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Template-Assisted Electrochemical Synthesis of CdSe Quantum Dots—Polypyrrole Composite Nanorods

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Abstract: Luminescent nanoparticles have reached a high level of maturity in materials and spectral tunability for optics and optoelectronics. However, the lack of facile methodology for heterojunction formation of the nanoparticles provides many challenges for scalability. In this paper we demonstrate a simple procedure to synthesize a nanoparticle-embedded polymer nanorod hybrid structure via a template-based electrochemical method using anodic aluminum oxide membranes. This method enables the formation of interactive nanostructures wherein the interface area between the two components is maximized. As a proof of concept, semiconducting CdSe nanoparticles were embedded in polypyrrole nanorods with dimensions that can be finely tuned. We observed enhanced photoluminescence of the hybrid structures compared with bare polypyrrole nanorods.

Keywords: nanorod; nanoparticles; electrodeposition; heterojunction; optoelectronics

1. Introduction

Since the report that polymers with conjugated backbone structures can become superconductors at room temperature, research on organic conductors has been extensively studied [1–3]. The structure of most conductive polymers has the characteristic of alternating single and double bonds, with the advantages of being able to control their electrical conductivity by doping and having an easy manufacturing process in thin film, powder, or in various nanostructures. The use of these conductive polymers includes electrode materials, static electricity removal, electromagnetic wave shielding and absorption, etc. Its great advantage is its very diverse workability which is lightweight and can be mass produced. However, since mechanical properties or thermal stability are insufficient in completely replacing metals or other materials, studies on manufacturing methods of various conducting polymer composites have been conducted to overcome this problem [4,5].

In the case of metal or semiconductor nanoparticles, when the size is reduced to less than 100 nm, the optical, electrical, magnetic, and chemical properties of the existing material may change, or the properties may be significantly improved due to the maximized surface area and quantum effects. For example, inorganic quantum dots (QDs) such as CdSe, InP, perovskite CsPbX₃, etc., are considered promising semiconductor nanoparticles because they have unique optical and electronic properties due to quantum effects [6–9]. Therefore, studies on the formation of heterojunctions using the unique physicochemical properties of these nanoparticles and, in particular, many attractive

methods applicable to optoelectronic devices have been reported [10–17]. Such heterojunctions can be formed by physical adsorption, growth on other nanostructures, electrostatic adsorption, and covalent bonding chemistry [18–20]. The optimal approach to form the maximum possible interface between two nanostructured materials is to embed one in another. Using this method, many researchers have fabricated various types of heterogeneous nanostructures using advanced technologies such as chemical vapor deposition (CVD) [21], atomic layer deposition (ALD) [22,23], electron-beam lithography (EBL) [24], and solution synthetic methods [25–27]. Previous studies focused primarily on the formation of the composite structure itself, and there remains room for improvement by controlling the shapes and dimensions of the hybrid nanostructures. Huynh et al. fabricated a composite nanowire of CdSe nanocrystal rod and poly(3-hexylthiophene) and applied it to photovoltaic devices. In manufacturing nanocomposite wires, they used a method of growing into nanowires by synthesis of a polymer material, but there were disadvantages in the difficulty to adjust the length of the nanowires and control the diameter [28]. Chen et al. have produced nano-patterned hybrid nanostructures by e-beam lithography and plasmon-assisted polymerization and observed enhanced optoelectronic properties; however, the materials' generality and scalability of this process present significant questions about its suitability to industry scale [29].

In this study, we describe an effective synthetic pathway based upon template electropolymerization to produce conducting polymer nanorods in which optically active quantum dots are embedded (Figure 1). Templated electropolymerization is renowned for the high throughput synthesis of conducting polymer nanostructures whose dimensions are confined in well-defined porous membranes. Anodic aluminum oxide (AAO) membranes have been widely used for this purpose owing to their vertically aligned, close-packed uniform nanopores whose diameters can be controlled from tens to hundreds of nanometers [30–33]. In addition to the well-known synthesis, in this study we embedded nanoparticles of choice, CdSe quantum dots, as proof of our concept by dispersing colloidal nanoparticles in the polymer precursor solution during the electropolymerization. Various combinations can be realized by slightly modifying this method and altering the types of associated nanostructures that can be synthesized through electrochemical synthesis.

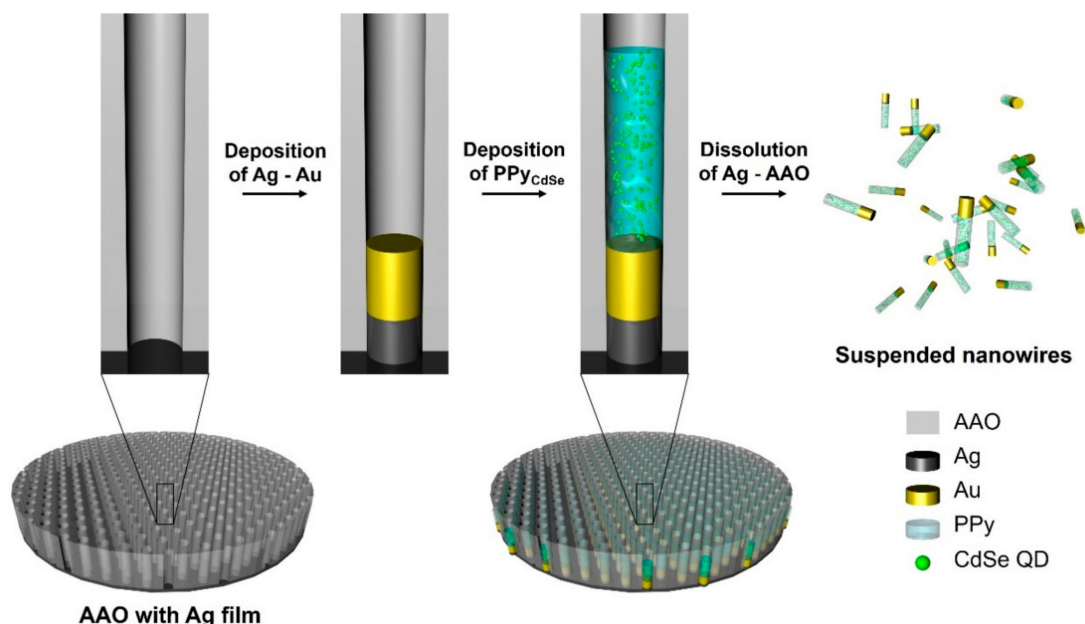


Figure 1. Schematic illustration of synthetic procedures for the CdSe-embedded PPy nanorods.

2. Materials and Methods

2.1. Materials

Commercial AnodiscTM wafers (13 mm wafer diameter and ~230 nm pore diameters, Whatman) were used for the synthesis of most nanorods in this study. For the synthesis of thinner nanorods, an AAO membrane was manually fabricated by anodizing Al foil (99.999%, from Sigma-Aldrich, Seoul, Korea) in 0.3 M oxalic acid solution at 47 DC V of applied voltage. The electro plating solutions, Orotemp 24 RTU for Au and Techni Silver 1025, were purchased from Technic Inc. (Seoul, Korea). Other chemicals, pyrrole, CdSe quantum dot nanoparticles, tetrahydrofuran, and tetrabutylammonium tetrafluoroborate were purchased from Sigma-Aldrich. Deionized (DI) water was purified to the resistivity of 18.2 M Ω through a Millipore water purification system (USA) and used for all the aqueous solutions and necessary steps.

2.2. Synthesis of CdSe-Embedded PPy Nanorods

PPy nanorods containing CdSe nanoparticles were synthesized by a method developed from the well-established templated electropolymerization on AAO substrates (Figure 1) [20,26].

Specifically, Ag film 100 nm thick was deposited on one side of a commercial (or home-grown) AAO membrane by an ion coater (IB-3, Eiko Engineering Co., Ltd., Ibaraki, Japan). Then, a three-electrode electrochemical setup (BAS 100, BASi, West Lafayette, IN 47906, USA) was configured in which the Ag layer, a Pt plate, and an Ag/AgCl electrode were used as the working, counter, and reference electrodes, respectively. A Teflon cell and an O-ring were used to prevent leakage of the plating solution. First, sacrificial Ag was electrochemically deposited by -800 mV potential for 5 min to cover defective pores located at the bottom of the AAO membranes. Au was deposited on top of the Ag rods by -750 mV potential for 30 min. Then, CdSe-embedded PPy nanorods were grown by 1200 mV potential for 2 h using 20 mL of a homemade tetrahydrofuran solution containing 0.1 M of pyrrole, 1 mg of CdSe nanoparticles, and 0.1 M of tetrabutylammonium tetrafluoroborate. Several methods reported to fabricate PPy in aqueous condition with LiClO₄ [34], but we chose the organic solvent to improve quantum yield of QDs [35]. It is important to note that this growth condition is optimized for growing CdSe-embedded polymer nanorods. When the concentration of CdSe was low (0.5 mg or 0.1 mg of CdSe), there was no fluorescence effect of CdSe, and when the concentration of CdSe was higher than 1 mg (2 mg of CdSe), the AAO hole was blocked by CdSe nanoparticles; therefore, CdSe-embedded nanorods were not formed (data not shown). Next, sacrificial Ag and AAO templates were sequentially removed by etchant 3 M HNO₃ and 3 M NaOH, respectively, for 3 h each; the hybrid nanorods from the AAO membrane were dispersed into solution. The nanorods were then rinsed with DI water three times using centrifugation and were transferred to ethanol for improved dispersion on substrates for characterizations. A control sample without the CdSe nanoparticles can be synthesized in a similar manner except for the inclusion of CdSe nanoparticles in the PPy electropolymerization step.

2.3. Characterization

Morphological analysis of control PPy nanorods and CdSe-embedded PPy nanorods were evaluated by scanning (SEM, LEO SUPRA 55, Zeiss, Germany) and high-resolution transmission electron microscopy (HRTEM, model JEM-3010, JEOL, Tokyo, Japan). The optical properties of the nanorods were studied using optical/fluorescence micrographs and photoluminescence spectra, and the samples were prepared by dropping onto the silicon substrate. A two-channel SMU (Keithely 2612) was used for electrical measurements of nanorods.

3. Results and Discussion

The successful synthesis of PPy-CdSe composite nanorods was verified by electron microscopy (Figure 2). As previous studies have shown, this method can synthesize well-defined polypyrrole nanorods where the diameters of the nanorods closely match the expected pore diameters of the AAO

membrane, as observed by scanning electron microscopy (SEM, Figure 2a). However, it was difficult to observe the embedded CdSe quantum dots with SEM because it mostly provides topographic surface analysis, and the size of quantum dots are similar or smaller than the resolution limit of SEM. Transmission electron microscopy (TEM) would be an acceptable substitute, but the nanorods are too thick to allow transmission of electrons in order to form an image. To characterize the hybrid nanorods with TEM, thinner nanorods were synthesized using a homemade AAO membrane with pore diameters of 25 ± 5 nm and a thickness of 30 μm . The synthesis of composite nanorods can be carried out via the same process with the homemade templates, and this results in thinner nanorods. TEM then enabled the observation of CdSe quantum dots embedded in polypyrrole nanorods (Figure 2b). Each component (PPy, Cd, and Se elements) was also confirmed by an energy-dispersive X-ray spectroscopic spectrum (Figure 2a, inset).

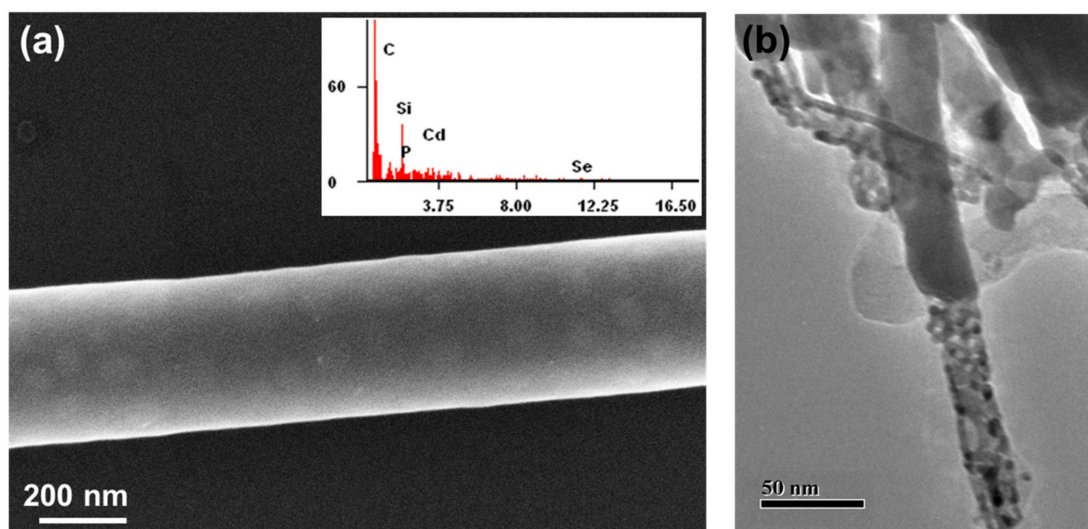


Figure 2. Electron micrographs of the CdSe-embedded PPy nanorods synthesized with different AAO template pore sizes, (a) 300 nm (SEM) and (b) 25 ± 5 nm (TEM). The inset in (a) is the EDS spectrum of CdSe-embedded PPy nanorod that shows the C, Cd, and Se elements.

Polypyrrole photoluminescence normally does not occur at wavelengths longer than 500 nm, and this is in agreement with our experimental result where no detectable signal was observed in the control polypyrrole nanorods with fluorescence microscopy (Figure 3a,b).

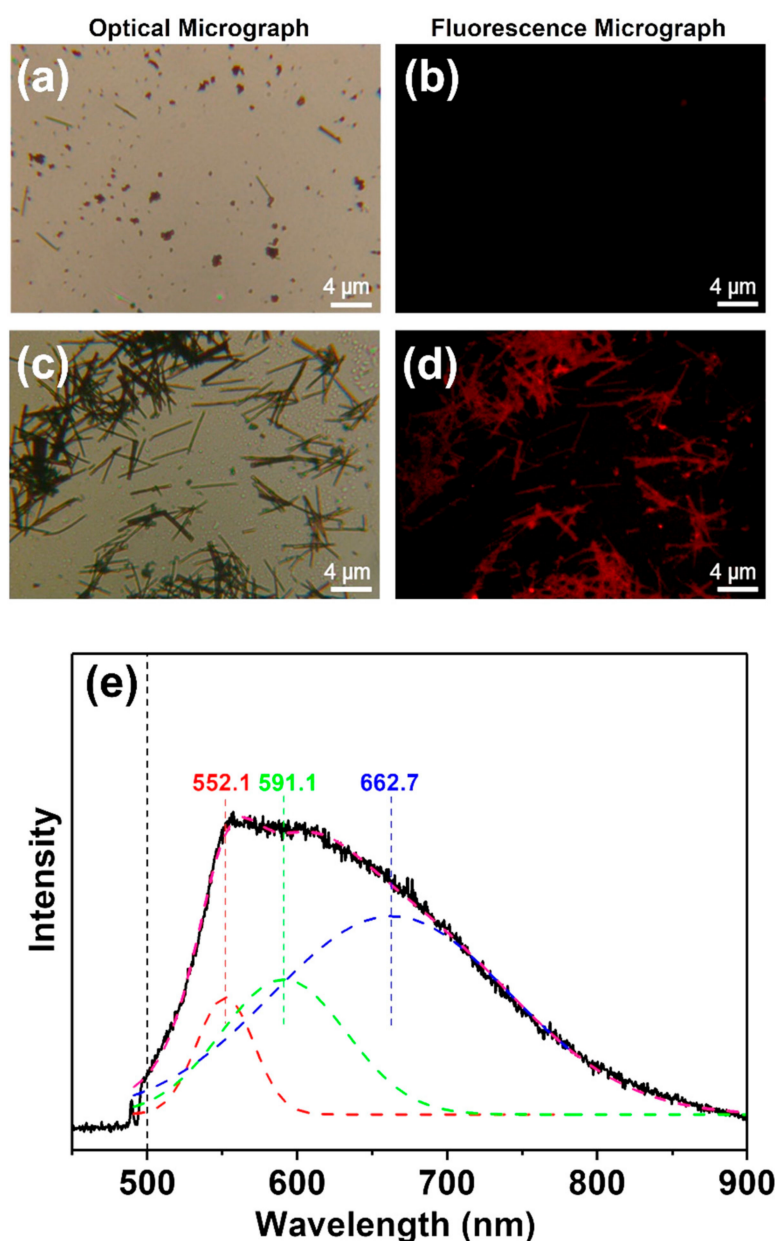


Figure 3. (a) An optical micrograph and (b) a fluorescence micrograph of the control sample, PPy nanorods without CdSe nanoparticles. No observable photoluminescence was detected for the control sample. (c,d) Respective data for CdSe-embedded PPy nanorods where emissions from the hybrid nanorods were captured. (e) A photoluminescence spectrum from the CdSe-embedded PPy nanorods (black), deconvoluted peak fittings (red, green, and blue dotted lines), and the cumulative peak fitting (magenta).

Interestingly, the CdSe-embedded polypyrrole nanorods showed photoluminescence signals along the nanowires (Figure 3c,d), which differed from the fluorescence of CdSe quantum dots (Figure 4b). The CdSe quantum dots showed a single photoluminescence peak at 594.5 nm, whereas the photoluminescence peak of the CdSe-embedded polypyrrole nanorods was much broader and could be deconvoluted into three different Gaussian curves ($R^2 = 0.996$); the wavelengths of the three peaks were 552.1, 591.1, and 662.7 nm (Figure 3e). To test any effect from the electrolyte during the synthesis, CdSe quantum dots were dispersed into the plating solution (w/o pyrrole monomer, 0.1 M) containing tetrahydrofuran and toluene before a dropcast film was prepared for spectroscopy, but no meaningful

change in photoluminescence was detected (Figure 4c). In contrast, when the CdSe quantum dots were mixed with the plating solution containing pyrrole monomer (the pyrrole molecules are presumably adsorbed onto the quantum dot surfaces), we observed a blue-shift of the single photoluminescence peak to 567 nm (Figure 4d).

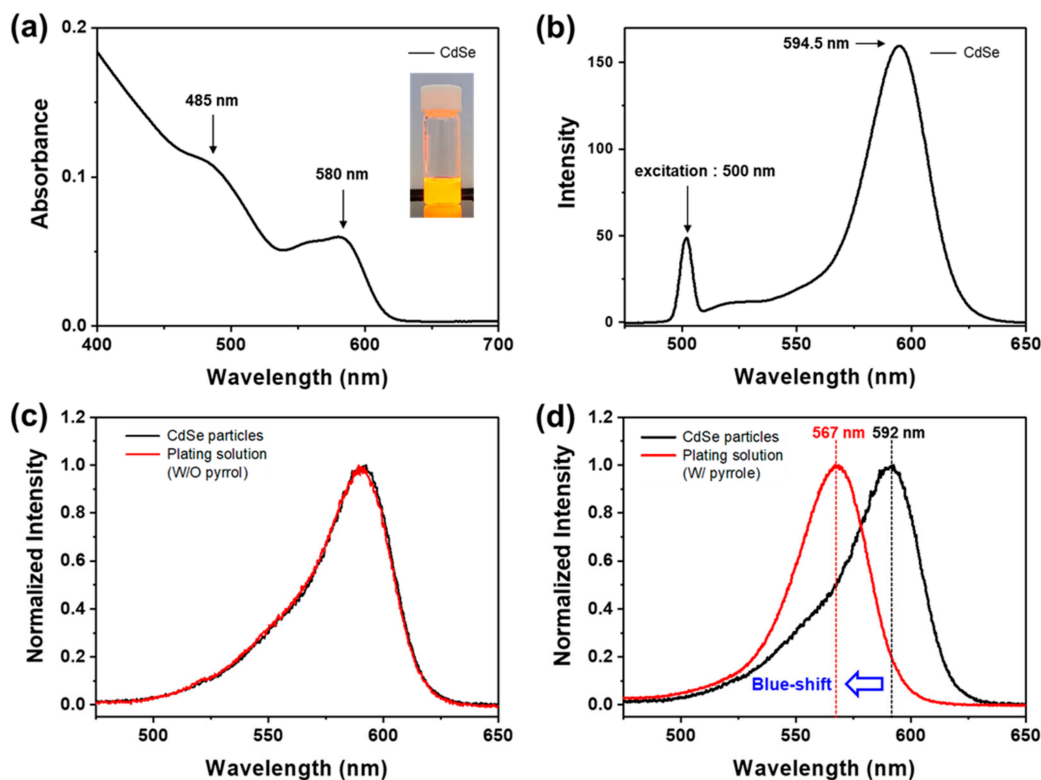


Figure 4. (a) UV-vis absorption spectrum of CdSe nanoparticles. (b) Photoluminescence (PL) spectrum of CdSe nanoparticles. The excitation wavelength of PL is 500 nm. PL spectra with (d) and without (c) pyrrole monomer in CdSe and plating solution mixtures.

These data indicate that the photoluminescence of CdSe has been affected by the hybridization with polypyrrole through the interface formation. There are several possible explanations for the observed change in photoluminescence. The changes in energy band structure of the quantum dots by interfacing with polypyrrole can induce chemical and/or physical modification of the surface states [20]. The energy transfers between the quantum dots and polypyrrole can also result in such a change [36]. If the photon energy is absorbed by the quantum dots and, instead of directly emitting light, the photon transfers to polypyrrole where excitons recombine, a similar effect to what is observed can occur. Lu et al. have shown that the CBM (conduction band minimum) of PPy is higher than that of CdSe, and the VBM (valence band maximum) of PPy is lower than that of CdSe. However, the oxidation-induced energy level is close to the VBM of CdSe [37]. The energy level places around 0.4–0.7 eV from VBM of PPy (5.7 eV). In our experimental result (Figure 4d), the photoluminescent peak shifted from 592 to 567 nm, and the value corresponded to 0.09 eV. The calculated value was close to the extracted value from the experiment. In addition, the insertion or adsorption of CdSe quantum dots to polypyrrole could be regarded as doping of the conducting polymer, providing an additional energy state for excitons to recombine and emit light [38]. Further studies, such as exploration into the transient photoluminescence spectrum, should be conducted to clearly identify the mechanism.

Finally, the current–voltage (I_{DS} – V_{DS}) characteristics were measured on a microchip where two Au electrodes (gap distance of 5 μ m) were bridged by a nanorod sample. The nanorod-based electronic devices were fabricated onto a SiO₂ substrate 300 nm thick by a conventional photolithographic

technique. The gap between the electrodes of the device was 5 μm and contacted with a gold (Au) electrode of 100 nm thickness (Figure 5a). Bare polypyrrole nanorods showed relatively low current with asymmetric $I_{\text{DS}}-V_{\text{DS}}$ characteristics, which resulted from the Au segment at one side of polypyrrole nanorods and contact resistance. In particular, because the PPy-Au segments were directly bonded, the Schottky characteristics were reflected, and a diode-shaped $I_{\text{DS}}-V_{\text{DS}}$ curve was shown on the bare polypyrrole nanorods [34]. Between the applied voltages -2 V to $+2\text{ V}$, the CdSe-embedded polypyrrole nanorods showed slightly higher current and quasi-linear ohm-like properties than the bare polypyrrole nanorods, which could be a result of increased carrier density by doping (Figure 5). However, above the applied voltage $+2.5\text{ V}$ the total current flow of CdSe-embedded polypyrrole nanorods was lower than that of the bare polypyrrole nanorods, which was probably due to the contact resistance of the embedded CdSe nanoparticles.

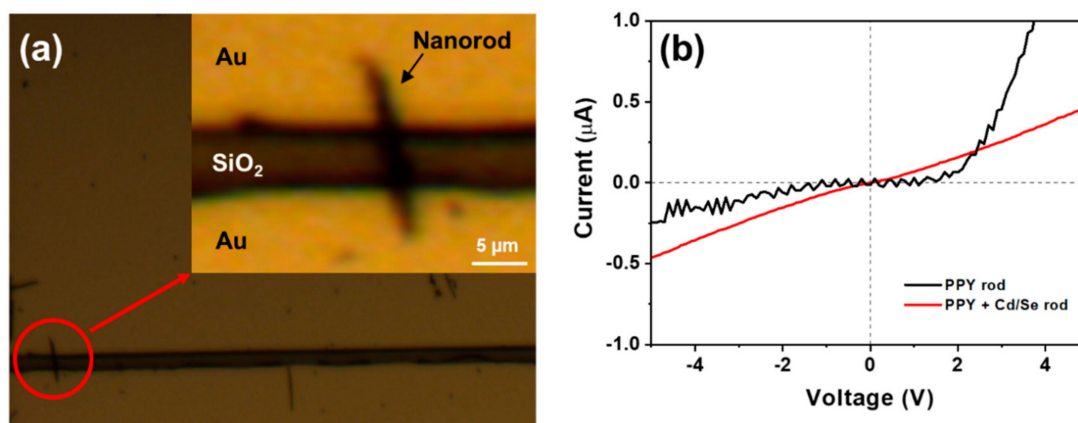


Figure 5. (a) Representative optical micrograph of a nanorod-bridged gapped Au electrode. (b) I-V characteristics of a CdSe-embedded PPy nanorod (black) and a control PPy nanorod without CdSe nanoparticles (red).

4. Conclusions

In conclusion, we have demonstrated the synthesis and characterization of CdSe quantum dot-embedded polypyrrole nanorods. The hybrid nanorods consisting of gold and PPy segments were electrochemically manufactured using a template synthesis method. Using this method we were able to successfully form nanostructures in which the interface area between the two components was maximized. The construction of the desired composite nanomaterials has been verified, and the hybrid structure exhibited optical and electronic properties distinguishable from each isolated component (polypyrrole and CdSe). Moreover, the fluorescence properties of CdSe-embedded PPy nanorods were confirmed, and their blue shift phenomenon was studied. Considering the wide variety of materials available for electrochemical synthesis and colloidal nanoparticles, scientists and engineers in the fields of photovoltaics, optoelectronics, catalysis, and biosensing may utilize this method for a variety of applications.

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Conflicts of Interest: The authors declare no conflict of interest.

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