Time-tunable autocatalytic lucigenin chemiluminescence initiated by platinum nanoparticles and ethanol

Chun-Feng Duan, Hua Cui*

Supporting Information

Other chemiluminescence (CL) reactions involving metal nanoparticles (NPs)

The direct catalysis by metal NPs was mainly observed for luminol CL reactions including luminol-H_2O_2, luminol-$K_3Fe(CN)_6$, luminol-$AgNO_3$ and luminol-hydrazine CL systems as the references cited in the text. Although our previous work has found some other CL reactions[1] initiated by gold NPs besides of luminol CL reactions, in these CL systems, gold NPs did not act as catalyst, but reductant, nanosized platform, or energy acceptor. Another CL from decomposition of peroxymonocarbonate catalyzed by gold NPs, to the best of our knowledge, was the only one metal NPs catalyzed CL system without luminol reported.[2] Because of the low quantum yield of these CL systems without luminol, it was difficult to use them for analytical application.

Experimental

Chemicals. Lucigenin (bis(N-methylacridinium) nitrate, $Luc^{2+}\cdot 2NO_3^-$) was obtained from Tokyo Chemical Industry Co., Ltd (Japan). *N*-Methyl-9-acridone (NMA) was purchased from Acros Organics. H_2PtCl_6, sodium citrate, sodium hydroxide, acetaldehyde (40% v/v) and chloroform were of analytical grade and purchased from Shanghai Reagent (Shanghai, China). Absolute ethanol (≥99.8%, guarantee reagent/GR) was obtained from Lingfeng Chemical Reagent (Shanghai, China). All reagents were used as received, and Mill-Q water (18.2 MΩ) was used throughout.

Synthesis and purification of Pt nanoparticles (NPs). The colloidal solutions of Pt NPs were synthesized by citrate reduction method reported by Henglein[3] with some modification. Briefly, 5.0 mL of 1% sodium citrate solution was added to 45 mL of boiling solution of H_2PtCl_6 (30 μmol). After boiling for 1 h, the solution was turned to brown color. Then it was cooled to room temperature with stirring. For the further purification, the free synthesis precursors left in the obtained Pt colloids were removed via thoroughly dialysis for 2 days in Mill-Q water with a membrane of 3500 molecular weight cutoff. The purified Pt colloids were used as the stock solution of Pt NPs for all the following experiments.

Procedure for CL measurements. The chemiluminescence (CL) detection was conducted on a BPCL Luminescence Analyze (Beijing, China) with a fixed voltage of -500 V. For a typically CL measurement, 0.5 mL of 5.0×10^{-5} M lucigenin and 0.5 mL of 0.05 M NaOH were successively added to a cylindrical CL cell. Then 0.5 mL of the mixture solution of Pt NPs and ethanol was injected into the cell to initiate the CL reaction. The CL intensity during the reaction along with time was recorded by the Luminescence Analyze.

Optical measurements. The CL spectra and fluorescence spectra were measured on a model F-7000 spectrofluorometer (Hitachi, Japan). UV-visible absorption spectra were obtained on a UV8453 spectrophotometer (Agilent, USA). A high resolution transmission electron microscope (HRTEM, JEM-2010, Hitachi, Japan) was used to characterize the size of Pt NPs. The surface states of Pt NPs before and after CL reaction were characterized by X-ray photoelectron spectrum (XPS) on a model ESCALAB MK II electron spectrograph (VG, England). ^{1}H-NMR spectra were recorded with an AVANCE 300 (300 MHz) NMR spectrometer (Bruker, Switzerland) in $CDCl_3$. TMS was used as a reference for ^{1}H-NMR.

Supporting figures

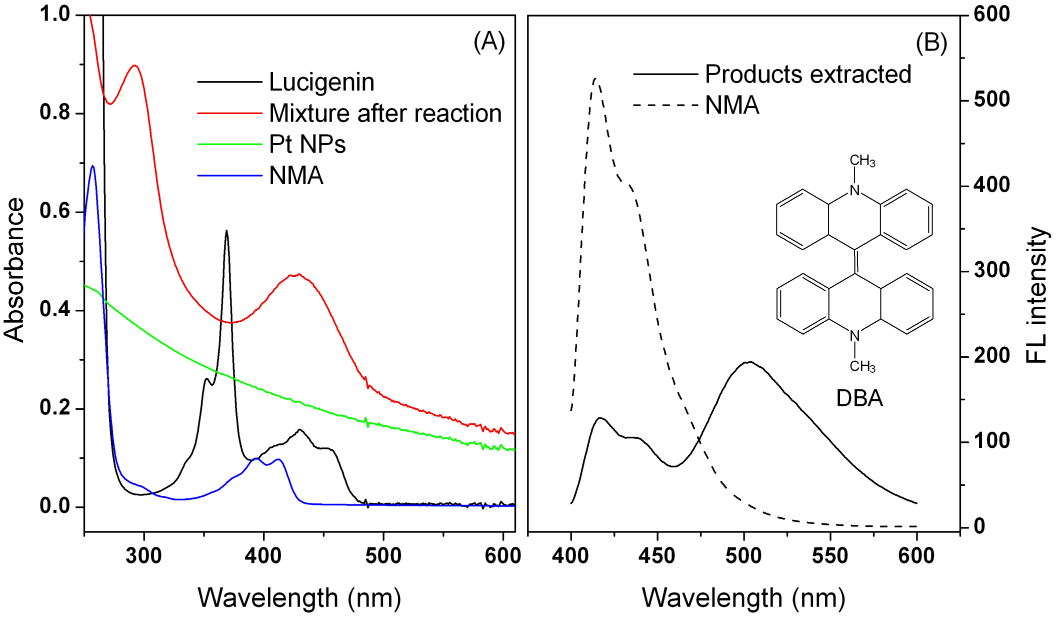

Figure S1 (A) UV-visible absorption spectra of lucigenin, NMA, Pt NPs and the resulted solution after CL reaction of lucigenin-NaOH-ethanol-Pt NPs. Lucigenin, 1.7 × 10^{-5} M in 0.017 M NaOH; NMA, 1.0 × 10^{-5} M in 10% (v/v) ethanol; Pt NPs, 17% (v/v). CL reaction condition: 1.0 mL of 5.0 × 10^{-5} M lucigenin mixed with 1.0 mL of 0.05 M NaOH, and then 1.0 mL of ethanol-Pt NPs solution. The concentrations of ethanol and Pt NPs in the injection solution were 30% and 50% (v/v), respectively. (B) Fluorescence emission spectra of NMA in chloroform and the products after CL reaction extracted by chloroform (excitation wavelength was at 380 nm). The concentration of NMA was 3.0 × 10^{-6} M in chloroform. In order to avoid the fluorescence quenching by Pt NPs, NaCl solid was first added to the mixture solution after CL reaction to salt-out Pt NPs, and then chloroform was added to extract the products. The emission spectra of extracted products not only exhibited the emission of NMA, but also another fluorescence emission around 500 nm, which is attributed to the byproduct DBA,[4] whose chemical structure is shown in the inset.

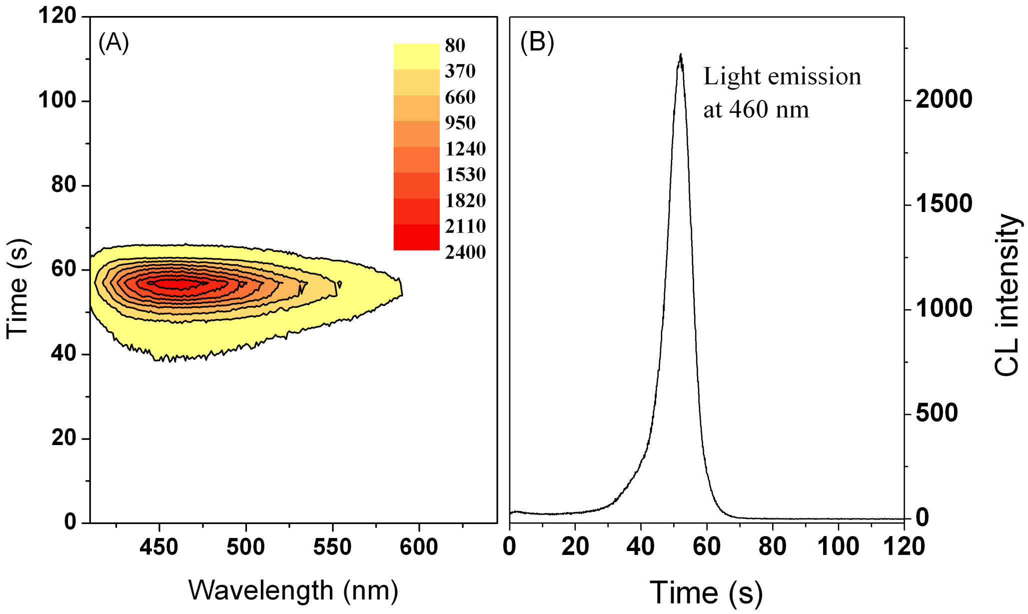

Figure S2 (A) Contour map of the CL spectra of lucigenin-NaOH system involving ethanol and Pt NPs. There is only one emission peak located at 460 nm, supporting that the emitter of the CL system is still the excited NMA. (B) Kinetic curve of light emission at 460 nm with time. CL reaction condition: 1.0 mL of 5.0 × 10^{-5} M lucigenin was mixed with 1.0 mL of 0.07 M NaOH, and then 1.0 mL of ethanol-Pt NPs solution was injected. The concentrations of ethanol and Pt NPs in the injection solution were 30% and 50% (v/v), respectively. The measurements started immediately after injection.

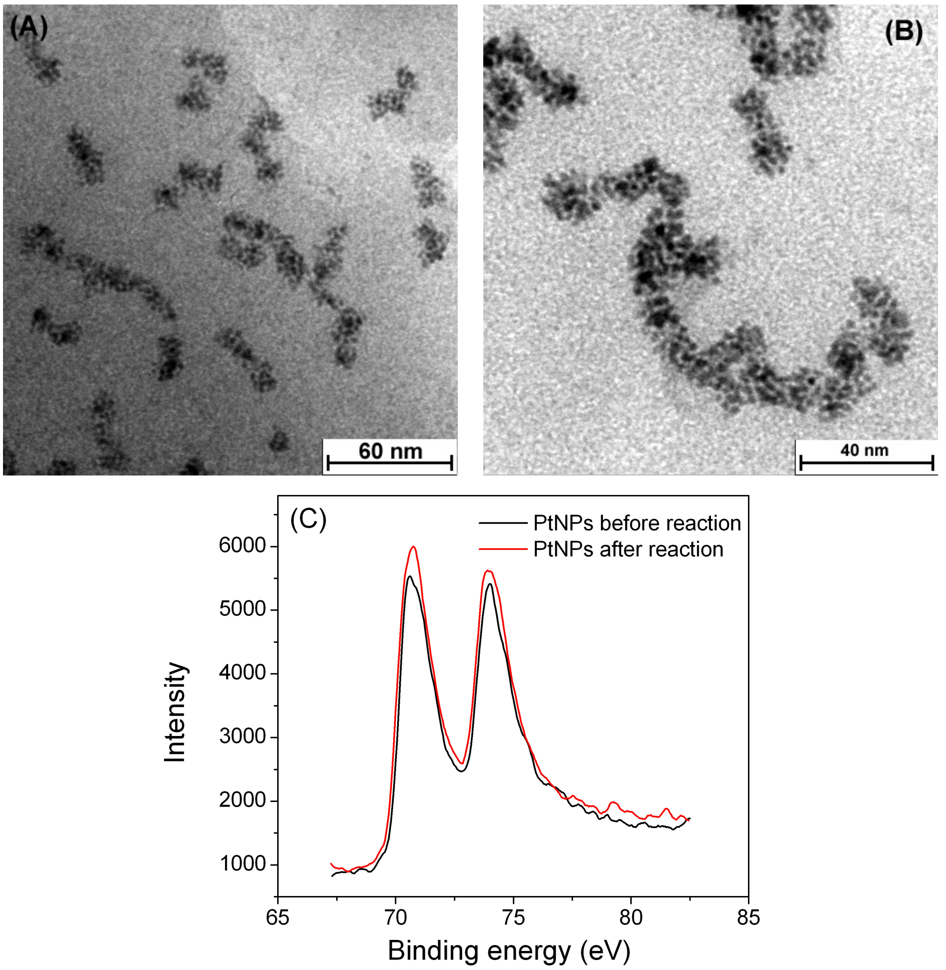

Figure S3 HRTEM of Pt NPs before (A) and after (B) CL reaction. The size of Pt NPs was 2-3 nm and did not change after CL reaction. (C) XPS of Pt NPs before and after CL reaction. The solid precipitates of Pt NPs was obtained by a salting out from the solutions with NaCl, collected after centrifugation and dried at room temperature. The CL reaction condition was the same as Fig.1

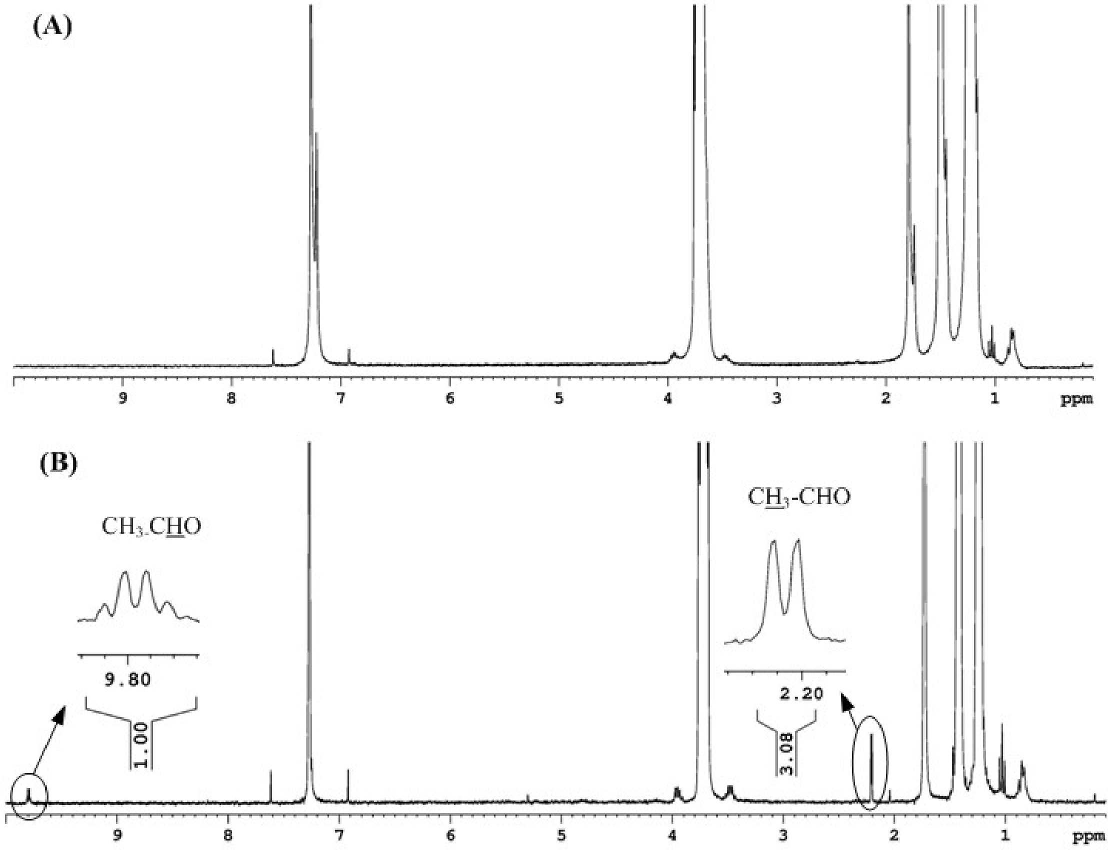

Figure S4 ^{1}H-NMR of the reaction products of lucigenin-NaOH-ethanol (A) and lucigenin-NaOH-ethanol-Pt NPs (B) system. The products were extracted from the reaction solution by $CDCl_3$. The reaction conditions were the same as Fig.1.

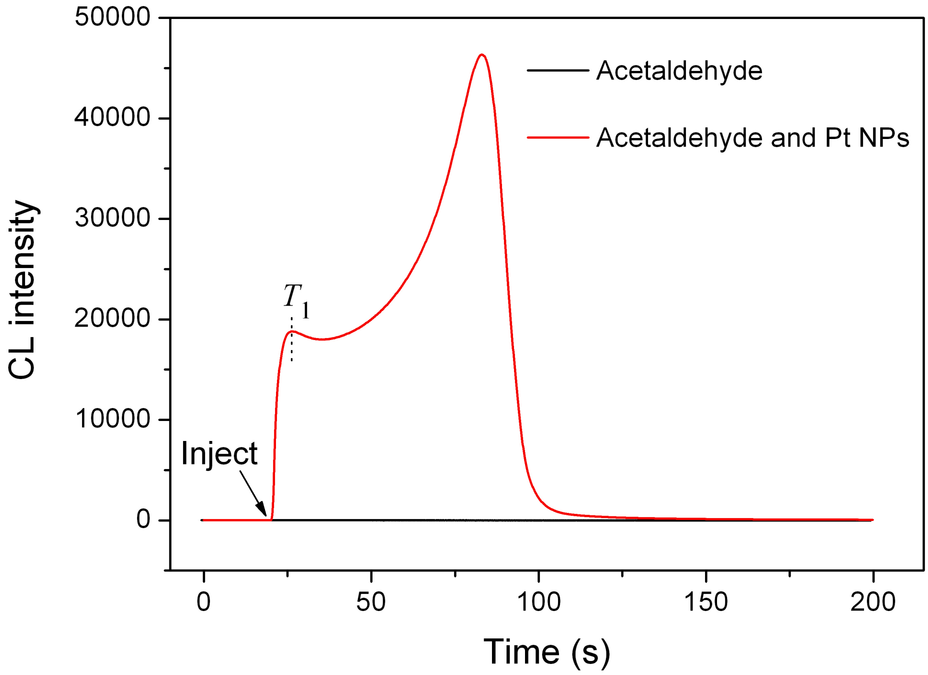

Figure S5 CL kinetic curves of lucigenin-NaOH system in the presence of acetaldehyde (20% v/v) and Pt NPs-acetaldehyde solution (with concentration of 50% and 20% (v/v), respectively). Other conditions were the same as Fig.1. The CL intensity at T_1 after injection (I ≈ 18800) was much higher than that in the presence of ethanol (50% v/v) shown in Fig.1 (I ≈ 2450).

References

[1] H. Cui, Z. F. Zhang and M. J. Shi, *J. Phys. Chem. C*, 2005, **109**, 3099; H. Cui, Z. F. Zhang, M. J. Shi, Y. Xu and Y. L. Wu, *Anal. Chem.*, 2005, **77**, 6402; Z. F. Zhang, H. Cui and M. J. Shi, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1017.

[2] J. M. Lin and M. L. Liu, *J. Phys. Chem. B*, 2008, **112**, 7850.

[3] A. Henglein, B. G. Ershov, and M. Malow, *J. Phys. Chem.*, 1995, **99**, 14129.

[4] K. Maeda, T. Kashiwabara and M. Tokuyama, *Bull. Chem. Soc. Jpn*, 1977, **50**, 473.