Electronic Supplementary Information

Development of Electrochemiluminecence Sensor for Verapamil Hydrochloride based on TiO_2 sol/ZnO@Ag/Silica sol-$Ru(bpy)_3^{2+}$ Modified Pyrolytic Graphite Electrode

Ying LUO[a], Yingshi HUANG[b]*, Yanqing LI[c]* and Jun FENG[c]

[a] *School of Food and Chemical Engineering, Liuzhou Institute and Technology, No. 99, Xinliu Road, Liuzhou, Guangxi 545616, China*

[b] *Library, Shanghai University of Engineering Science, No. 333, Longteng road, Shanghai 201620, China*

[c] *College of Biological and Chemical Engineering, Guangxi University of Science and Technology, No. 268, Donghuan Road, Liuzhou, Guangxi 545006, China*

**Corresponding author*: *liyanqing@gxust.edu.cn, 26120002@sues.edu.cn*

Contents

1. Preparation of nano-TiO_2 sol

Nano-TiO_2 sol was prepared by sol-gel method with $TiCl_4$ as a precursor. In a typical experiment, 4 mL of $TiCl_4$ was first pumped into 100 mL ethanol (EtOH) solution with magnetic stirring to form a kind of semi-transparent green-yellowish sol. 20 mL of this dispersion was subsequently treated with 37 mL of 2.5 wt% ammonia drop by drop. The precipitate was filtered and washed with distilled water several times to neutral. The washed products were then dissolved into 30 mL of H_2O_2 solution, and then mixed with 5 mL of silica sol and 65 mL water. Nano-TiO_2 sol was obtained by refluxing at 90 ℃ for 4 h.

2. Preparation of nano-Ag

Silver seeds were prepared by using silver nitrate as precursor and PVP as stabilizer and reductant. 0.169 g silver nitrate and 1 g PVP were added respectively to 50 mL ethanol with vigorous stirring, both of which reacted individually at 40 ℃ and 60 ℃ for about 10 min. Silver nitrate solution, then, was introduced into the PVP solution, and Ag sol was obtained as the mixture was stirred vigorously for 2 h (Fig. S1).

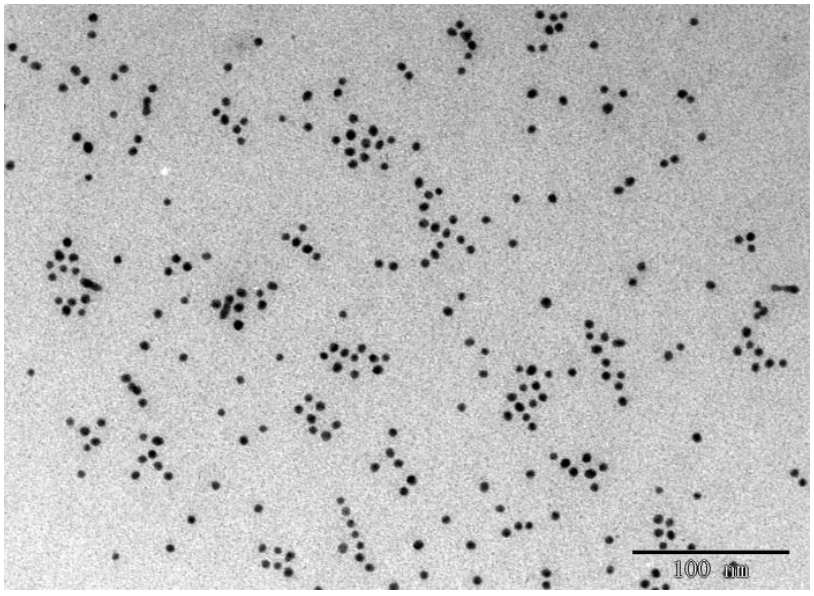

Figure S1. TEM image of nano-Ag

3. Preparation of nano-ZnO

0.2195 g zinc acetate dehydrate was dissolved into 50 mL of ethanol solution under constant stirring at 60 ℃ for 20 min. Meanwhile, 1×10^{-2} mol L^{-1}NaOH solution was prepared by dissolving 0.04 g NaOH in 50 mL ethanol under stirring at 50 ℃ for 20 min. The zinc acetate dehydrate solution was heated to 50 ℃ and 5.0 mL of PEG 200 was doped under even stirring for 10 min, and then the NaOH solution was rapidly added into the mixed solution of zinc acetate dehydrate and PEG 200 under the conditions of reaction temperature 50 ℃, reaction time 10 min and fully stirred, and the nano-ZnO solution was obtained (Fig. S2).

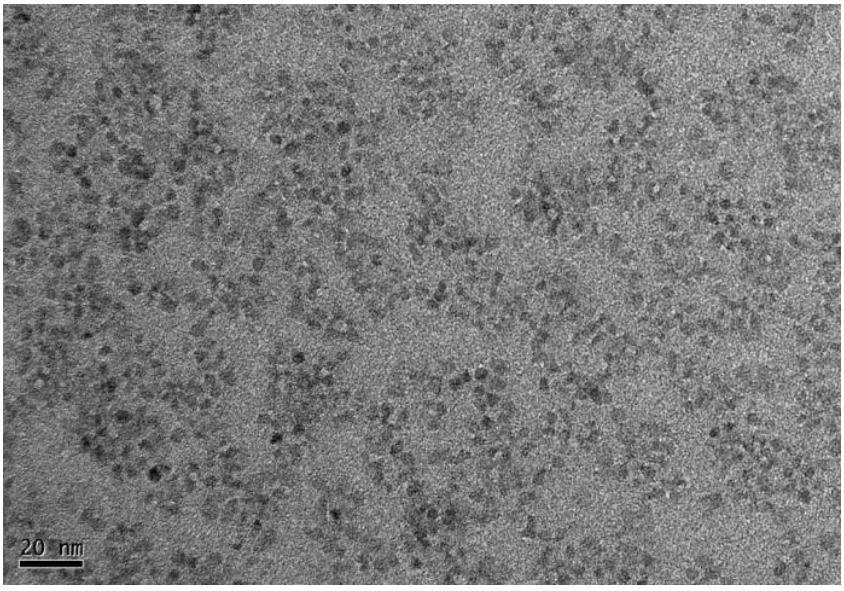

Figure S2. TEM image of nano-ZnO

4. Synthesis of ZnO@Ag core-shell quantum dot

The ZnO@Ag core-shell structures were fabricated by a simple and convenient method in the ethanol at relative low temperature. Firstly, Ag sol was prepared according to “2 Preparation of nano-Ag”. Secondly, 0.04 g NaOH was dissolved in 50.0 mL ethanol under stirring at 50 ℃ for 20 min, and 0.2195 g zinc acetate dehydrate was dissolved into 50.0 mL of ethanol solution under constant stirring at 60 ℃ for 20 min. Moreover, zinc acetate dehydrate solution was well-mixed with Ag sol with the color of solution changing from yellow to grey. Finally, 5.0 mL of PEG

200 was doped into the compound solution for another 10 min at 50 ℃, and then 1×10^{-2} mol L^{-1} NaOH solution was rapidly added (within 30 s) at 40 ℃ under constant stirring for 1 h, and ZnO@Ag core-shell structures were gained (Fig. S3).

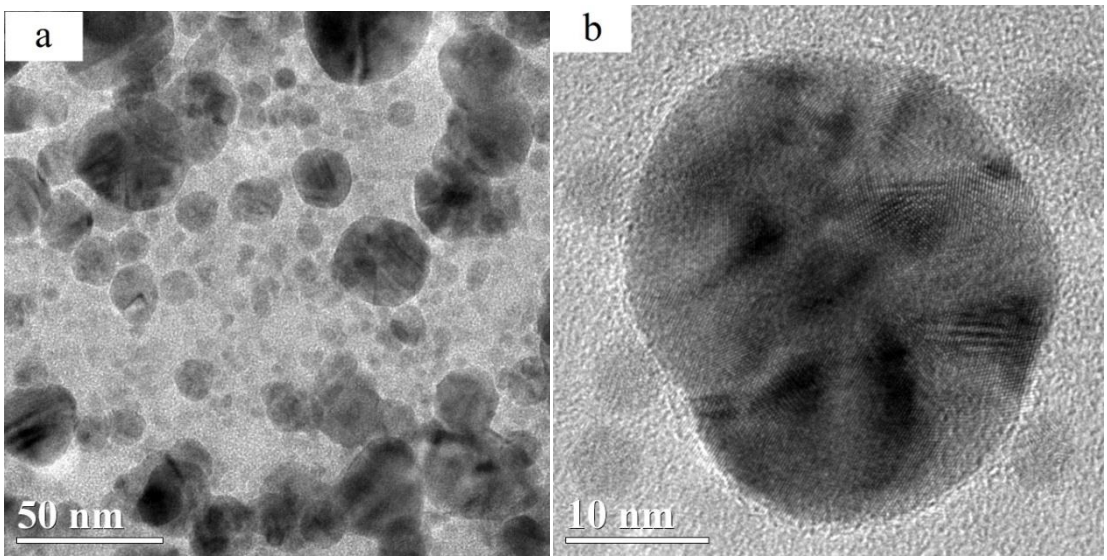

Figure S3. TEM images of ZnO@Ag core-shell quantum dot

5. Optimization of instrument parameters

The influences of different negative high voltage (600-900 V) and potential scan rate (40-140 mV s^{-1}) on the ECL intensity and stability were studied. The results demonstrated the ECL response of $Ru(bpy)_3^{2+}$-VpCl system increased on increasing negative high voltage and potential scan rate. It was widely known that the ratio of anode current to cathode current increased with increasing of the PMT volage when incident luminous flux reached a certain level, so enhancing supply voltage was benefited to amplify optical signal and promote the ECL intensity. Whereas noise signal was simultaneously increased and the instrument could be damaged possibly. Thus a negative high voltage of -800 V and a scanning rate of 100 mV s^{-1} were selected.

6. UV/Vis absorption spectra of ZnO@Ag

The UV/Vis absorption spectra of ZnO@Ag has two distinct absorption peeks (333 nm and 412 nm), and the wavelength range of ZnO@Ag was 300-500 nm.

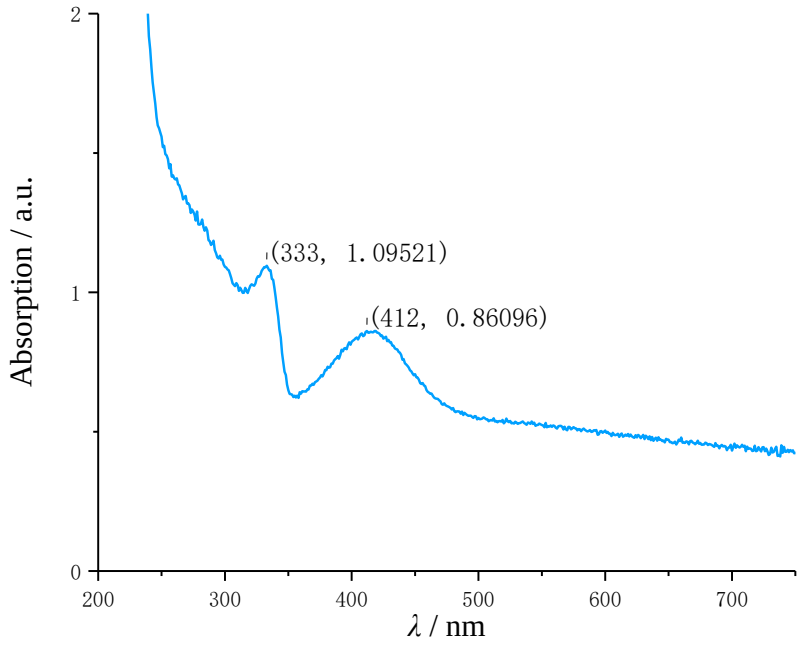

Figure S4. UV/Vis spectrum for ZnO@Ag solution