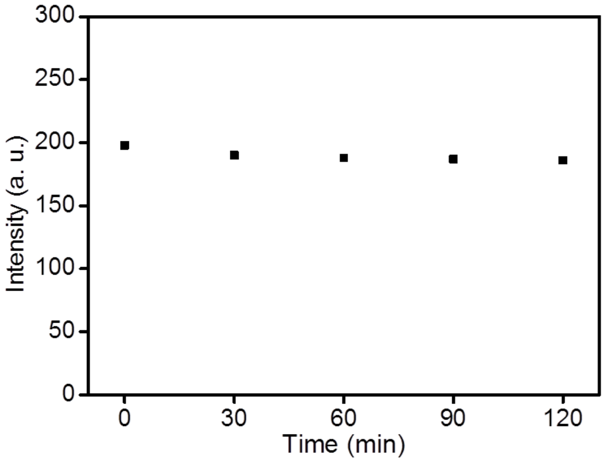

Fig. S3 Stability of PA-AuCu NCs under illumination with an Xe lamp. Excitation and emission wavelengths: 280 and 625 nm, respectively.

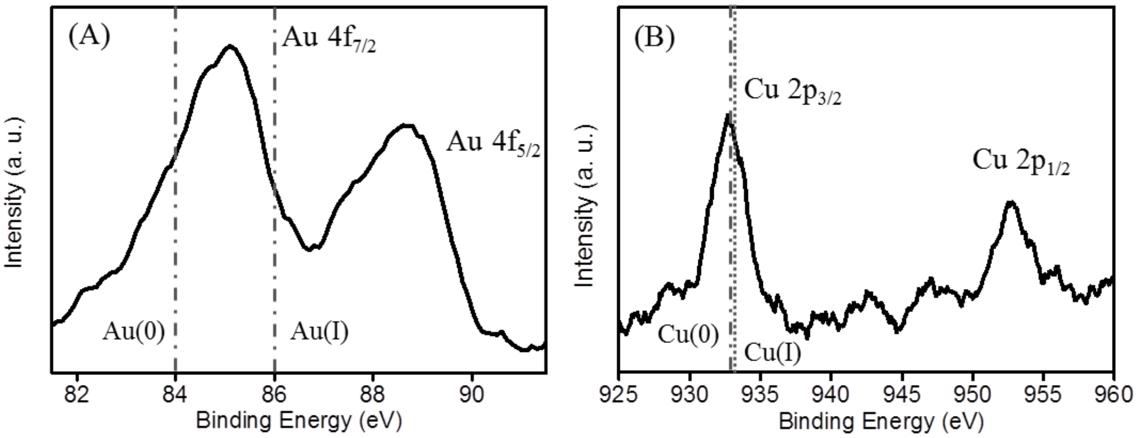

Fig. S4 X-ray photoelectron spectra of (A) Au 4f and (B) Cu 2p electrons in PA-AuCu NCs.

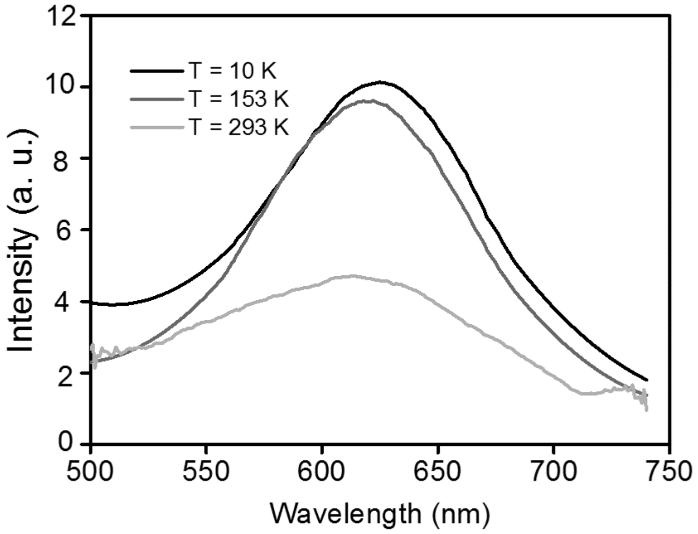

Fig. S5 PL spectra of PA-AuCu NCs at different temperatures. Excitation wavelength was set at 270 nm.

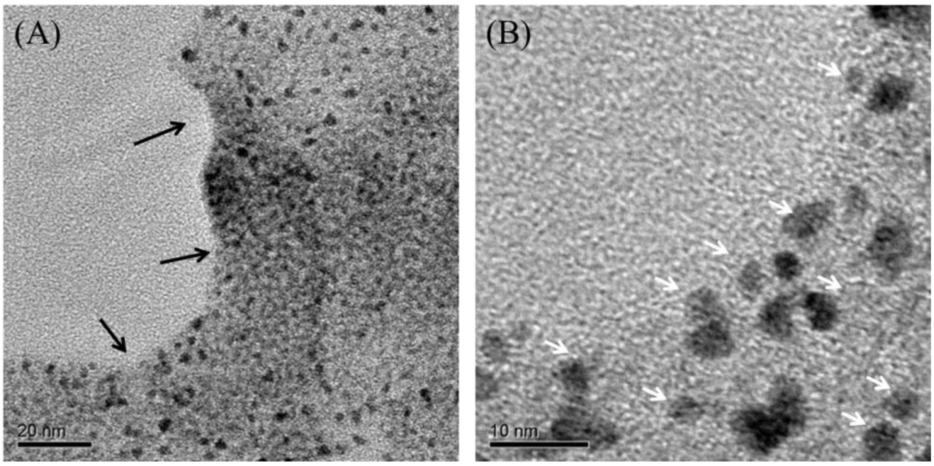

Fig. S6 TEM image of PA-AuCu NCs at pH 3.0. The black arrows indicate PA-AuCu complexes in (A). (B): an enlarged TEM image of (A). The white arrows indicate AuCu NCs in (B).

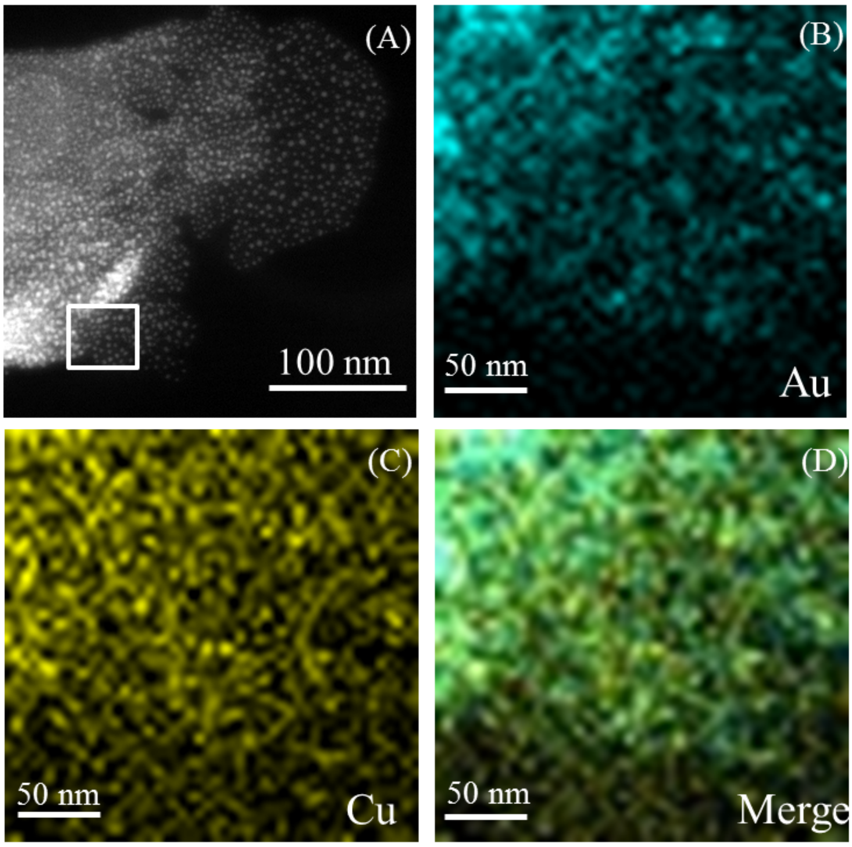

Fig. S7 (A) HAADF STEM image of PA-AuCu NCs, and (B)-(D) their corresponding EDS mappings. (B): Au (blue), (C): Cu (yellow), and (D): merge of (B) and (C) mappings. The EDS element mapping was taken in the white square area as indicated in (A).

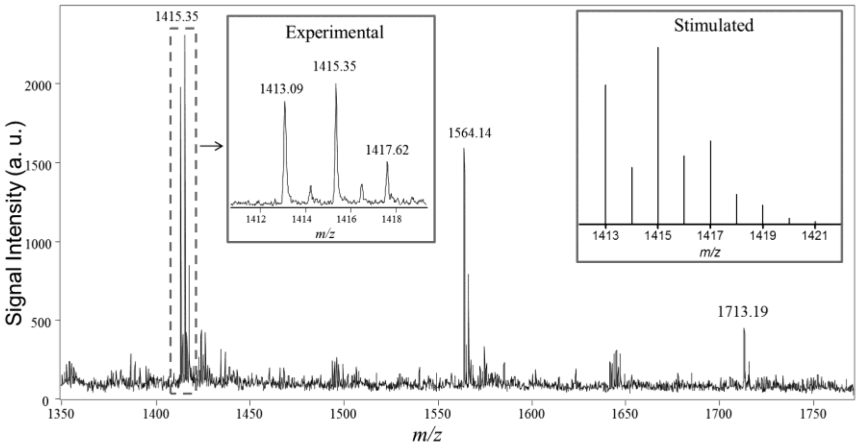

Fig. S8 MALDI-TOF MS spectrum of PA-AuCu NCs. The peaks at *m/z* 1413.09, 1564.14 and 1713.19 are assigned to be PA_6-Au_2Cu_2, PA_7-Au_2Cu_2 and PA_8-Au_2Cu_2, respectively. Inset: the experimental and simulated isotopic patterns of $[Au_2Cu_2PA_6\text{-}H]^-$.

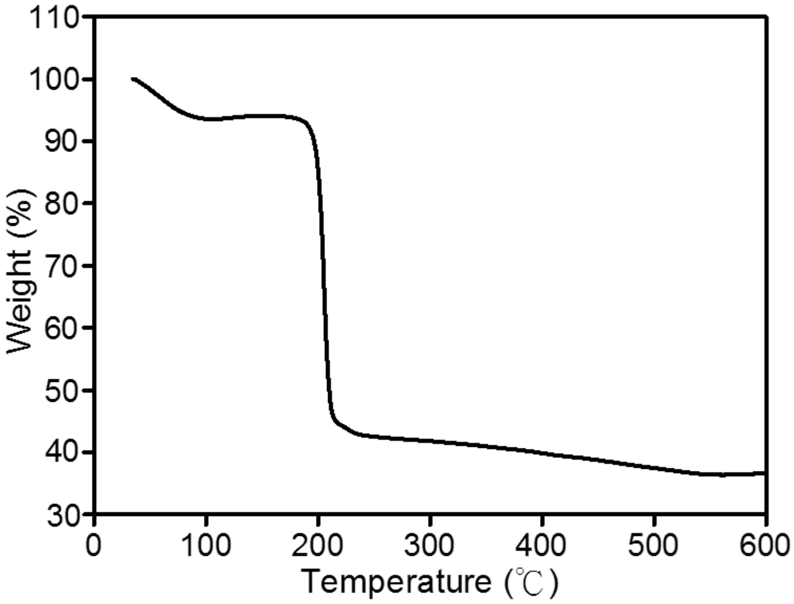

Fig. S9 TGA curve of PA-AuCu NCs.

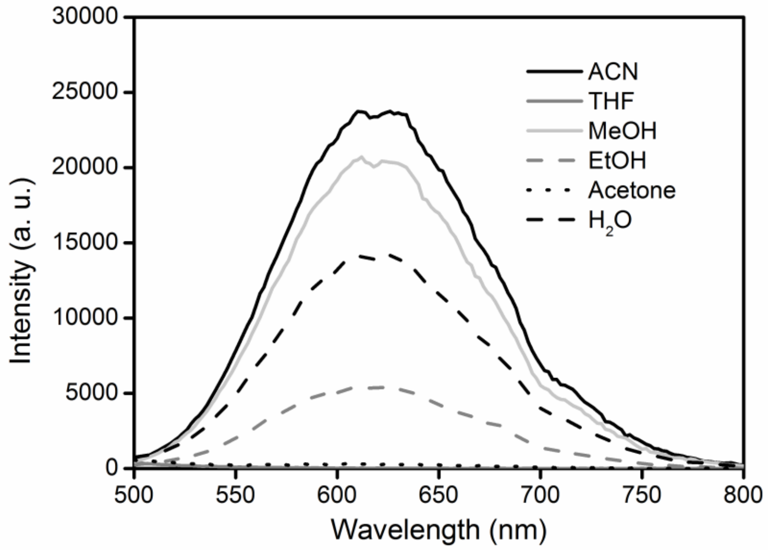

Fig. S10 PL spectra of PA-AuCu NCs in various organic solvents. Excitation wavelength was set at 270 nm.

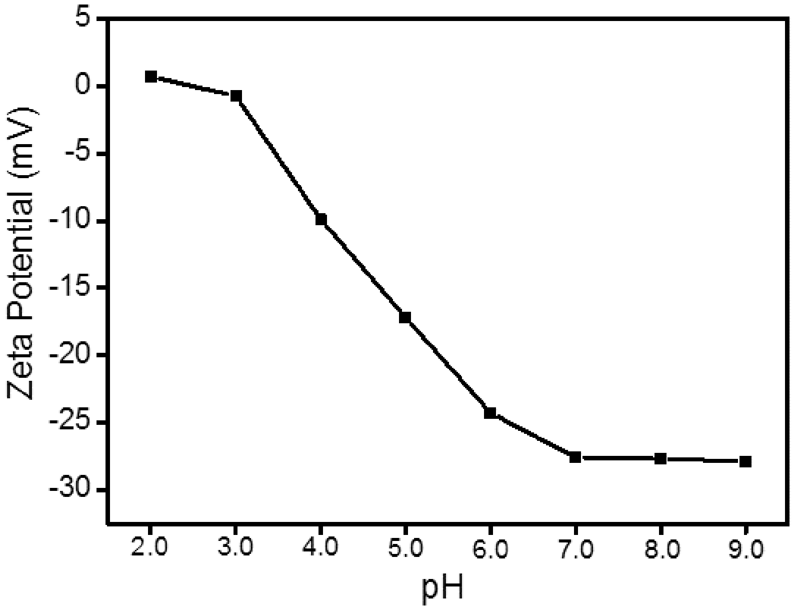

Fig. S11 Zeta potential of PA-AuCu NCs at various pH values.

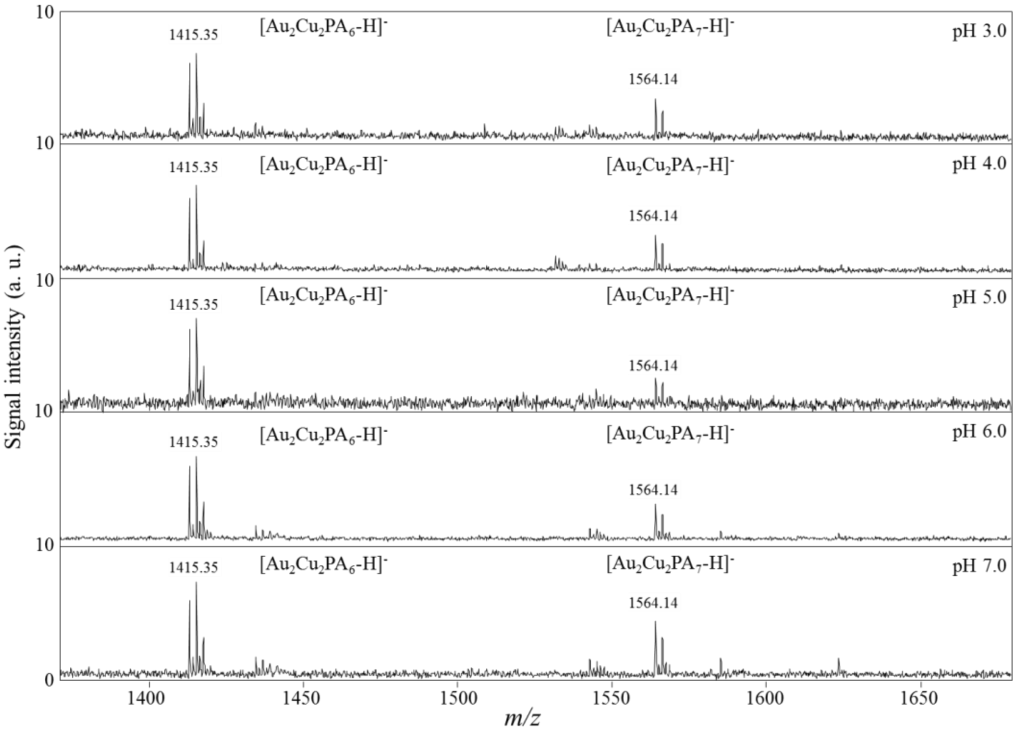

Fig. S12 MALDI-TOF MS spectra of PA-AuCu NCs at various pH values. The peaks at *m/z* 1413.09 and 1564.14 are assigned to PA$_6$-Au$_2$Cu$_2$ and PA$_7$-Au$_2$Cu$_2$, respectively.

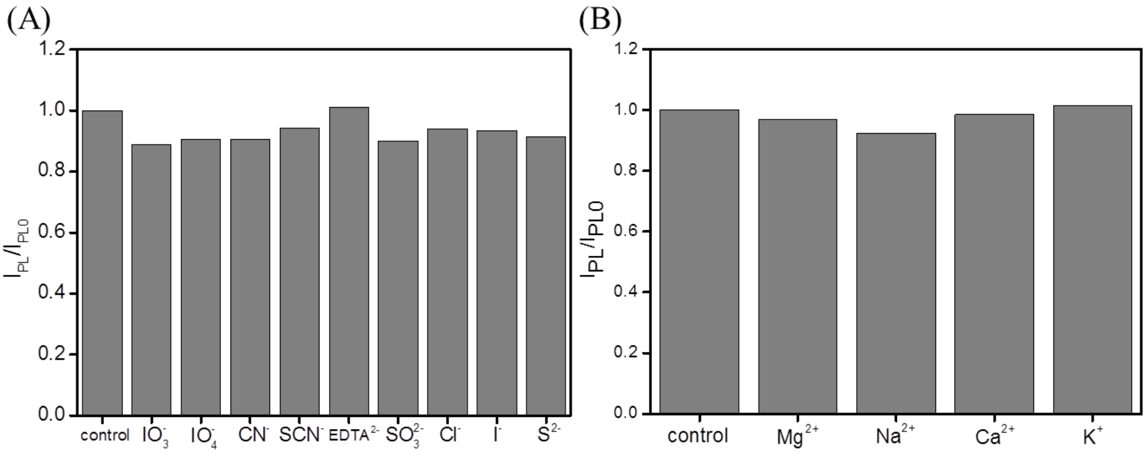

Fig. S13 I_{PL0} and I_{PL} are the PL intensities of PA-AuCu NCs (0.02X) at 625 nm in the absence and presence of (A) anions (0.5 mM) and (B) cations (5 mM). Excitation wavelength was set at 270 nm.

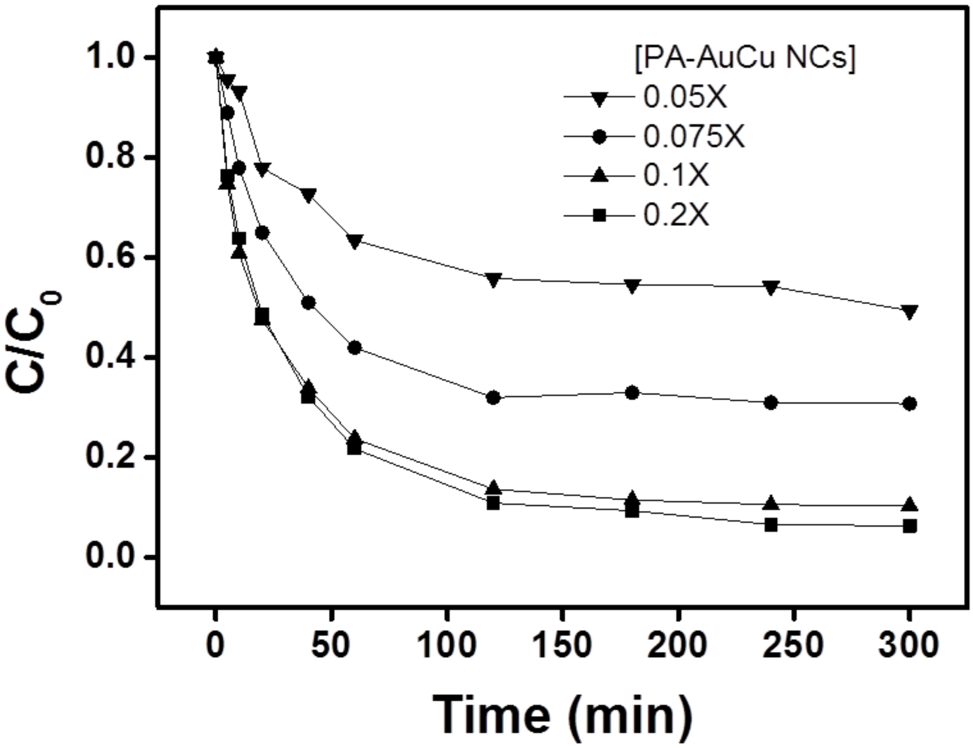

Fig. S14 Degradation of MB in the presence of PA-AuCu NCs as a function of time. C and C_0 (10 μM) are the concentrations of MB at the initial and various reaction times, respectively. MB concentrations at various times were calculated from the corresponding absorbance values at 662 nm according to the Beer's law.

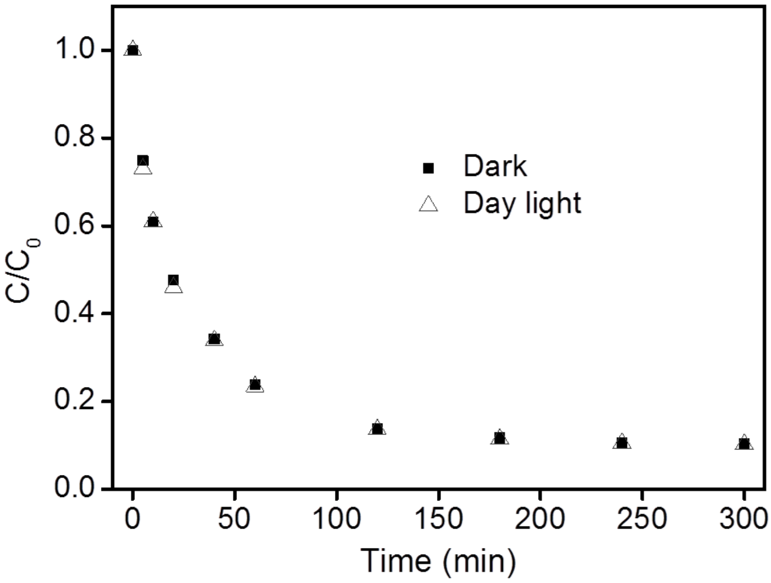

Fig. S15 Reduction of MB in the presence of PA-AuCu NCs in the dark and daylight, separately. C$_0$ (10 uM) and C are the concentrations of MB at the initial and various reaction times, respectively.

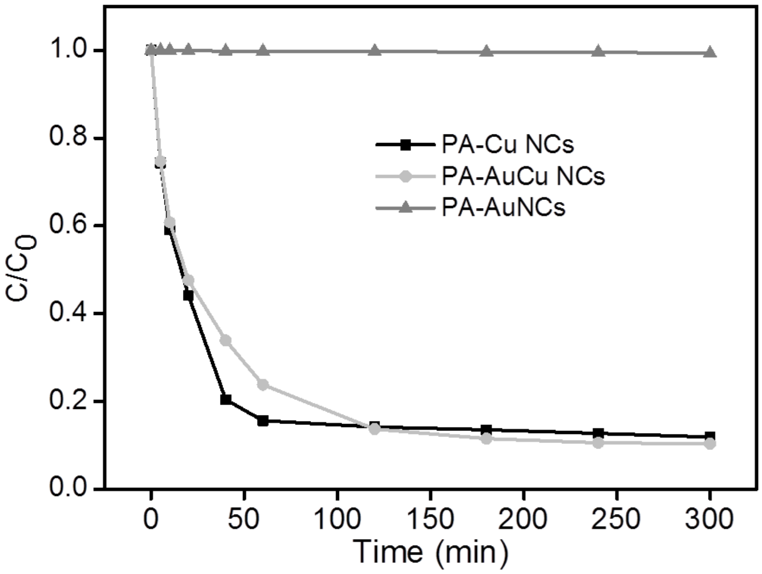

Figure S16. Degradation of MB in the presence of PA-AuCu NCs (0.1X), PA-Au NCs (0.1X) and PA-Cu NCs (0.1X) separately as a function of time. C and C$_0$ (10 μM) are the concentrations of MB at the initial and various reaction times, respectively. MB concentrations at various times were calculated from the corresponding absorbance values at 662 nm according to the Beer's law.