Supplementary Material (EIS)

pH-dependent Catalytic Properties of Pd-Ag Nanoparticles for Luminol Chemiluminescence

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Experimental

Chemicals. A 1.0 × 10^{-2} mol/L stock solution of luminol was prepared by dissolving luminol (Sigma, America) in 0.10 mol/L sodium hydroxide solution. ABTS was obtained from Bio Basic Inc. (Ontario, Canada). Poly vinyl pyrrolidone (PVP, Mw=36000), $AgNO_3$, $Pd(NO_3)_2$, and ascorbic acid were obtained from Shanghai Reagent (Shanghai, China). All reagents were of analytical grade, and used as received. Ultra-pure water obtained by a Direct-Q 3 UV water purification system (Millipore, USA) was used throughout.

Preparation of Pd-Ag Colloid. Pd-Ag Colloid were synthesized by chemical reduction method in a solution. In brief, 0.04 g PVP was dissolved in 4.0 mL water. Subsequently, 1.0 mL $AgNO_3$ (5.0×10^{-3} mol/L), 1.0 mL $Pd(NO_3)_2$ (5.0×10^{-3} mol/L) were added to this solution, and the formed suspension was mechanically stirred and diluted by 10.0 mL water to allow dissolution. HNO_3 (1.0 mol/L) was used to adjust the pH of the solution to 4.0. Then, 4.0 mL ascorbic acid (0.02 mol/L) containing 80 μL NaCl (0.05 mol/L) was added in the solution slowly, and the color of the mixture visibly changed to brown after 5 minutes. The reaction was conducted at room temperature for 30 min and the raw colloid was purified as follows: the raw colloid was centrifuged at 6000 rpm for 30 min (Universal 320, Hettich, Germany). The soft sediment was rinsed and resuspended by PVP buffer solutions (0.01 g/mL), which could adjust colloid to different pH value. The size and shape of the synthesized nanoparticles were characterized by high resolution transmission electron microscope (HRTEM, JEM-2010, Hitachi, Japan) and scanning electron microscope (SEM, JEOL JSM-6700F, Japan) as shown in Fig. S1 (Supporting Figures). Statistical analysis of HRTEM data revealed that the average diameter of the colloids was 40.0 ± 10.0 nm. The energy dispersive X-ray (EDX) spectroscopy was carried on the high resolution transmission electron microscope (HRTEM, JEM-2010, Hitachi, Japan). The XRD sample was prepared as follows: purified Pd-Ag colloid was centrifuged, and the precipitates obtained were thoroughly washed by water and alcohol. Then, they were dried at room temperature and were used for the studies of X-ray powder diffraction (XRD). XRD pattern was obtained with a model D/max-rA diffractometer (Rigaku, Japan).

CL Measurements. The CL was detected by a microplate luminometer (Centro LB 960, Berthold, Germany). In a typical experiment, 50 μL of Pd-Ag colloid was pipetted into each well of microtiter plate, and then 50 μL of luminol was injected into each well successively. The light emission was measured by the microplate luminometer immediately.

When investigating the effects of nitrogen and oxygen, the experiments were conducted on a flow injection CL system (Ruimai Electronic Science Co., China), including a model IFFM-D flow injection system, a model IFFS-A luminometer and a computer. Pd-Ag colloid carried by water mixed with luminol. The high potential of the photomultiplier tube was set as –800 V.

Optical Measurements. The CL spectra were measured on a model FL 5401 spectrofluorometer (Shimadzu, Japan). UV-visible spectra were measured on a model UV-2401 PC spectrophotometer (Shimadzu, Japan).

Supporting figures

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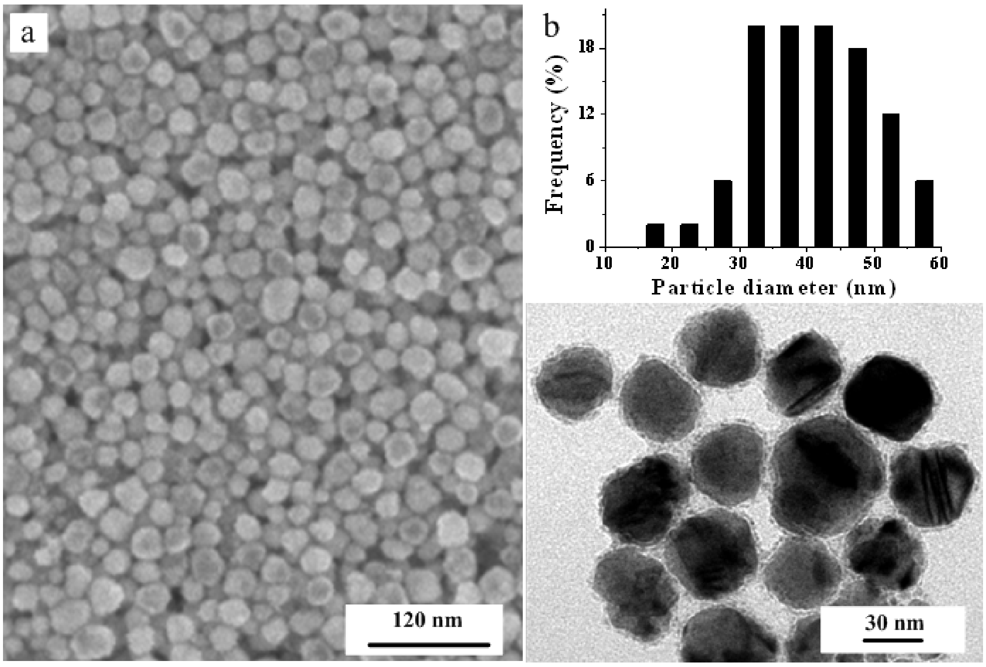

Figure S1. (a) SEM and (b) TEM image and the corresponding size distributions of Pd-Ag bimetallic nanoparticles.

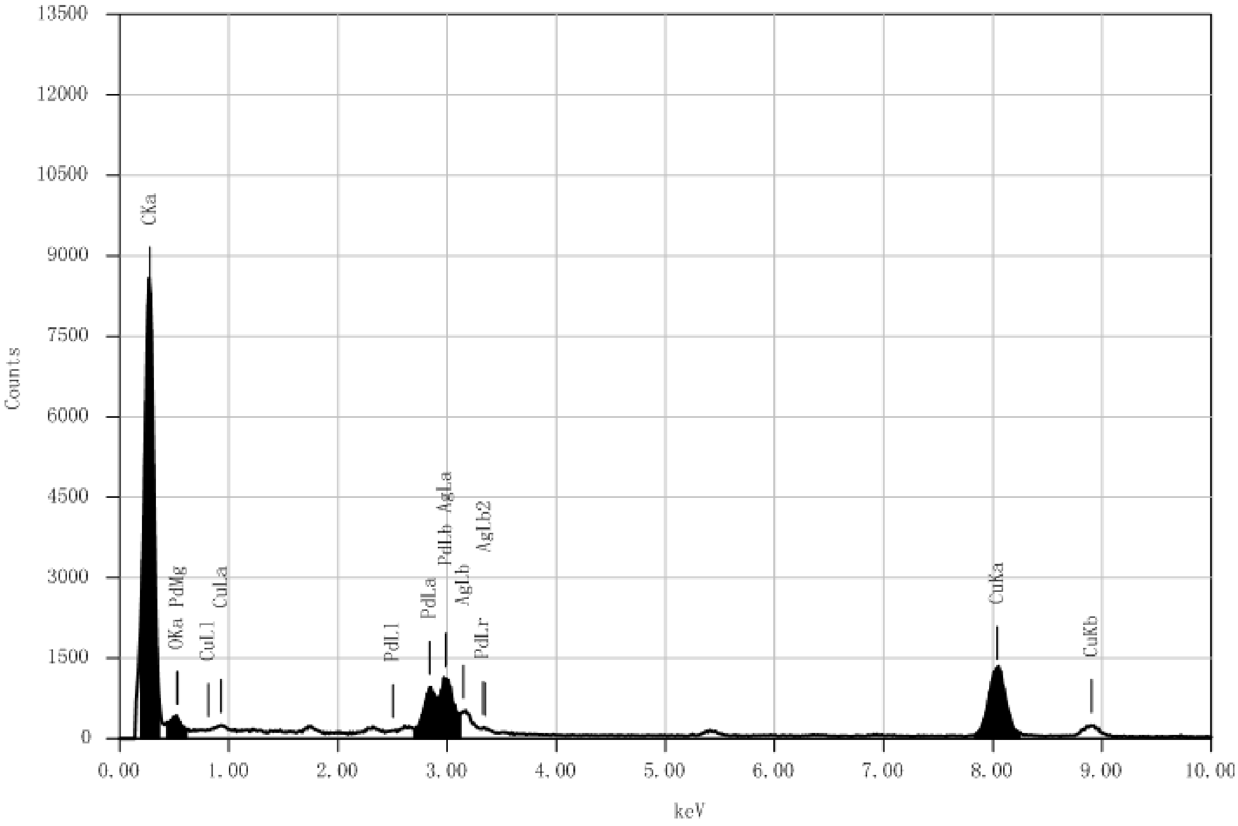

Figure S2. EDX spectrum of Pd-Ag NPs.

Based on the EDX analysis, the atomic ratio (Pd/Ag) was 1.1 : 1.

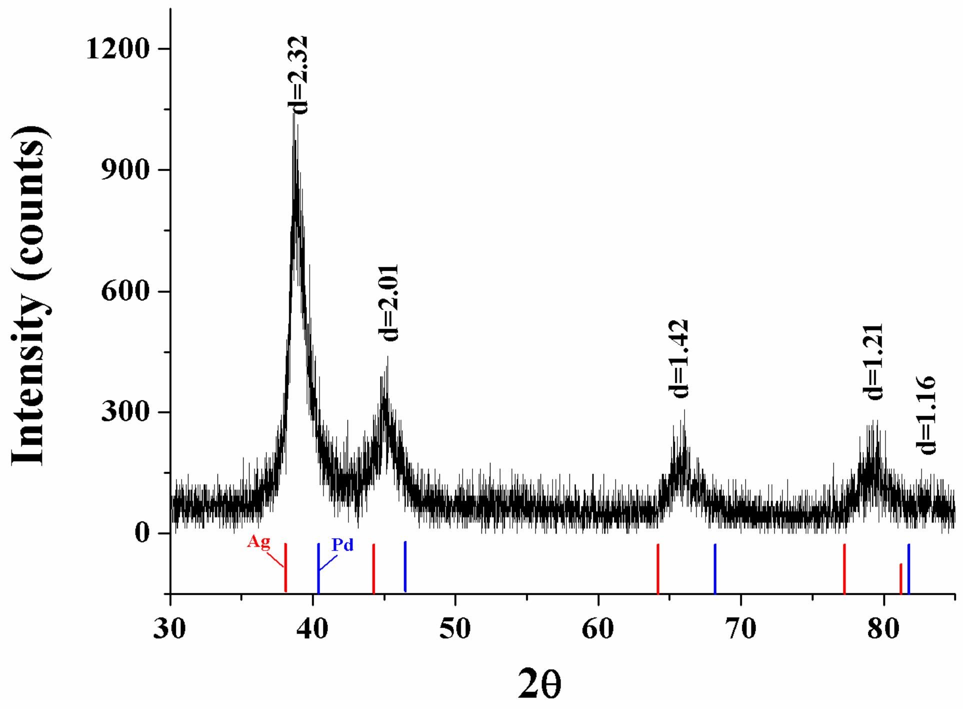

Figure S3. XRD patterns of the Pd-Ag NPs.

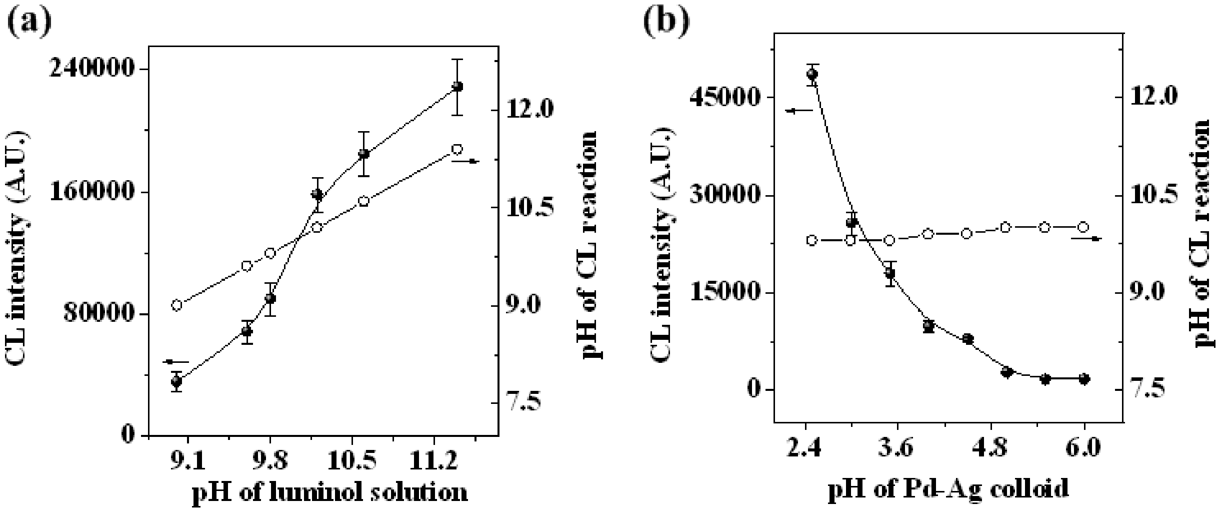

Figure S4. Effects of pH of (a) luminol solution and (b) Pd-Ag colloid on the CL intensity and the pH of the CL reaction. (a) Condition: Pd-Ag colloid dissolved in 0.01 g/mL PVP at pH 4.0 adjusted by HNO_3; 1 × 10^{-4} mol/L luminol in 0.1 mol/L carbonate buffer with different pH values. (b) Condition: 1 × 10^{-4} mol/L luminol in 0.1 mol/L carbonate buffer (pH 10.0); Pd-Ag colloid dissolved in 0.01 g/mL PVP with 0.02 mol/L acetic acid/sodium acetate buffer with different pH values.

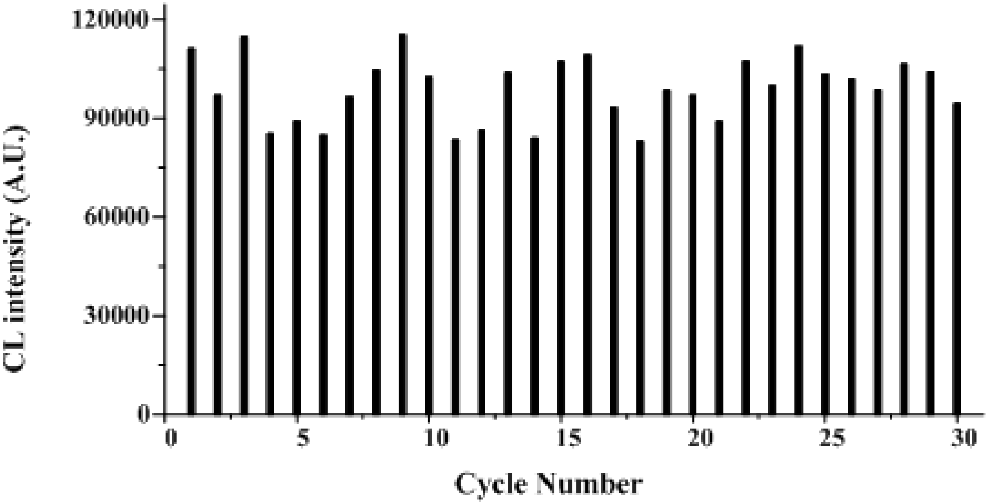

Figure S5. Reversible CL emission response of 30 consecutive acid/base cycles. Cycle step: (a) 50 mL of Pd-Ag colloid in 0.05 mol/L phthalic acid buffer (pH 4.0) reacted with 250 μL of 2.0×10^{-3} mol/L luminol in ~ 10 mol/L NaOH; (b) the colloid was acidified by ~ 10 mol/L HCl to pH 4.0; (c) 50 μL of the resulted colloid mixed with 50 μL of 1×10^{-5} mol/L luminol in 0.05 mol/L NaOH to produce CL. An acid/base cycle was finished. 30 consecutive acid/base cycles from (a) to (c) was executed.

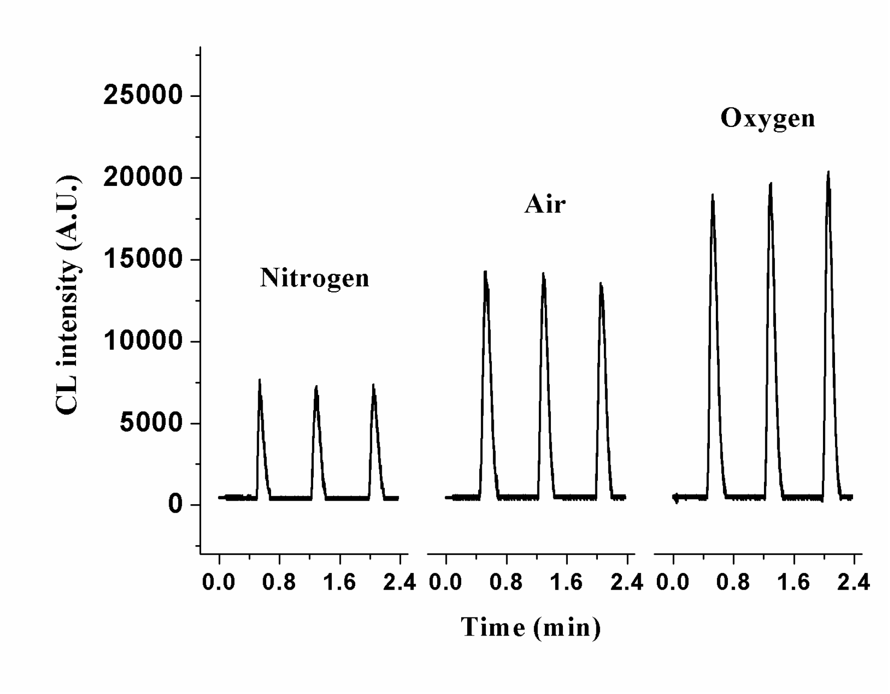

Figure S6. Effect of nitrogen and oxygen on the CL intensity on a flow injection CL system. Conditions: 1 × 10^{-4} mol/L luminol in 0.1 mol/L carbonate buffer (pH 10.0).

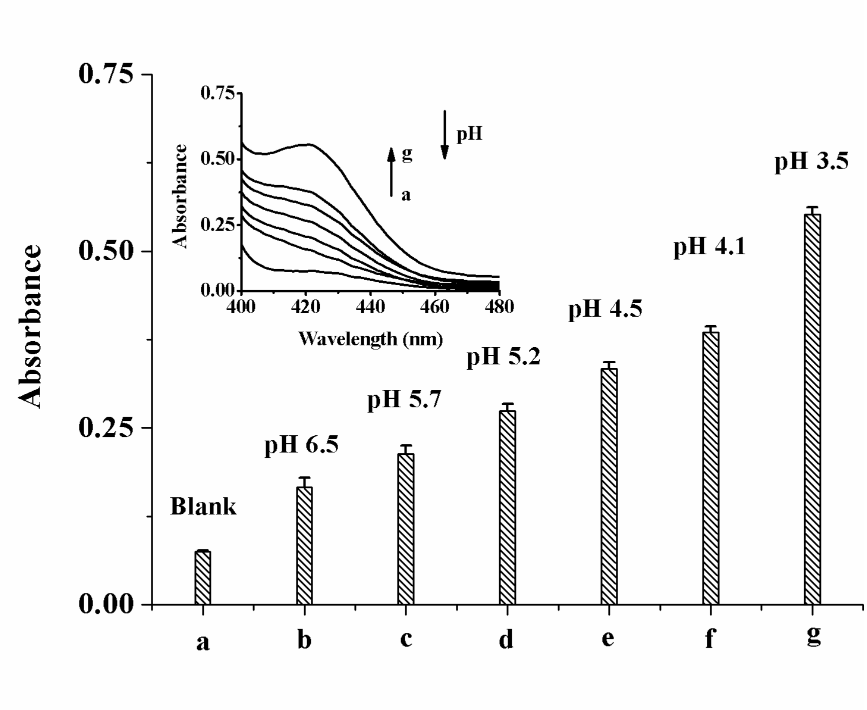

Figure S7. Absorbance at 418 nm of ABTS mixed with 0.02 mol/L acetic acid/sodium acetate buffer (pH 4.0) (a) or acidic Pd-Ag colloid in 0.02 mol/L acetic acid/sodium acetate buffer with various pH values, including 6.5(b), 5.7(c), 5.2(d), 4.5(e), 4.1(f). and 3.5(g). The inset is absorption spectra of ABTS mixed with blank (a) and acidic Pd-Ag colloid(b-g).

It was reported that ABTS could be oxidized by hydrogen peroxide by virtue of HRP catalysis and an increase in the absorbance at ~ 420 nm due to oxidation of ABTS could be monitored to obtain the reaction rate. We supposed that Pd hydroperoxide species might be similar to hydrogen peroxide in oxidative activity. Therefore, the acidic Pd-Ag colloid instead of hydrogen peroxide was used to oxidize ABTS by the bubbling of oxygen. After the oxidation reactions, the reacted mixture was centrifuged and the supernatant was employed to measure the absorbance at ~420 nm to avoid the interference of Pd-Ag colloid. The absorbance at ~ 420 nm increased after reaction for all of the acidic Pd-Ag colloids, demonstrating acidic Pd-Ag colloid with different pH could indeed oxidize ABTS. Moreover, the absorbance at ~420 nm increased with the decrease of pH, indicating that Pd hydroperoxide species had stronger oxidative activity under acidic conditions due to that more Pd hydroperoxide species in the acidic Pd-Ag colloids were formed. These results supported that the acidic Pd-Ag colloids in the presence of oxygen could produce oxidative species. Besides, this experiment also implied that Pd-Ag NPs may be used as pH-controllable catalysts for the aerobic oxidation of other organic compounds than luminol.

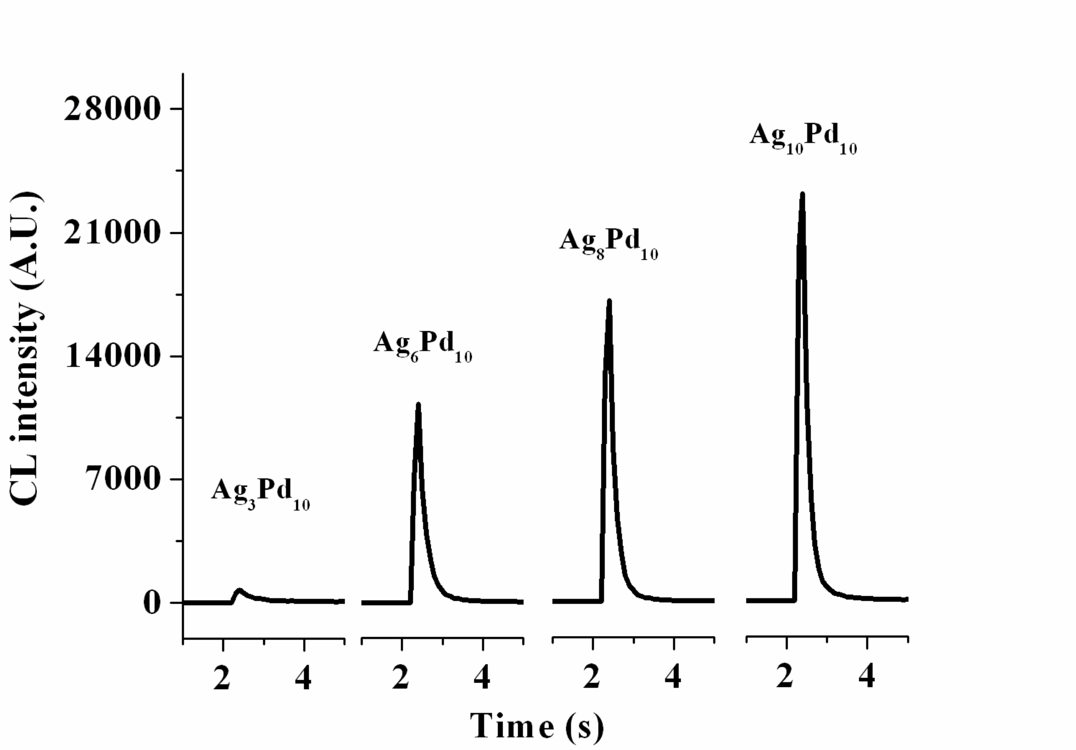

Figure S8. Effect of Ag content in Pd-Ag nanoparticles on the CL intensity. Conditions were the same as Fig.1.