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Electrogenerated chemiluminescence of novel TiO_2/CdS nanocomposites for sensitive assays of cancer cells

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ABSTRACT

A novel TiO_2/CdS nanocomposite was prepared and used to fabricate an electrochemiluminescence (ECL) biosensor for the detection of cancer cells for the first time. The nanocomposite exhibited a strong cathodic ECL signal. Folic acid for targeting cell membranes was bound to a TiO_2/CdS/3-aminopropyltriethoxysilane film, and specific recognition of folic acid to targeting cells was achieved, leading to a significant decrease in ECL intensity. The decrease in ECL signal was logarithmically related to the cell concentration in the range of 150–9600 cells mL^{-1}. The ECL biosensor could provide a sensitive, selective, and convenient approach for early and accurate detection of cancer cells.

Electrogenerated chemiluminescence (ECL) is the process in which electrogenerated radicals form excited species emitting light without the need of an external light source [1]. Advantages of ECL include simultaneous generation of radical cations and anions and the control of electrode potentials that drive light emission processes. ECL has great potential in biological applications such as detection in immunoassays, food and water testing, trace metal determination, sensors, and biomolecules [1]. Semiconductor nanomaterials with excellent optical properties have been the focus of widespread research and are used in applications such as optoelectronics, biological labeling, and biomedical devices [2–4]. Since the ECL of Si quantum dots (QDs) was first observed by Bard and colleagues[5], the ECL properties of semiconductor nanomaterials have attracted more and more attention; especially II–VI nanocrystals containing CdS, CdSe, and CdTe have become the most popular ECL emitters in aqueous systems [6–9]. Recently, some relatively environmentally friendly nanomaterials such as carbon nanocrystals and gold clusters [10,11] have been used in ECL biosensors.

Our motivation is to explore ECL of various compounds [12,13] toward application in biosensors and bioanalytical chemistry. Core–shell nanocomposites (CSNs), including multiphase semiconductors, metal–semiconductors, and metal–metal nanocomposites, have been the subject of extensive research in the past decades, because of their tunable surface properties; enhanced optical, electronic, and catalytic properties; and potential applications in many areas such as microelectronics, optoelectronics, optical devices, and catalysis [14–17]. As two of the most studied semiconductor photocatalysts in practical applications, CdS and TiO_2 have attracted great attention. These two semiconductors are often coupled to each other, because of their matched band structures. Hitherto, many attempts have been made to fabricate andutilize CdS/TiO_2 one-dimensional (1D) CSNs as photocatalysts [18–20]. For instance, nanorods of CdS, CdSe, and CdSeS have been deposited by chemical vapor deposition onto TiO_2 nanorod arrays [21]. Misra and co-workers synthesized 1D CdS/TiO_2 CSNs by filling 1D TiO_2 nanotubes with CdS nanoparticles [22]. It is of great interest to study the ECL of CdS/TiO_2 CSNs, since no ECL research, to the best of our knowledge, has been reported.

In addition, cancer is today's most pressing health concern. It has been reported that very sensitive monitoring of cancer cells could provide an easier and more effective way to monitor progression of the disease [23–25]. Consequently, the research into accurate and sensitive recognition and detection of cancer cells is extremely important for cancer diagnosis and therapy. Furthermore, QD ECL has been used for DNA and cell detection [26,27]. However, the ECL of TiO_2/CdS has not been reported or applied to the detection of cancer cells.

Folic acid is a ligand that is useful for targeting cell membranes and enhancing nanoparticle endocytosis via the folate receptor. It is a stable, inexpensive, and generally poorly immunogenic chemical with a high affinity for the folate receptor [28]. The folate receptor is a well-known tumor-associated receptor that is overexpressed in many tumors, including those of the breast, lung,

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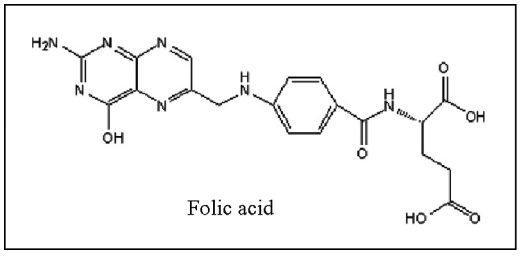
kidney, and brain [29]. Previous studies have shown the potential targeting abilities of folic acid due to the overexpression of folate receptors in cancer cells [30]. In general, tumors overexpressing folate receptors are better suited as candidate targeting moieties for folic acid [31].

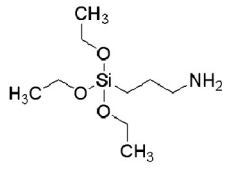
In this work, we prepared a novel TiO_2/CdS nanocomposite with strong and efficient ECL signal and fabricated an ECL biosensor for the detection of cancer cells for the first time. 3-Aminopropyltriethoxysilane (APS) was used as a cross-linker and could greatly enhance the ECL of the nanocomposite. Folic acid as a ligand was applied to specifically recognize and target cancer cells. The prepared ECL biosensor could be used to detect the concentration of cancer cells in the range of 150–9600 cells mL^{-1} We anticipate that the TiO_2/CdS nanocomposite will become a promising ECL emitter because of its excellent properties, which have great potential in the development of ECL biosensors. The ECL biosensor could provide a sensitive and selective approach for early detection of cancer cells.

Experimental procedures

Reagents

Sodium sulfide (Na_2S), cadmium chloride ($CdCl_2{\cdot}2.5H_2O$), APS polyelectrolyte, and folic acid (FA) were obtained from Shanghai Bailingwei Biochemical Co., Ltd. (Shanghai, China). The structures of FA and APS are shown below.





All other reagents were of analytical grade and used as received without further purification. Phosphate-buffered saline (PBS; 0.1 M) of various pH's was prepared by mixing the stock solutions of NaH_2PO_4 and Na_2HPO_4 and then adjusting the pH with 0.1 M NaOH and H_3PO_4. Unless otherwise mentioned, ultrapure fresh water obtained from a Millipore water purification system (MilliQ; specific resistivity >18 MV cm^{-1}; S.A. Molsheim, France) was used throughout this work. TiO_2 nanoparticles (30–40 nm) were obtained from Henan Huier Nanotechnology Co.

Cells

Ramos cancer cells and control normal cells were obtained from the Chinese Academy of Medical Sciences. The cell density was determined using a hemocytometer, and this was performed prior to any experiments. During all experiments, the cells were kept in a refrigerator at 4 °C.

Apparatus

Transmission electron microscopy (TEM) images were recorded using a Jeol JSM-6700F instrument (Hitachi). Scanning electron microscopy (SEM) was carried out on a Jeol JSM-6340F instrument. UV absorption spectra were acquired with a Ruili 1200 photospectrometer (Peking Analytical Instrument Co., Beijing, China).

Preparation of the TiO_2/CdS nanocomposite and folic acid

TiO_2 (0.01 g) was transferred into a 1.5-ml Eppendorf tube, and 500 μl of $CdCl_2$ solution (0.1 M) was added and sonicated thoroughly for 5 min to get a homogeneous mixture. They were then centrifuged at 3000 rpm for 3 min to remove superfluous Cd^{2+}. The resulting TiO_2/Cd^{2+} nanocomposites were subsequently dispersed in a solution of Na_2S (0.1 M) for another 5 min. They were then sonicated and centrifuged to remove unbound sulfur ion. This process was repeated three times until the desired TiO_2/CdS nanocrystallites were achieved.

The TiO_2/CdS nanocomposite obtained was then mixed with APS solution (4/1, v/v) under gentle shaking to get a homogeneous TiO_2/CdS/APS mixture.

The folic acid was soluble in dimethyl sulfoxide (Me_2SO), and a solution of 1.84 mM folic acid in Me_2SO was prepared.

Fabrication of the ECL biosensor for cell assay

The fabrication principle of the ECL biosensor for cells assay is illustrated in Scheme 1. The Au electrode was polished carefully with 1.0-, 0.3-, and 0.05-μm α-Al_2O_3 powder on fine abrasive paper and washed ultrasonically with water. Six microliters of TiO_2/CdS/APS nanocomposite solution was dropped onto the electrode surface and dried in air. Then 8 μL of Me_2SO solution of FA was dropped onto the electrode surface, and the electrode was put in a moist environment (37 °C) overnight.

For cell assay, the cell density was determined using a hemocytometer, after which, 1×10^6 cells dispersed in RPMI 1640 cell medium buffer were centrifuged at 3000 rpm for 5 min and redispersed in 1 mL of PBS (10 mmol). During all experiments, the cells were kept in an ice bath at 4 °C.

After the TiO_2/CdS/APS/FA-modified electrodes were washed with 0.01 M PBS to remove superfluous FA, the electrodes modified with TiO_2/CdS/APS/FA were covered with 200 μL PBS containing various numbers of cells in a moist environment for 50 min. Then the electrodes were washed and ECL measurements were performed.

ECL detection

ECL emission was detected with a Model MPI-A electrochemiluminescence analyzer using a three-electrode system at room temperature. The electrodes were a modified magnetic Au disk working electrode (4-mm diameter), a saturated calomel reference

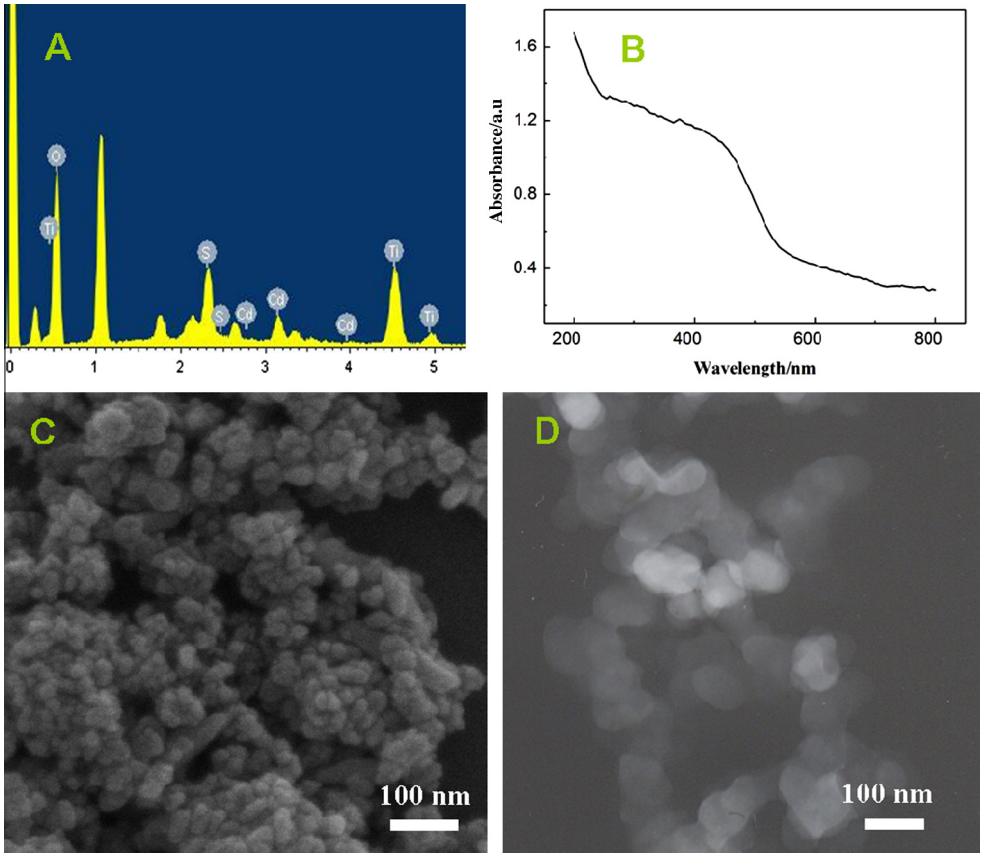


Fig.1. (A) Energy-dispersive X-ray spectroscopy and (B) UV–Vis spectra of the TiO_2/CdS nanocomposites. (C) SEM image of TiO_2 nanoparticles, (D) TEM image of TiO_2/CdS nanocomposites.

electrode, and a Pt counterelectrode. The electrodes modified as above were in contact with 0.1 M PBS (pH 7.4) containing 0.05 M $K_2S_2O_8$ and 0.1 M KCl and scanned from 0 to −1.5 V. The spectral width of the photomultiplier tube (PMT) was 200–800 nm, the voltage of the PMT was −800 V, and the scan rate was 100 mV s^{-1} in the detection process. ECL signals related to the cell concentrations could be measured.

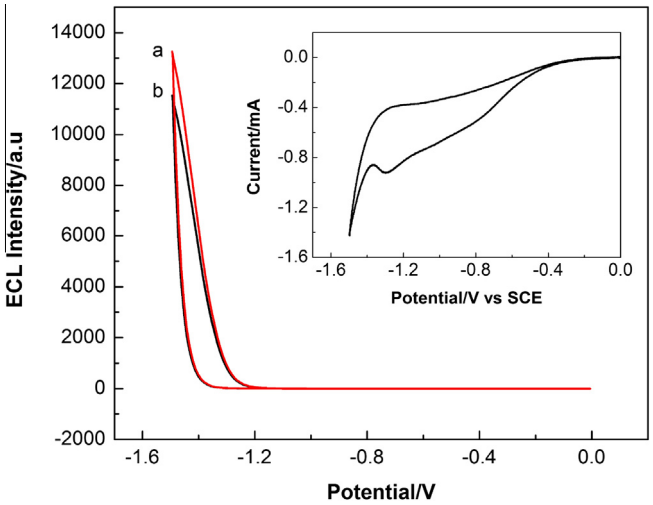


Fig.2. ECL-potential curves of TiO_2/CdS/APS (curve a) and TiO_2/CdS/APS/folic acid (curve b) nanocomposites on the electrode. Inset is the cyclic voltammogram of TiO_2/CdS/APS/folic acid on the electrode.

Results and discussion

Preparation and characterization of TiO_2/CdS nanocomposites

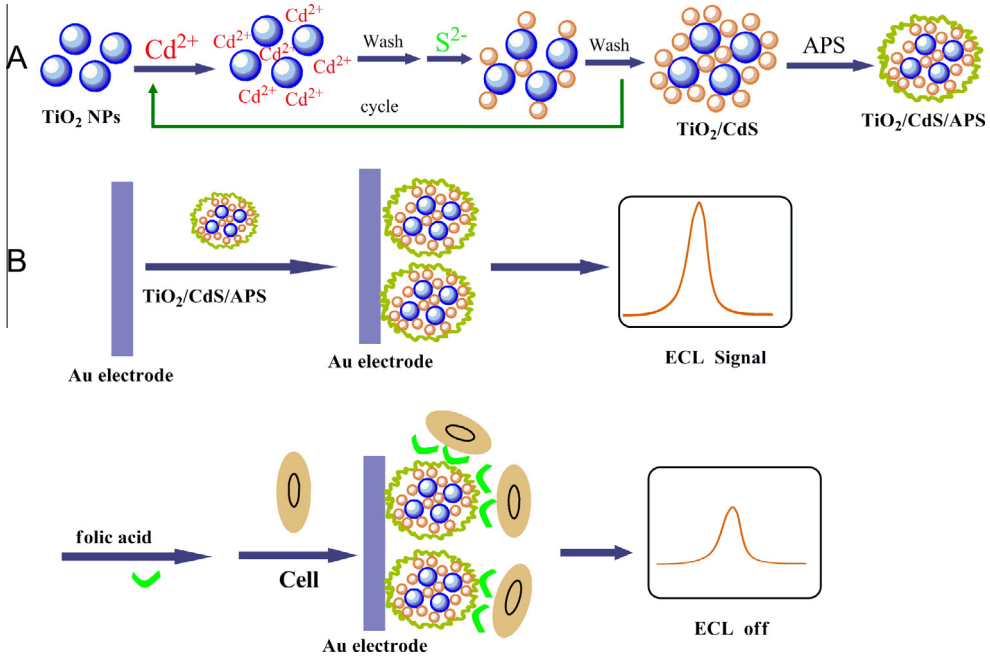
It is reported that solution-based deposition of CdS and CdSe quantum dots on oxide surfaces has been successfully employed by Hodes and co-workers [32–34]. As shown in Scheme 1A, the TiO_2 nanoparticles were sequentially exposed to solutions of $CdCl_2$ and Na_2S to deposit CdS on the TiO_2 surface. We have now succeeded in growing CdS nanocrystallites on TiO_2 nanoparticles by the successive ionic layer adsorption and reaction technique.

To confirm the elemental composition of the TiO_2/CdS core shell nanocomposites, energy-dispersive X-ray spectroscopy (EDX) has also been carried out. The results (Fig. 1A) demonstrate that the core shell TiO_2/CdS nanocomposite contains the elements Ti, O, Cd, and S. In addition, the TiO_2/CdS composite nature is further evidenced by UV–Vis spectra (Fig. 1B). The composite sample exhibits two absorption edges corresponding to TiO_2 (at 370 nm) and CdS (at 549 nm), with strong absorbance in the visible light region.

The morphology and microscopic structure information of TiO_2 was determined by a SEM (Fig. 1C). The average diameter of the TiO_2 nanoparticle was about 30–40 nm. Fig. 1D shows the TEM image of the TiO_2/CdS nanocomposites; the nanocomposites have an average diameter of 60–80 nm and are uniform in size and morphology. The results indicate that CdS nanocrystallites were successfully formed on the TiO_2 nanoparticles, which was consistent with the EDX and UV–Vis spectra of the TiO_2/CdS nanocomposites.

ECL behavior of the TiO_2/CdS core shell nanocomposites

Fig. 2 (curve a) shows an ECL-potential curve and cyclic voltammogram (inset) of TiO_2/CdS nanocomposites on the electrode. One



Scheme 1. Schematic representation strategy for (A) preparation of TiO_2/CdS/APS nanocomposites and (B) cell assay based on ECL of TiO_2/CdS nanocomposites.

ECL peak was observed at −1.49 V in the cathodic process, resulting from the reaction of TiO_2/CdS with $S_2O_8^{2-}$. When the potential was scanned in the negative direction, TiO_2/CdS immobilized on the electrode was reduced to nanocrystalline species ($TiO_2/CdS^{\cdot-}$), while the coreactant $S_2O_8^{2-}$ was reduced to the strong oxidant $SO_4^{\cdot-}$. Then $SO_4^{\cdot-}$ could react with the negatively charged $TiO_2/CdS^{\cdot-}$ through electron transfer, leading to the excited state (TiO_2/CdS^*), which emits light. The possible ECL mechanisms are as follows:

$$TiO_2/CdS + e^- \rightarrow TiO_2/CdS^{\cdot-} \quad (1)$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\cdot-}, \quad (2)$$

$$TiO_2/CdS^{\cdot-} + SO_4^{\cdot-} \rightarrow TiO_2/CdS^* + SO_4^{2-}, \quad (3)$$

$$TiO_2/CdS^* \rightarrow QD + h\nu. \quad (4)$$

Fabrication and characterization of the ECL biosensor for cell assays

The fabrication principle of the ECL biosensor for cancer cells is shown in Scheme 1B. The obtained TiO_2/CdS nanocomposite was covalently conjugated to APS by the reaction of carboxyl groups of CdS with amino groups of APS. After the TiO_2/CdS/APS film was formed on the electrode, the TiO_2/CdS/APS nanocomposites displayed high and stable ECL signal (Fig. 2, curve a). Then the folic acid with carboxyl groups as the ligand for targeting cell membranes was covalently conjugated to APS with amino groups, and the ECL signal slightly decreased (Fig. 2, curve b). Subsequently, specific recognition of folic acid to targeting cancer cells was achieved, which led to an obvious decrease in ECL signal. The reason was that the targetingcancer cells with large volume greatly inhibited the ECL reaction of TiO_2/CdS on the electrode and thus decreased the ECL intensity, which suggested that the target cancer cells can be detected by the ECL signal.

SEM images (Fig. 3) were used to characterize the morphology of the electrode surface in the fabrication process of the ECL biosensor. The bare gold surface was clean and smooth (Fig. 3A). By comparison, when the TiO_2/CdS/APS nanocomposites were immobilized on the electrode, the nanocomposite film spread over the surface very uniformly, and the nanoparticles' morphology on the surface was observable (Fig. 3B).

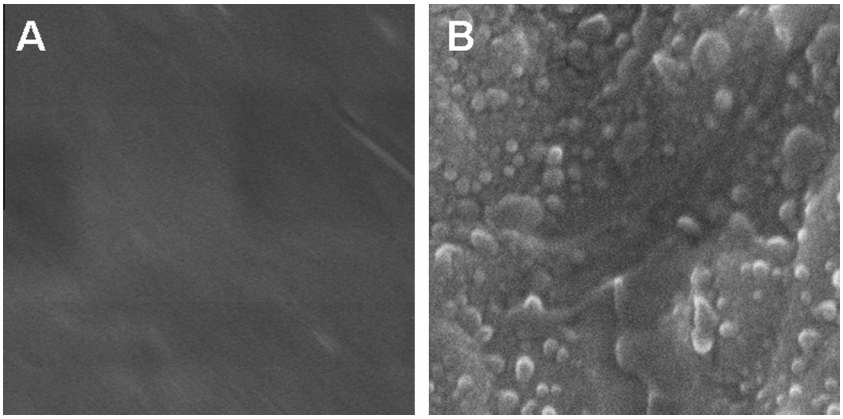


Fig.3. SEM images of (A) bare gold electrode surface and (B) the electrode surface with TiO_2/CdS/APS nanocomposites.

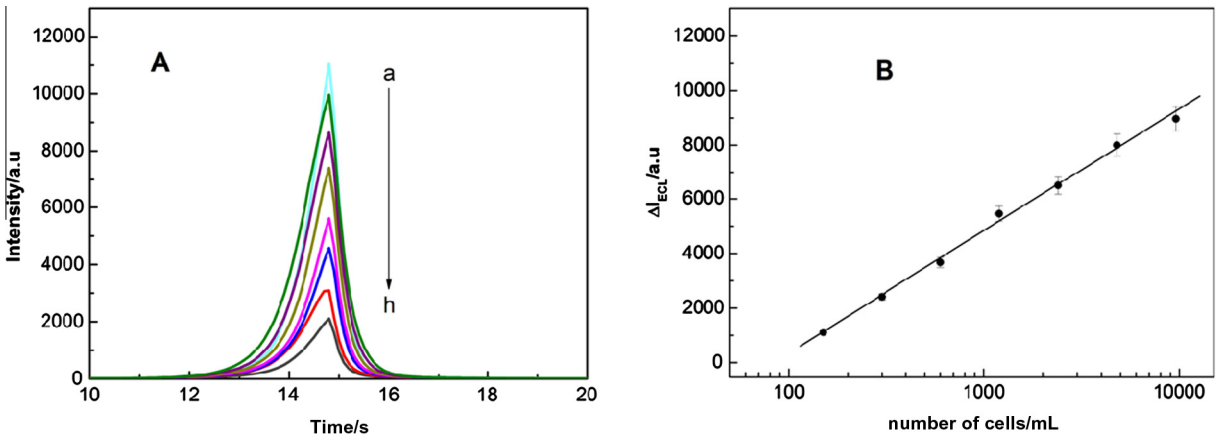


Fig.4. (A) ECL signals for detection of various numbers of target cells. (B) Calibration curves for detection of cells from 150 to 9600 cells ml^{-1}.

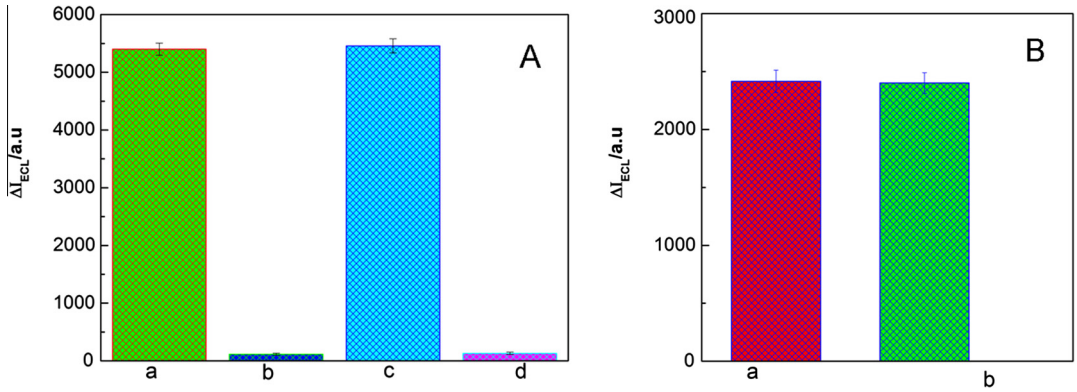


Fig.5. (A) The ECL response in bar graph form to (lane a) the Ramos target cancer cells in serum, (lane b) the control normal cells in serum, (lane c) the Ramos target cancer cells in cell medium, and (lane d) the control normal cells in cell medium. The number of cells was 1200 cells mL^{-1}. (B) The ECL response in bar graph form to (lane a) the pure target cells (300 cells mL^{-1}) and (lane b) the mixture of cancer cells (300 cells mL^{-1}) and normal cells (3000 cells mL^{-1}). Graph (A) indicates that the target cancer cells in both sample and medium obviously show a significantly higher signal compared to the normal cells. Graph (B) indicates that the normal cells cannot exert an obvious effect on ECL response.

ECL assay of the cells based on TiO_2/CdS nanocomposites

Fig. 4A shows the ECL signals of the biosensor that were responsive to various concentrations of target cancer cells. When the TiO_2/CdS/APS nanocomposites and then folic acid ligand were immobilized on the electrode, the ECL signal was very high (curve a). However, after the target cells were captured by the folic acid ligand on the electrode, the ECL peak intensity remarkably decreased owing to the increased inhibition effect of cells on the electron transfer. The ECL signal decreased gradually with increasing cell concentrations (from curve b to h), indicating that the cell concentrations could be detected by ECL.

The standard calibration curve for cell detection is shown in Fig. 4B. The increase in ECL signal was proportional to the cell concentrations in the range from 150 to 9600 cells mL^{-1} The detection limit was 96 cells mL^{-1} at 3σ. As 200 μL of cells in PBS was used for our experimental detection, this detection limit was equivalent to 20 cells/200 μL, suggesting that this strategy is highly sensitive and has great potential for early and accurate detection of cancer cells. A series of five duplicate measurements of 300 cells mL^{-1} was used for estimating the precision, and the relative standard deviation was 6.1%, showing good reproducibility.

The feasibility of the ECL assay for actual applications was investigated, as shown in Fig. 5. Target cancer cells and normal cells at the same concentration (1200 cells mL^{-1}) were spiked into two different samples and then measured using the ECL method (Fig. 5A, lanes a and b). For comparison, the signals of the same amount of cells in cell medium were also measured (Fig. 5A, lanes c and d). The target cancer cells in both sample and medium obviously show a significantly higher signal compared to the normal cells. In addition, small amounts of cancer cells (300 cells mL^{-1}) were mixed with large numbers of normal cells (3000 cells mL^{-1}),and the ECL response was compared with that of the pure target cells (300 cells mL^{-1}). As shown in Fig. 5B, the normal cells cannot exert an obvious effect on the ECL response. The results indicate that this ECL assay has good selectivity for target cancer cells and can be applied in actual samples. As the receptor for folic acid in cancer cells was about 300 times higher than that in normal cells, the folic acid-based ECL cytosensor can be introduced for highly sensitive cell-based sensing and might be useful for clinical cancer detection, with the advantages of easy construction, quick detection, high sensitivity, and free additional labeling.

Conclusions

In this work, we fabricated a novel TiO_2/CdS nanocomposite and successfully used it to develop an ECL biosensor for the detection of cancer cells. The TiO_2/CdS nanocomposite exhibited intense cathodic ECL signal on the Au electrode. Folic acid as a ligand for targeting cell membranes was first applied to the ECL biosensing, making the cell immobilization and target sensing convenient and rapid. The TiO_2/CdS nanocomposite could be a promising candidate emit-

ter of ECL biosensors because of its intense ECL and good stability. This strategy opens a new approach for cancer cell assay based on ECL of the TiO_2 nanocomposite and folic acid ligand, which has great potential for early and accurate detection of cancer.

Acknowledgments

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