

CdTe quantum dot sensitized hexaniobate nanoscrolls and Photoelectrochemical properties

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Experimental Methods

Synthesis of niobate nanosheets

Layered potassium niobate ($K_4Nb_6O_{17}$) was prepared by a conventional solid-state method. The mixture of Nb_2O_5 and K_2CO_3 was calcined at 1473K for 15 min in a Pt crucible. The final product of $K_4Nb_6O_{17}$ powder was pulverized in a mortar to decrease particle size. The powder was treated with 0.5M H_2SO_4 for 24 h in order to protonate the interlayers. The proton exchanged powder was exfoliated by introducing tetrabutylammonium (TBA) or ethylamine (EA) molecules into the interlayer. The reaction was carried out in an aqueous tetra(n-butyl)ammonium hydroxide solution for 24 h. The subsequent centrifugation of the solution at 2000 rpm for 30 min yielded colloidal suspension of individual $[Nb_6O_{17}]^{4-}$ sheets.

Synthesis of Cysteamine-Coated CdTe QDs

Cysteamine-coated CdTe quantum dots were prepared in water according to the similar procedure described by Chen Qi-Fan *et al*¹. Typically, cysteamine was added into an aqueous $Cd(Ac)_2 \cdot 2H_2O$ solution purged with Ar. The pH of the solution was adjusted to 5.6 with 1M NaOH and/or concentrated acetic. Na_2Te was dissolved in previously boiled water under Argon flow and then transferred to the cadmium-cysteamine solution under Ar flow. The reaction mixture was refluxed at 110°C for the desired duration and then stored at 4°C, in the dark. Cd^{2+} : cysteamine: Te^{2-} ratio was fixed at 2:4:1.

Synthesis of Cys-CdTe QD/NbO hybrid films

Films were fabricated by Electrophoretic Deposition Methods. In order to prepare the hybrid materials 5 ml of Quantum Dot solution was added into 5 ml of the exfoliation solution of hexaniobate nanosheets. The pH of the exfoliation solution was adjusted to 6.5-7 prior to QD addition. CdTe/NbO hybrid material was precipitated as soon as two solutions were mixed. The precipitate was isolated by centrifugation under 3000 rpm for 3 min and washed three

times with acetonitrile. After last washing, the hybrid material was redispersed in acetonitrile by applying ultrasonic treatment for 5 min. This resulted in a dispersion of CdTe/NbO hybrid material. The dispersion was used to prepare the thin films.

Prior to the deposition, Indium Tin oxide coated glass (ITO, $R_s < 10 \text{ ohm/sq}$) (Teknoma Ltd, Izmir Turkey) electrodes were washed with acetone, ethanol and nitric acid solutions, subsequently. ITO electrodes were rinsed with water and two ITO electrodes were dipped into the dispersion solution. The distance between the electrodes was 1 cm and the area for electrophoretic deposition on the films was 1 cm^2 . Electrophoretic deposition was carried out under 50 V for 10 sec. Keithley 2400 Model sourcemeter was used for deposition experiments. Following the deposition, the film was rinsed with ethanol and dried naturally.

Characterization

The crystal structure and orientation of the films were analyzed from X-Ray Diffraction (XRD) patterns (using $\text{CuK}\alpha$ radiation, Bruker D8, ADVANCE with DaVinci design). The topography of the films was analyzed by Zeiss ULTRA PLUS Field Emission Scanning Electron Microscope (FE-SEM). Bright Field images of the CdTe/NbO hybrid materials were taken in the Scanning Transmission Electron Microscopy (STEM) mode of the microscope by using high resolution STEM detector coupled to the FESEM. The hybrid material was taken with a pipette from the dispersion solution and a couple of drops were dried on a Cu grid for sample preparation. The chemical composition of the films was analyzed by Bruker X-flash6 Energy Dispersive X-ray Fluorescence (EDX) Detector on the FE-SEM. Chemical state of CdTe on the film was analyzed by Thermo K-Alpha X-ray Photoelectron Spectrometer (XPS) with $\text{AlK}\alpha$ source. Optical absorption spectra of the deposited films were recorded by measuring the diffuse reflection spectra (Shimadzu UV-3600) and converting them by using the Kubelka-Munk function.

All electrochemical experiments were carried out in a conventional three-electrode electrochemical cell with a Pt counter electrode and a saturated Ag/AgCl reference electrode. A 250W Xe-Hg lamp (Newport) was used as the light source to measure the photoelectrochemical properties. Photocurrent experiments on films were recorded in a $0.1\text{M Na}_2\text{S} + 0.1\text{M Na}_2\text{SO}_3 + 0.1\text{M Methanol}$ at 0 V on working electrode with respect to the Ag/AgCl reference electrode. Photocurrents were recorded by Bio-Logic VSP model Potentiostat/Galvanostat.

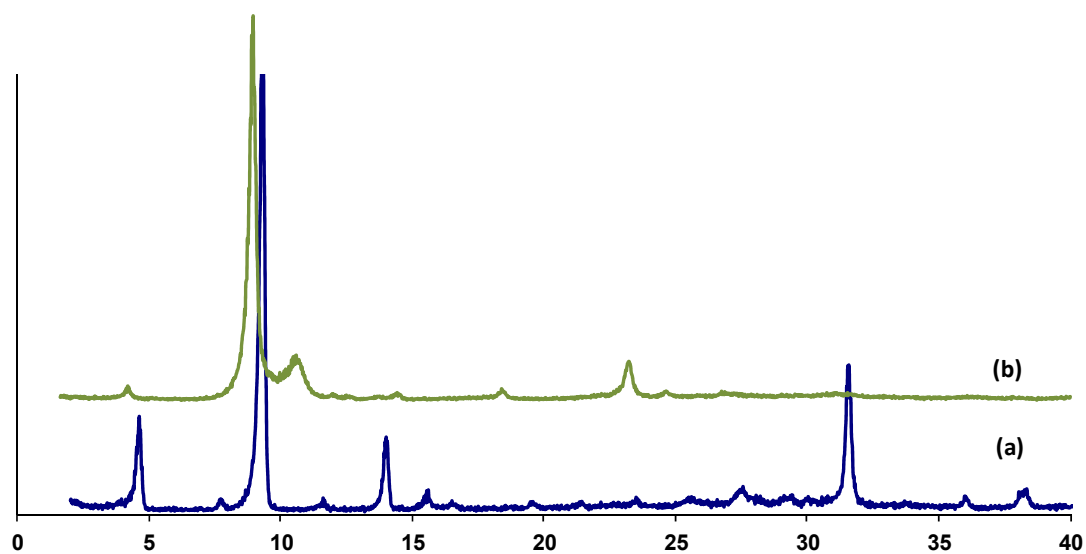


Fig 1. X-ray diffraction patterns of a) K₄Nb₆O₁₇·3H₂O and b) its proton exchanged form

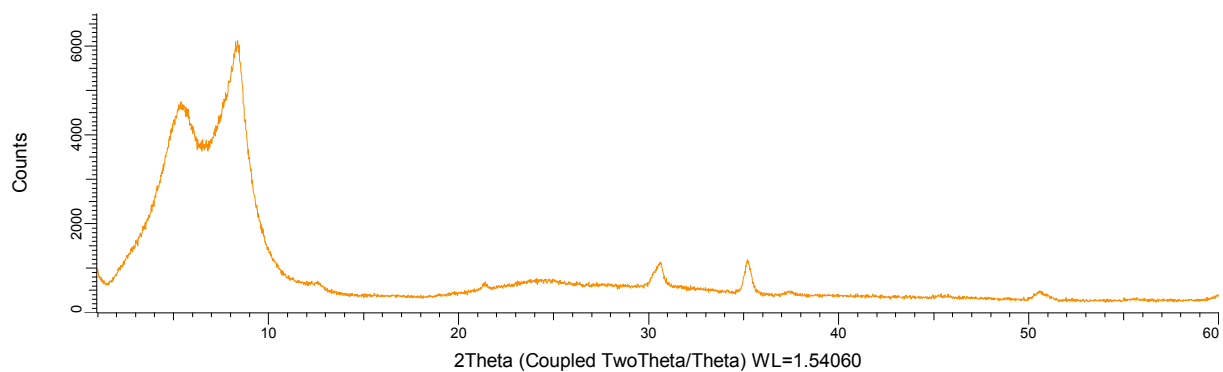


Fig 2. X-ray Diffraction pattern of CdTe/NbO film deposited on ITO electrode.

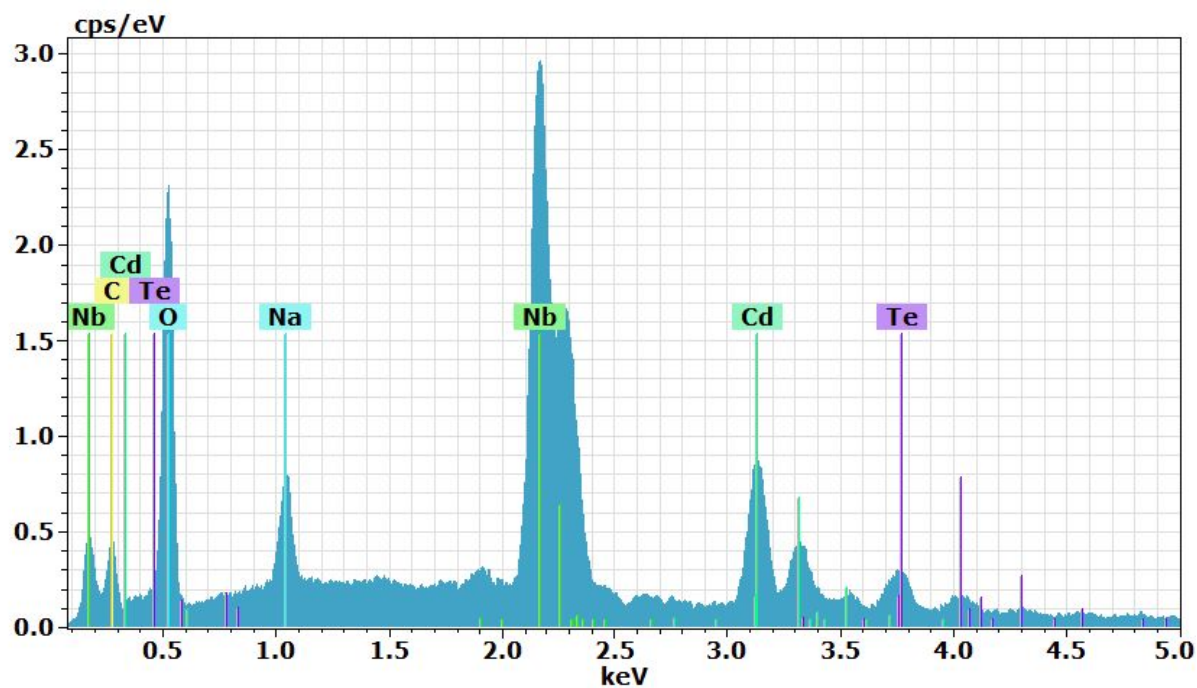


Fig 3. EDX spectrum of CdTe/NbO film

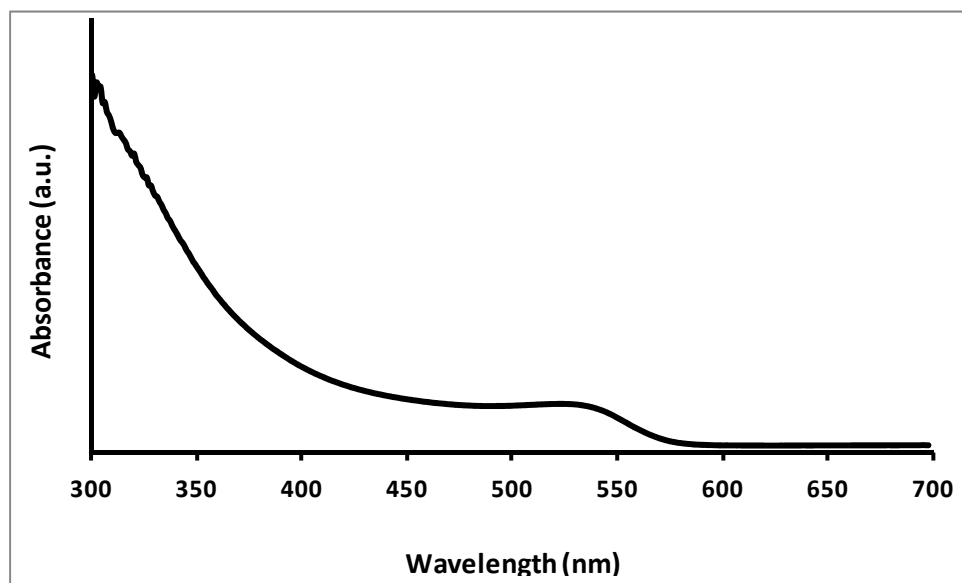


Fig 4. Visible Absorption spectrum of aqueous Cysteamine capped CdTe quantum dot solution

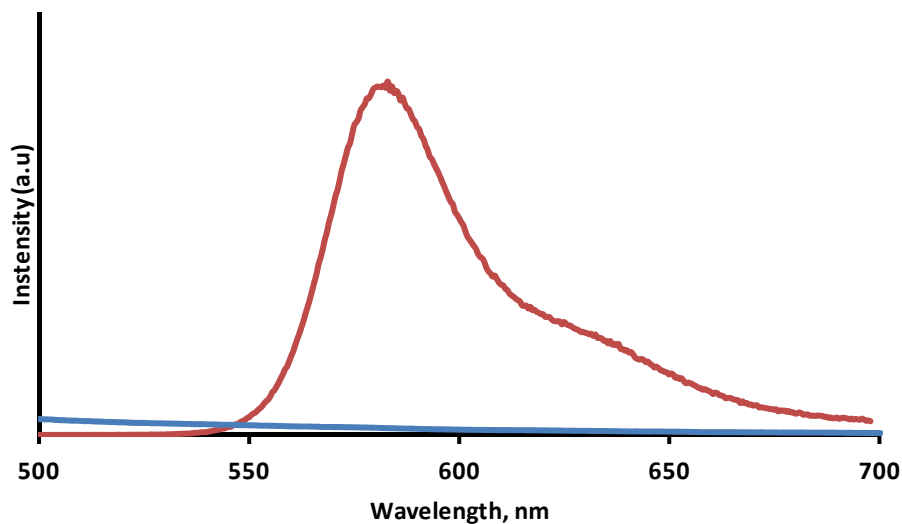


Fig. 5 Photoluminescence spectrum of Cysteamine capped CdTe quantum dots (red curve) and film of Niobate nanosheets sensitized with cysteamine capped quantum dots (blue curve) ($\lambda=400$ nm)

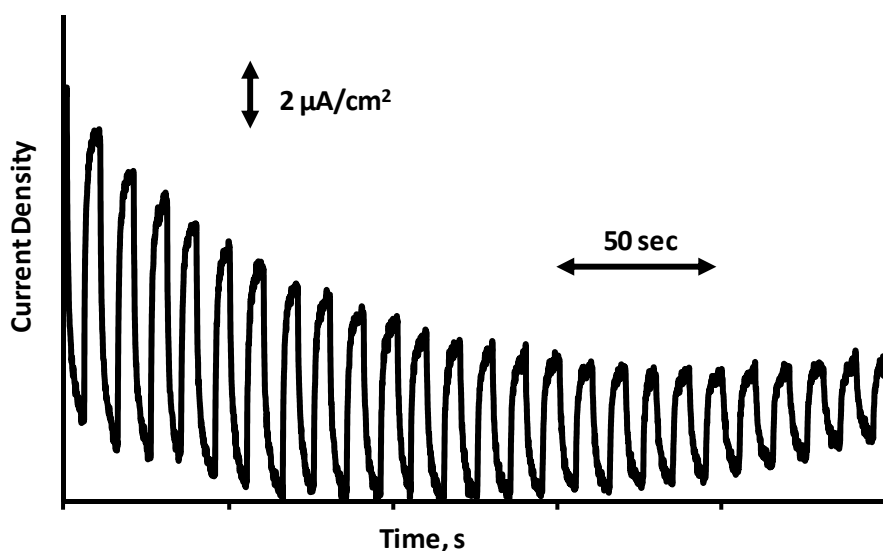


Fig 6. Photocurrent produced by Cys-CdTe film in a solution of 0.1 M Na_2S + 0.1M Na_2SO_3 + 0.1 Methanol. Films were electrophoretically deposited from a solution of the quantum dots in acetonitrile. Photocurrent experiments were performed by 250 Watt Hg-Xe Light source with 1.5 AM filter ($100 \text{ mW}/\text{cm}^2$)

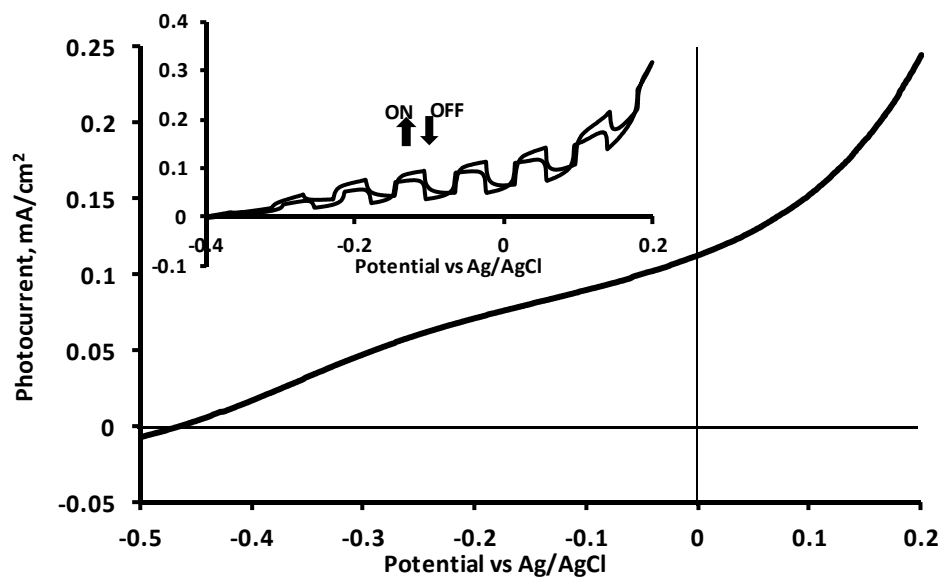


Fig 7. I-V curve of Cysteamine-CdTe sensitized niobate films in a solution of 0.1 M Na₂S + 0.1M Na₂SO₃ + 0.1 Methanol under illumination. The inset graph shows the I-V curve of the same electrode under chopped illumination. Source is 250 Watt Hg-Xe Light source with 1.5 AM filter (100 mW/cm²).