Supporting Information
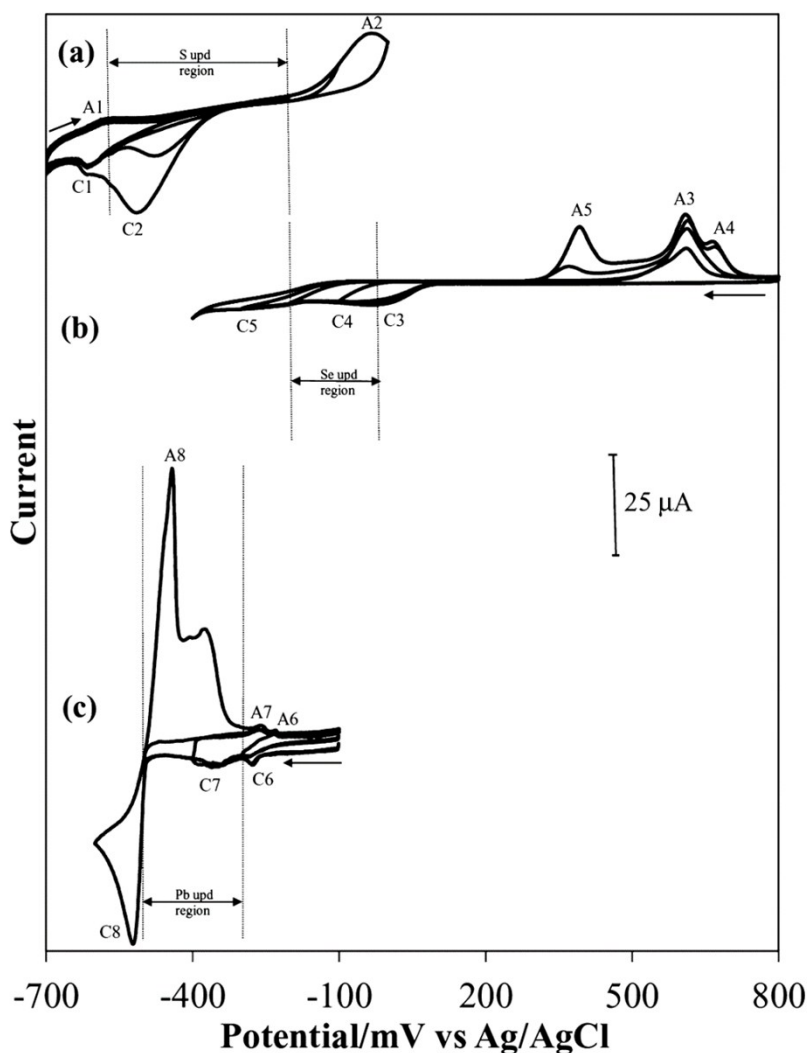
Fabrication of free-standing graphene paper decorated with flower-like $PbSe_{0.5}S_{0.5}$ structures

Ümit Çağrı Üst, Şemsi Betül Demir, Kader Dağcı, Murat Alanyalıoğlu*

Atatürk University, Sciences Faculty, Department of Chemistry, 25240, Erzurum, Turkey

* Corresponding author; E-mail: malanya@atauni.edu.tr; Phone: +90 442 231 4283; Fax: +90 442 231 4109

Fig. S1. Cyclic voltammograms of 1.0 mM Na_2S (a), 1.0 mM SeO_2 (b) and 1.0 mM $Pb(CH_3COO)_2$ (c) in 0.1 M ABS (pH: 5.9) on polycrystalline Au electrode. Cell temperature: 70°C. Scan rate: 50 mV.s^{-1}.
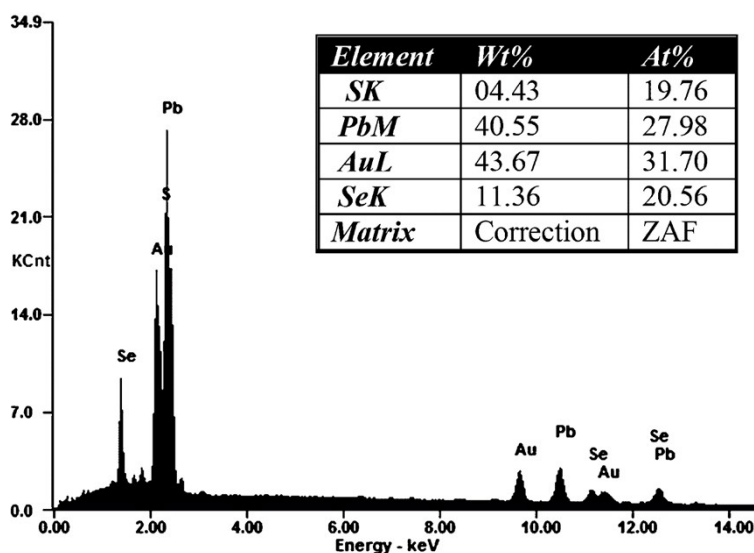
Fig. S1 exhibits the cyclic voltammograms of 1.0 mM Na_2S, 1.0 mM SeO_2, and 1.0 mM $Pb(CH_3COO)_2$ in 0.1 M ABS (pH: 5.9) on Au electrode. Dissolution of PbS and PbSe is very low and temperature is required to be elevated to increase the solubility of PbS and PbSe precipitates and to form sufficient amount of Pb^{+2}, S^{-2}, and Se^{+4} in the solution. So, cyclic voltammetry experiments have been applied at the same temperature with thin film preparation (electrodeposition) process and fixed at 70°C. The voltammetric behavior of sulfur is shown in Fig. S1.a and is very similar to previously obtained results. [1,2] When potential cycling of the working electrode is applied between -700 mV and 0 V, two peak pairs are observed at -575

mV/-630 mV (A1/C1) and -50 mV/-510 mV (A2/C2), which are attributed to upd and bulk deposition/desorption of sulfur, respectively. [1,2] Electrochemical investigation of selenium is represented in Fig. S1.b and is characterized by three peak pairs at -10 mV/+595 mV (C3/A3), -270 mV/+665 mV (C4/A4), and -470 mV/+400 mV (C5/A5). Peak pairs of C3/A3 and C4/A4 are assigned to surface-confined deposition/desorption of selenium, while peak pair of C5/A5 is due to bulk deposition/desorption. [3,4] Stickney et al. have investigated electrochemical behavior of selenium and they have reported that electrodeposition kinetic of Se is very low and electrodeposition of Se is composed of chain of chalcogenide atoms with about three monolayers, held together by van der Waals forces. [4]
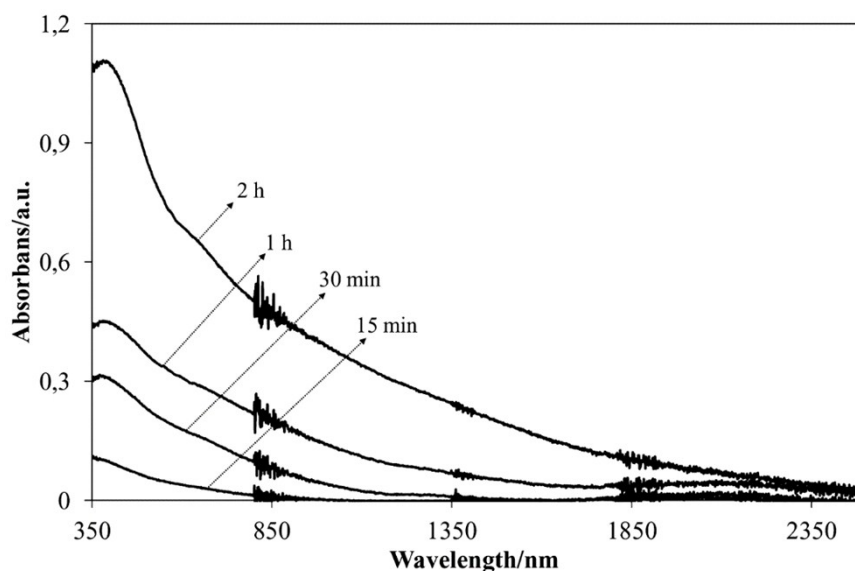
Fig. S1.c demonstrates voltammetric behavior of lead and it includes the peak pairs at -280 mV/-230 mV (C6/A6), -345 mV/-280 mV (C7/A7), which are assigned to underpotential deposition/desorption of lead, while peak pair at -520 mV/-445 mV (C8/A8) is associated with bulk deposition/desorption. [5] In order to obtain single crystal $PbSe_xS_{(1-x)}$ thin films with a highly-oriented structure, atom-by-atom electrodeposition of Pb, Se, and S is needed and electrodeposition potential must be suitable with upd of each element. As shown with dashed vertical lines in Fig. S1, potential regions of -575 mV/-200 mV, -200 mV/-10 mV, and -490 mV/-300 are associated with upd of S, Se, and Pb, respectively. Based on these limit potentials, electrodeposition potential has been determined as -300 mV. This constant potential value is fitted to upd of both Pb and S but it is clear that -300 mV is at the region of bulk deposition of selenium as seen in Fig. S1.b. Number of layers of electrodepositied selenium is highly related to selenium concentration in the electrochemical cell. Kazacos and Miller have reported that electrode surface is rapidly covered with red metallic selenium, if electrodeposition is carried out at bulk deposition region in a solution, which includes higher than 2.0 mM Se^{4+}. At the lower concentrations than 2.0 mM Se^{4+}, it is supposed that electrodeposition of Se at even bulk deposition region occurs via slow surface-limited reaction and results with a few layers of chain structure. [4,6] In our experimental setup, Se^{4+} species form with dissolution of PbSe at 70°C and it is obvious that Se^{4+} concentration in this solution is supposed to be considerably lower than the reported critical concentration of 2.0 mM.

EDS spectrum of $PbS_{0.5}Se_{0.5}$ thin film on Au(111) electrode (Fig. S2) indicates that there are four components; Au, Pb, Se, and S. Because Au comes from electrode, it is subtracted from all data

and the chemical composition of the thin film is calculated as 30.10% of Se, 28.93% of S, and 40.97% of Pb.

Element	Wt%	At%
SK	04.43	19.76
PbM	40.55	27.98
AuL	43.67	31.70
SeK	11.36	20.56
Matrix	Correction	ZAF

Fig. S2. EDS spectrum of $PbS_{0.5}Se_{0.5}$ thin film on Au(111) electrode.


Fig. S3. UV-vis.-NIR absorption spectra of ITO-coated glass electrode modified with $PbS_{0.5}Se_{0.5}$ thin film after 15, 30, 60, and 120 minutes electrodeposition time.

Fig. S3 shows UV-vis.-NIR absorption spectra of ITO-coated glass electrode modified with $PbSe_{0.5}S_{0.5}$ thin film after 15, 30, 60, and 120 min. electrodeposition time. It is obvious that the absorbance value in the spectra increases by increasing the film thickness (electrodeposition

time) as expected. Bandgap (E_g) value of each sample can be calculated by following equation;

$$E_g = 1240 / \lambda_g \qquad (1)$$

where, λ_g is the wavelength-axis (nm) while absorption coefficient is zero ($\alpha \rightarrow 0$) [7]. λ_g is determined as about 2200, 2380, 2530, and 2580 nm for 15 min, 30 min, 1 h, and 2 h electrodeposition times, respectively. E_g values have been calculated by using absorption spectra and equation 3.1 as 0.56, 0.52, 0.49, and 0.48 eV, respectively.
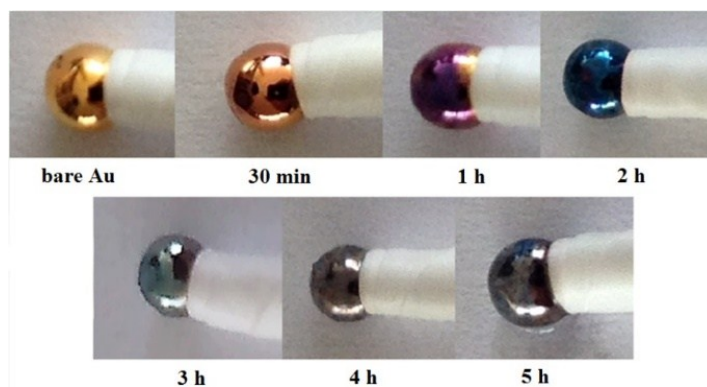

Fig. S4. Electrodeposited $PbS_{0.5}Se_{0.5}$ thin films on polycrystalline Au electrode from 0.1 M ABS (pH: 5.9) including 10 mg PbS + 10 mg PbSe. Electrodeposition potential: -300 mV. Cell temperature: 70°C.
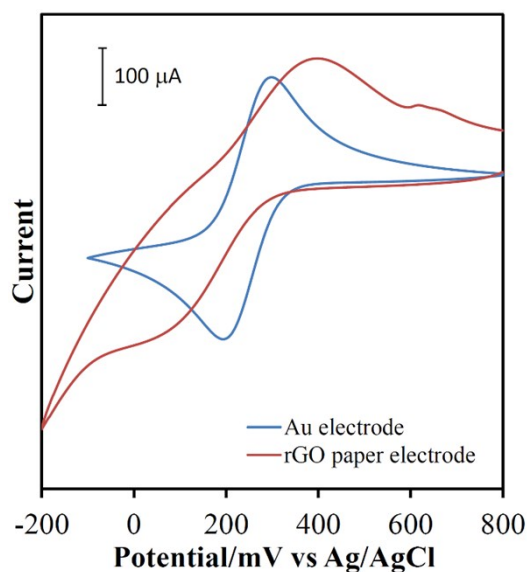
Fig. S5. Cyclic voltammograms of Au and rGO paper electrodes in a solution containing 0.1 M KNO_3 and 0.01 M $K_3Fe(CN)_6$. Scan rate: 50 mVs^{-1}.
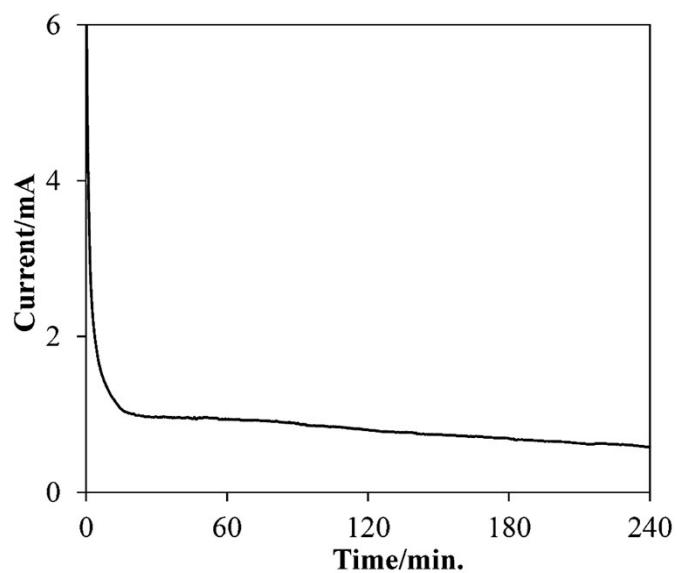
Fig. S6. Current-time data obtained for electrodeposition of PbSe$_{0.5}$S$_{0.5}$ thin films on rGO paper electrode. Applied potential: -450 mV.
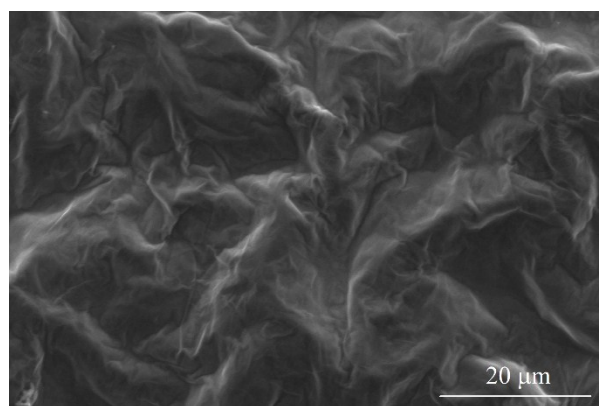
Fig. S7. SEM image of rGO paper

Determination of particle size from XRD data

Scherrer equation: $\tau = \dfrac{\kappa\lambda}{\beta\cos\theta}$

where:

τ is the mean size of the ordered (crystalline) domains in nm,

κ is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9 and varies with the actual shape of the crystallite,

λ is the X-ray wavelength in Å

β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radian,

θ is the Bragg angle.

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