

Ion Selective Polymer Dots for Photoelectrochemical Detection of Potassium Ion

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Experiential Section.

Reagents and Apparatus. Poly(styrene-co-maleic anhydride) (PSMA) was obtained from Tianjin Heowns Biochem LLC (China), and the conjugated polymer poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-{2,1,3}-thiadazole)] (PFBT), sodium tetrakis [3,5-bis-(trifluoromethyl)phenyl]borate (NaTFPB), poly(diallyldimethylammonium chloride) (PDDA, 20 %, w/w in water, MW = 200000 – 350000), potassium chloride (KCl) and lithium chloride (LiCl) were obtained from Sigma-Aldrich. Sodium chloride (NaCl) and calcium chloride dihydrate (CaCl₂·2H₂O) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Other chemicals were of analytical reagent grade and used as received. A solution of 0.1 M Tris-HCl (pH = 7.4) was used to dilute the stock solution when needed. All aqueous solutions were prepared using ultrapure water (Milli-Q, Millipore).

PEC properties were measured by a homemade PEC system which had a 450 nm LED lamp as illuminator. Photocurrent was measured on a CHI 750E electrochemical workstation (China). A three-electrode system, including a modified ITO electrode as the working electrode, a Pt wire as the counter electrode and a saturated Ag/AgCl electrode as the reference electrode, is used for the measurement. Transmission electron microscopy (TEM) image was obtained by a JEOL model 2000 instrument (Japan) operated under a 200 kV accelerating voltage. Thermo Scientific Varioskan Flash spectral scanning multimode reader (USA) was used for the measurement of absorption spectra and fluorescence measurements.

Preparation of K-Pdots. The K-Pdots were prepared by the reprecipitation method. The PFBT polymer, functional polymer PSMA, ion-exchanger (NaTFPB) and potassium ion carrier (Potassium ionophore III) were separately dissolved in THF and then mixed to form a solution with a PFBT concentration of 100 µg/mL and a PSMA concentration of 20 µg/mL. Subsequently, 0.5 mL of the mixture was added to a total of 4.5 mL sonicated deionized water quickly. THF was then removed from the mixing solution by nitrogen stripping and the solution was filtered through a 0.22 µm filter. Eventually, the solution was concentrated by rotary evaporation at 55 °C.

Fabrication of Pdots-ITO Electrode. The K-Pdots modified multilayer film was fabricated by alternately immersing the cleaned ITO slides (3.3 × 0.7 cm) into a solution of 0.5 M NaCl with 2 % PDDA, and the solution with K-Pdots nanoparticle for 30 min. After repeating the above-mentioned process for 4 times, the electrodes were washed carefully with doubly distilled water.

PEC detection. The photocurrents of K-Pdots/ITO electrodes were detected in 50 mM Tris-HCl containing different concentrations of potassium ions. The potential applied was 0 V. The excitation light of 450 nm turned on/off every 10 seconds as the repeated illumination.