

Production and Identification of Highly Photoconductive CdSe-based Hybrid Organic-Inorganic Multi-Layer Materials¹

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Abstract—Highly photoconductive thin multi-layers of new hybrid organic-inorganic semiconductors have been developed. They result by the combination of an inorganic semiconductor with ferrocene, a commercially available compound, applying the electrodeposition and spin coating techniques, introducing sodium oxalate as an additive in the electrolytic bath. The organic layer of the hybrid system is enveloped between two inorganic layers in a sandwich-like structure. The full characterization of the final products by XRD, SEM-EDAX, band gap and photo electro chemical cell (PEC) measurements confirmed the development of the hybrid semiconducting system. The outer electrodeposited CdSe layer of the sandwich-like materials exhibits a definite hexagonal structure, whereas, as derived from the XRD and band gap data, the development of a new semiconducting compound has been confirmed. Thus, due to a synergic action, the three-layer materials present a remarkably improved photoresponse compared to that of the pure cubic CdSe electrodeposited in the presence of the oxalate additive as well as the three-layer hybrid CdSe-based products developed in our previous work in additive-free electrolytic baths.

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1. INTRODUCTION

Hybrid semiconductors are well-known for their particular semiconductive behavior due to the synergic combination of the properties of their components. These novel materials could find several interesting applications into various scientific fields, some of them presenting considerable industrial interest, as in photoconductors, photovoltaic devices, opto-electronics, sensors, photodetectors, etc. [1–3].

As presented in our previous works [4, 5], hybrid semiconducting products may be developed by deposition of an appropriate thin organic film (specifically ferrocene, commercially obtained) placed between two CdSe thin films in a sandwich-like construction presenting remarkably improved photoresponding behavior [4]. On the other hand, CdSe semiconducting thin films electrodeposited in the presence of some selected organic additives, such as glutamates, oxalates, choline, etc., also exhibit remarkable photoconductive character. This fact may be attributed to the creation of crystal defects on the CdSe deposits by the organic chemical species derived from the additives, impacting positively or negatively the photoconductivity of the final products [5].

CdSe, constituting the inorganic part of the hybrid system, is a well-known semiconductor, as referred in our previous works [2, 4–7] with a direct energy gap (1.7 eV). When electrodeposited, CdSe presents a well-developed cubic zinc-blende structure with a strong (111) preferred orientation [6, 8], behaving as a metastable kinetically controlled phase, which can easily be transformed to the thermodynamically stable hexagonal one (wurtzite) by annealing [6]. However, hexagonal CdSe exhibits a better photoresponse in a photoelectrochemical cell (PEC) and higher resistance in photocorrosion partly due to its stronger bonding [6, 7, 9]. A pure hexagonal structure of CdSe has been obtained in the hybrid three-layer materials previously prepared [4]. The organic part, being an electron donor, had induced a significant change in the semiconductive behavior to the final hybrid as compared to the pure inorganic material [2].

In the frame of this work, the development and study of new three-layered hybrid semiconducting systems, involving CdSe thin films and pure ferrocene in the presence of sodium oxalate in the bath, was attained. It is expected that the presence of the organic part, in particular when placed between two CdSe thin films, in a sandwich-like construction, in combination with the favorable action of the oxalate species should lead to hybrid materials presenting modified crystal structure and higher efficiencies in photo conversion.

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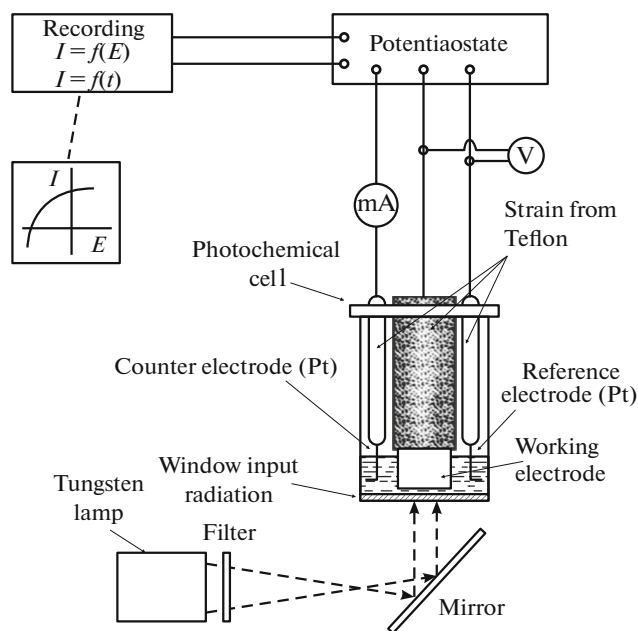


Fig. 1. Device for the electrochemical measurements.

It is also assumed that a new chemical semiconducting compound between the organic and the inorganic part of the hybrid system (CdSe and ferrocene, respectively) should be formed.

2. EXPERIMENTAL

CdSe thin films were developed potentiostatically, using a potentio-scan system with a conventional three electrode set-up (Fig. 1) [10]. The cathode was a rotating Ti disc electrode (diameter 12 mm; cathode's rotation rate: 500 rounds per minute, rpm). The counter electrode was a large platinum plated grid. The potential of the working electrode was monitored against an Hg/HgSO₄ saturated sulfate reference electrode (S.S.E.). The electrolytic bath for CdSe plating was an aqueous solution containing typically 0.2 mol/L CdSO₄ and 2×10^{-3} mol/L SeO₂ being kept constant at $85 \pm 1^\circ\text{C}$. The concentration of the additive (disodium oxalate) was set to 2×10^{-3} mol/L. The bath pH value was adjusted to 2.2.

The organic layers were deposited dropwise from solution of ferrocene (Fc) in toluene onto the rotating inorganic electrode (spin coating technique). In this way, a thin film of the organic substance was formed.

The three-layered products were prepared by applying a second CdSe layer over the organic one to give a sandwichlike structure. The inner CdSe layer of all specimens was electrodeposited at the potential of -1.0 V vs. S.S.E, whereas the outer one at three different potentials (-0.9 , -1.0 , -1.1 V vs. S.S.E.).

All deposits were examined by X-Ray Diffraction (XRD) with the Bruker D8 Advance using a CuK_α

X-ray source and Scanning Electron Microscopy (SEM) with the FEI-Quanta 200. Compositional data were obtained by Energy Dispersive X-ray (EDAX) analysis. The band gap widths were evaluated by spectrophotometry of the reflected light with the V-770 Jasco Spectrophotometer equipped with an integrating sphere. Photoresponse studies were performed in a PEC with a three electrode configuration comprising platinum wire rods as counter and reference electrodes. An alkaline sulfide-polysulfide solution (S_x^{2-} ; 1M NaOH, 1M Na₂S, 1M S solution) was used as the working red-ox electrolyte. The PEC measurements were conducted under a white illumination generated by a halogen lamp and focused in front of the quartz window of the cell. Illumination intensity was 1000 W/m².

3. RESULTS AND DISCUSSION

In all three-layered specimens, SEM-EDAX investigations (Fig. 2) confirmed the presence of cadmium and selenium and in addition, the spot analyses confirmed the coexistence of carbon and iron elements, due to the ferrocene moieties and consequently the preparation of a hybrid system.

Figure 3 summarizes the XRD diagrams of the as-prepared hybrid semiconductors (CdSe-Fc/oxalate), in comparison with the diagrams of pure CdSe and of CdSe electrodeposited from a bath, containing the oxalate additive.

It is found that, both CdSe deposits exhibit a cubic zinc blende structure with a predominant crystalline orientation towards the [111] crystallographic axis. On the other hand, all three-layered specimens present a clear hexagonal wurtzite structure of the outer CdSe layer. The less intense diffraction peaks corresponding to a cubic or a mixed cubic hexagonal structure are obviously derived from the inner CdSe layer. In addition, a new chemical compound, a reaction product between CdSe and ferrocene (CdSe · Fc) has been formed during the electrodeposition of the outer layer, as derived by the "new" lines appeared in the XRD diagrams of all the three-layered specimens.

Figure 4 describes the band gap width calculations for ferrocene and the CdSe/Ferrocene/CdSe three-layered hybrid semiconductors electrodeposited at different potentials. All three-layered materials present an additional band gap of about 2.0 eV (different of that of pure ferrocene, found at 2.45 eV), confirming the development of a new semiconducting compound, which has replaced their intermediate organic layer.

Table 1 summarizes the parameters of the photoconversion curves (short circuit current, j_{sc} , open circuit potential, V_{OC} , fill factor, FF , and photoelectrochemical efficiency, η) for CdSe and the three-layered products, used directly as absorbed electrodes in a conventional PEC. Figure 5 illustrates the respective current-potential photoresponses.

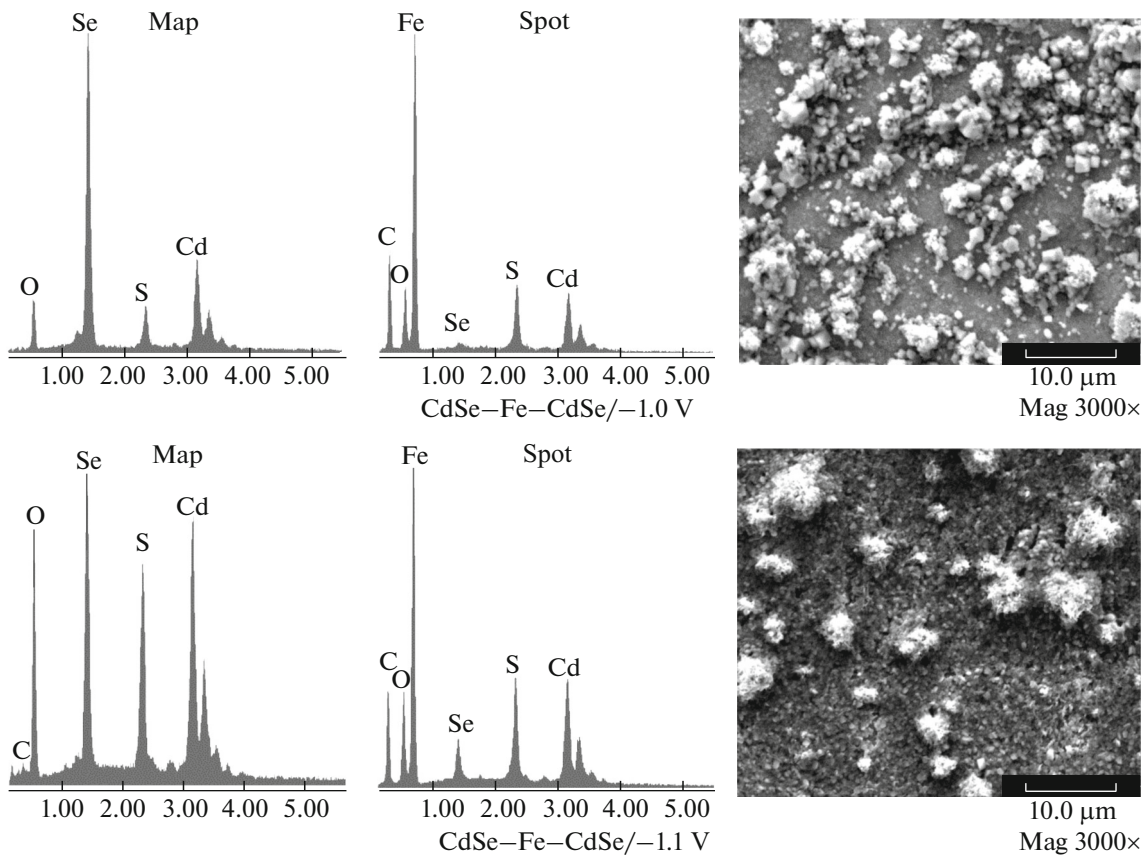


Fig. 2. EDAX diagrams and SEM micrographs of hybrid three-layered specimens prepared by electrodeposition at -1.0 and -1.1 V vs. SSE in the presence of disodium oxalate.

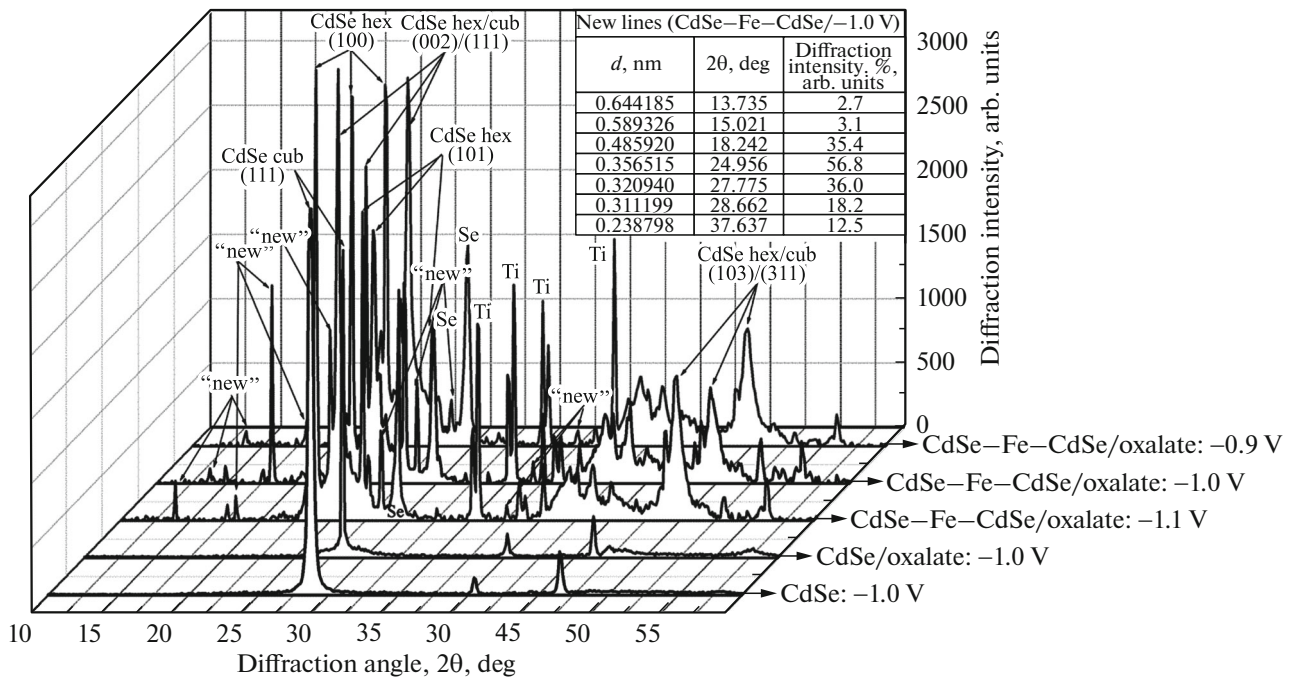


Fig. 3. XRD diagram of CdSe and CdSe/Ferrocene/CdSe three-layered hybrid semiconductors prepared by electrodeposition/spin coating/electrodeposition in the presence of sodium oxalate as an additive in the electrolytic bath.

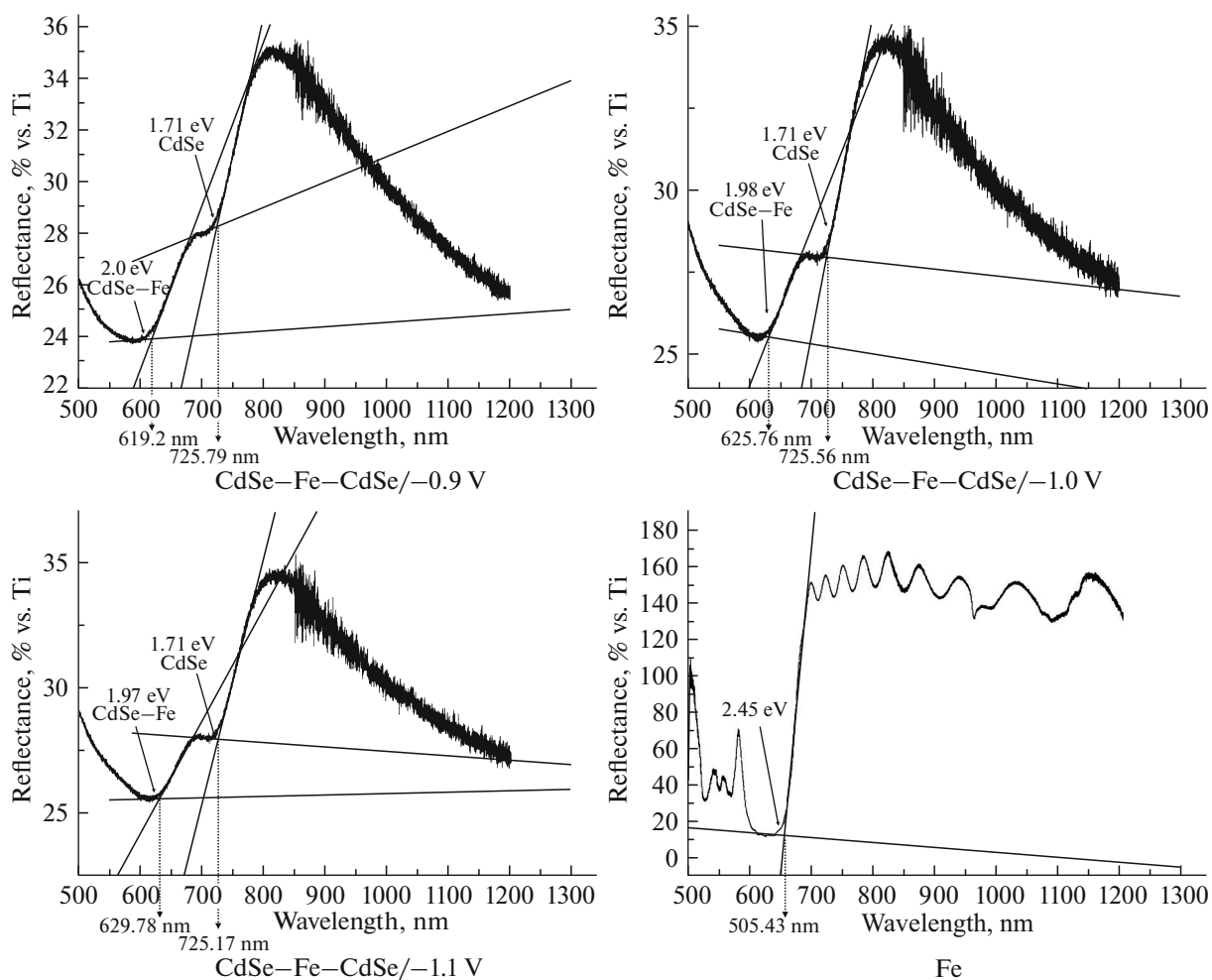


Fig. 4. Band gap width (E_g) measurements taken by spectrophotometry of the reflected light for the pure ferrocene and the CdSe/Ferrocene/CdSe three-layered hybrid semiconductors.

All photocurrents are anodic, that is characteristic of an n -type behavior. It is observed that CdSe/oxalate deposits present improved properties, such as short circuit current and photoelectrochemical efficiencies, compared to pure CdSe as well as CdSe electrodeposited using other additives in the bath, as glutamates [5]. These improved properties are attributed to the smaller size of oxalate species, which are capable to create more crystal defects, when incorporated in the CdSe lattice.

All three-layered specimens regardless of the deposition potential exhibit, remarkably improved semiconducting properties, displaying approximately seven times higher short circuits current and five times higher photo conversion efficiencies. This behavior is attributed to the development of a definite hexagonal structure in combination with the organic additive and the formation of the new semiconducting compound.

Table 1. Photoelectrochemical parameters of CdSe and CdSe/Ferrocene/CdSe three-layered products

	CdSe (-1.0 V)	CdSe/oxalate (-1.0 V)	CdSe-Fc-CdSe/oxalate (-0.9 V)	CdSe-Fc-CdSe/oxalate (-1.0 V)	CdSe-Fc-CdSe/oxalate (-1.1 V)
J_{SC} ($\mu A cm^{-2}$)	2160	6153	14763	14618	14726
V_{OC} (mV)	-412	-316	-344	-344	-329
FF	0.356	0.318	0.312	0.302	0.326
η (%)	0.317	0.617	1.582	1.519	1.579

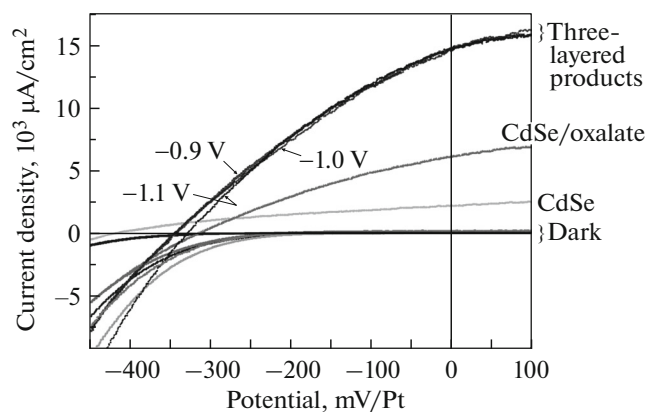


Fig. 5. Current density vs. electrochemical potential given by CdSe/Ferrocene/CdSe three-layered specimens in comparison with pure CdSe layers, used directly as absorbed electrodes in a conventional PEC in the dark and under illumination of 1000 W/m^2 .

4. CONCLUSIONS

New hybrid organic-inorganic semiconducting systems have been developed by the combination of a CdSe semiconductor with ferrocene prepared in the presence of an oxalate additive. In the preparation procedure, the organic layer is enveloped between two inorganic layers in a sandwich-like structure. The full characterization of the products confirmed the development of the hybrid semiconducting system. Their inner layer is a pure cubic (zinc blende) CdSe. The organic part of all three-layered products has been fully transformed during the electrodeposition of the outer layer to a new chemical compound ($\text{CdSe} \cdot \text{Fc}$),

presenting a clear semiconducting character with $E_g \approx 2 \text{ eV}$. Over this layer a pure hexagonal (wurtzite) CdSe has been developed. It is worth noting that all three-layered systems exhibit an exceptionally improved photoresponse attributed to the synergic action of three factors: the clear hexagonal structure of the outer inorganic film which accepts photons the incorporation of the additive into the CdSe lattice facilitating the development of crystal defects, and the formation of the new semiconductive compound ($\text{CdSe} \cdot \text{Fc}$), permitting a better photoconversion of the photons.

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