Supporting Information

Correlation at Two-Dimensional Charge-Transfer FeSe Interface

Yulong Huang, Yong Hu, Feng Hu, Ruizhe Yang, Changning Li, Jason N. Armstrong and Shenqiang Ren*

Department of Mechanical and Aerospace Engineering, Research and Education in Energy Environment & Water (RENEW) Institute, University at buffalo, The State University of New York, Buffalo, NY 14260, USA

E-mail: shenren@buffalo.edu

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FeSe synthesis. Polycrystalline FeSe was synthesized from high-purity iron (Alfa Aesar, 99.9%) and selenium (Alfa Aesar, 99.999%) powder by solid state reaction. 0.70 g iron and 0.99 g selenium with an atomic ratio of 1 : 1 were mixed and grinded using an agate mortar and pestle for one hour. The mixture was pressed into pellets and then loaded into a glass tube that would be pumped into a high vacuum state of about 2 mTorr. The sealed glass tube was then placed in a furnace to run a sintering process. According to the iron-selenium phase diagram,[1] superconducting β-FeSe forms below 457 °C. To avoid the formation of other phases of FeSe system and protect the glass tube from melting, a relatively low temperature of 380 °C was chosen to sinter the FeSe pellets. The raw materials were heated to 380 °C at a ramping rate of 100 °C/h and held for 2 days to get a homogenous product. Then, the sample was slowly cooled down to 150 °C at 50 °C/h followed by furnace cooling to room temperature.

Exfoliation of 2D FeSe nanosheets. 15 mg FeSe powder sample was loaded into 50 ml centrifuge, then 20 ml acetonitrile was added as solvent. Fisher Scientific Power Gen 125 Homogenizer was used to exfoliate FeSe powder by immersing the machine head into the bottom of solution. Homogenization process was kept for half an hour at the highest rotation speed which are the best homogenizer power and time to obtain fully exfoliated nanosheets in a large size. Then, homogenously exfoliated FeSe nanosheets suspended in the acetonitrile solvent, resulting a grey solution with FeSe concentration of 0.75 mg/ml. In order to protect FeSe sample from oxidation by heat produced during the homogenization, the centrifuge was kept in a beaker that is full of ice. Besides, acetonitrile solvent is also especially selected to isolate oxygen and decrease moisture to protect nanosheets. Water is a bad solvent for preventing oxidation.

KTCNQ crystal synthesis. 0.18 g KI and 0.22 g TCNQ were dissolved in 25 ml acetonitrile centrifuges respectively. After 10 minutes ultra-sonication, the two centrifuges of KI solution (colorless) and TCNQ solution (orange) were placed in 90°C water bathing to totally dissolve the KI and TCNQ grains. When the KI solution and TCNQ solution were clean without residues, KI solution was poured slowly into the centrifuge of TCNQ solution whose color turned into green at the meantime. The centrifuge of green mixed solution was placed vertically to cool down and evaporate acetonitrile solvent naturally. When 10 ml acetonitrile was evaporated, the rest solution was poured out carefully from the centrifuge and abundant purple crystallized grains were collected from the bottom of the centrifuge. To obtain a big crystal with a size of 1 mm * 0.5 mm, recrystallization of KTCNQ is needed. All the processes were conducted in a fuming hood.

FeSe-KTCNQ device for light illumination. The exfoliated FeSe nanosheets solution was dropped by a 20 μL pipetter onto 50 μm gap finger electrodes of an integrated ITO glass substrate (Ossila). After several drops coating and solvent evaporation, a FeSe nanosheet layer covered the ITO electrodes and presented a resistance of $1\sim10^3$ kΩ. Then, KTCNQ acetonitrile solution was dropped and dried out to recrystallize KTCNQ wires on FeSe nanosheets during which the KTCNQ-FeSe interface was formed. The solar light was applied by a LCS-100 solar simulator with an electronic shutter from Oriel instruments. Using two-electrode method, the light-induced current evolution and *I-V* curves were recorded by Keithley 2450 sourcemeter.

KTCNQ-FeSe nanosheets dimerization measurements. 50.8 mg KTCNQ was dissolved in acetonitrile solvent, then different amounts of FeSe nanosheet solution was added into KTCNQ solution by three steps with a molar ratio of n(FeSe) : n(KTCNQ) = 0.0032, 0.0096 and 0.0141, respectively. After each step, acetonitrile solvent was evaporated completely and two compounds contacted together to form the coupling interface. The mixture of FeSe nanosheets and KTCNQ was collected and mounted into a quartz cell to measure the magnetic susceptibility from 300 K to 450 K under an external magnetic field of 1 Tesla. All the magnetic measurements above 300 K were conducted on MicroSense line of Vibrating Sample Magnetometer with Nitrogen gas flow as sample protection.

Structure characterizations and low temperature magnetic properties measurements. The scanning electron microscopic image of surface morphology of FeSe and KTCNQ was taken on the Carl Zeiss AURIGA Cross Beam Focused Ion Beam Electron Microscope with an accelerating voltage of 200 KV, and a point resolution of 0.19 nm. The TEM image of exfoliated FeSe nanosheets was taken on a high-resolution electron microscope-JEOL JEM 2010. X-ray diffraction experiments were conducted on the Rigaku Ultima IV with operational x-ray tube power of 1.76 kW (40 kV, 44 mA). Low temperature magnetic properties measurements were conducted on a Physical Properties Measurement System (PPMS, Quantum Design) equipped with a Vibrating Sample Magnetometer (VSM).

Light illumination of KTCNQ, 2D FeSe and KTCNQ-coated 2D FeSe. Figure S1 shows the raw data of light illumination of 2D FeSe nanosheets, KTCNQ and KTCNQ-coated 2D FeSe nanosheets for which the same ITO patterned substrates are used as electrodes and holder. Their light-induced current enhancements are synchronously tuned by the on-off circle of light illumination. The current in KTCNQ is smaller than those in 2D FeSe and KTCNQ-coated 2D FeSe under a voltage of 1 V as well as the current enhancement (Fig. S1a). After coating a layer of KTCNQ, current enhancement in 2D FeSe is larger than before under light illumination (Fig. S1b). The current versus voltage curve of KTCNQ-coated 2D FeSe shows the current enhancement in the whole voltage range of – 20 V ~ + 20 V, compared to that of only 2D FeSe (Fig. S1c). All the light illumination data were analyzed by subtracting the slopes of current versus time (*I-t*) curves, as shown by dash lines in Fig. S2a-S2c, to exclude the thermal effects. A longer on-off circle period is needed to relax the samples to initial states (Fig. S4). After the slope subtraction, a large current enhancement is obvious in KTCNQ-coated 2D FeSe by KTCNQ of a little bit current enhancement where the *I-t* curves are re-plotted in Fig. S2d. Therefore, the net current enhancement by charge transfer from KTCNQ is obtained by subtracting the *I-t* curve of 2D FeSe from that of KTCNQ-coated 2D FeSe. To confirm the charge transfer at the FeSe-KTCNQ interface, another FeSe-KTCNQ device was prepared by mechanically putting KTCNQ crystals onto the top of 2D FeSe where no atomically bonded interface was formed. In this case, there was no extra current enhancement in the 2D FeSe after covering some KTCNQ crystals as shown in Fig. S3. Thus, the large current enhancement in 2D FeSe by coating KTCNQ (Fig. 3b and Fig. S2e) is contributed by the charge transfer at their interface.

Spin coupling at the interface of FeSe-KTCNQ

Magnetic properties of KTCNQ and FeSe are studied by magnetic field and temperature dependent magnetization as shown in Fig. S5 and S6. For KTCNQ, a linear magnetization versus magnetic field (*M*-*H*) curves show a diamagnetic behavior at 290 K and 450 K (Fig. S5a) that is consistent with the magnetization versus temperature (*M*-*T*) curve with a negative background under an external magnetic field of 1 Telsa (Fig. S5b). The dimerization transition in KTCNQ appears at 389 K and 370 K for zero-field cooling (ZFC) and field cooling measurements respectively. For the spin coupling study of FeSe-KTCNQ, all the *M*-*T* measurements above 300 K were conducted in ZFC mode. As shown in Fig. S7, the dimerization behavior is influenced by the 2D FeSe nanosheets by shifting the dimerization temperature from 389 K to 395 K with a molar ratio of n(FeSe) : n(KTCNQ) = 0.0096. Even only a little 2D FeSe nanosheets were added into KTCNQ, the magnetization of KTCNQ increased rapidly.

In order to confirm the spin coupling effect on dimerization temperature, only FeSe powder of same molar ratio was added into another batch KTCNQ powder and the dimerization temperature was not changed and kept at 386 K (Fig. S8). Therefore, the FeSe-KTCNQ interface is important for tunable dimerization and formed only by mixing their acetonitrile solution and the evaporating the solvent.

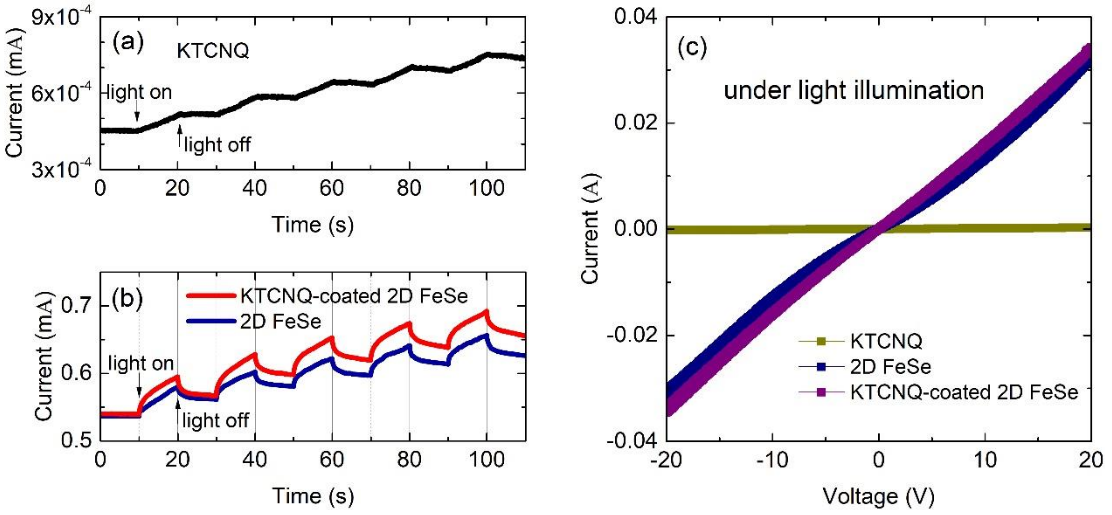

Figure S1. (a) Light illumination effect of KTCNQ crystal under a voltage of 1 V; (b) Current enhancement in FeSe nanosheets and KTCNQ-coated FeSe nanosheets under periodic light switching on-off circles; (c) the *I-V* curves of KTCNQ, FeSe nanosheets and KTCNQ-coated FeSe nanosheets under solar light illumination.

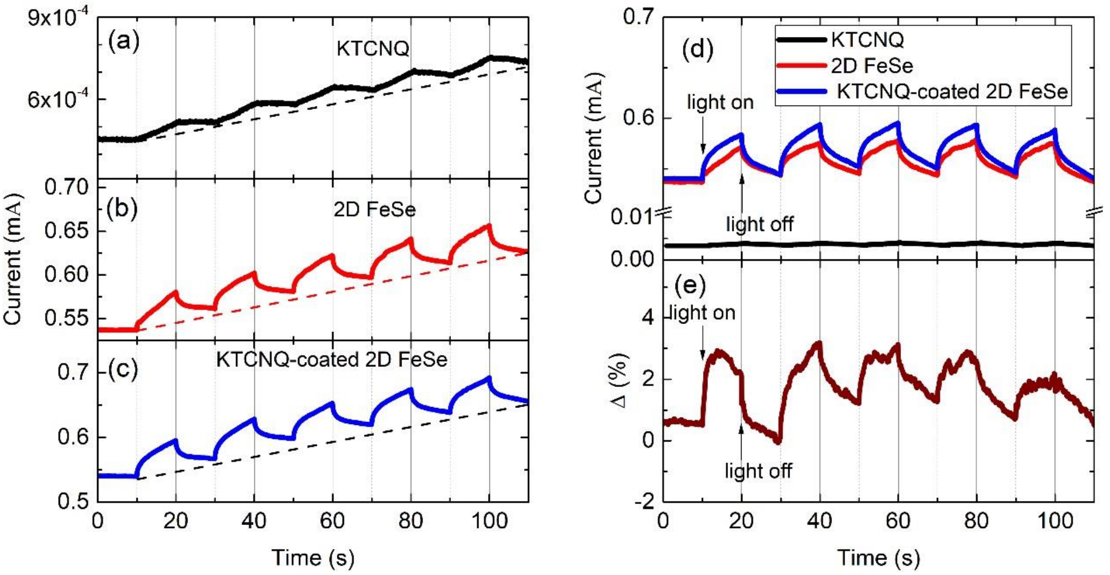

Figure S2. Calculation processing of photoinduced current enhancement in 2D FeSe layer coated with KTCNQ under light illumination. (a-c) Time dependent photoinduced current (*I-t*) curves of KTCNQ, 2D FeSe and KTCNQ-coated 2D FeSe. The dash lines are background base-lines whose slopes is used to be subtracted from the raw data. (d) *I-t* curves after subtracting the slopes of background base-lines. (e) The current enhancement of KTCNQ-coated 2D FeSe layer due to charge transfer that is calculated by subtracting the *I-t* curve of 2D FeSe from that of KTCNQ-coated 2D FeSe.

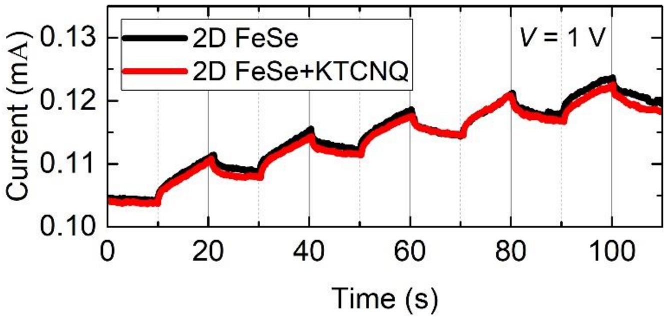

Figure S3. The comparison of photoinduced current of 2D FeSe nanosheets before and after KTCNQ crystals was directly covered on the top instead of KTCNQ solution. The two curves are almost equal, showing no current enhancement by KTCNQ crystal where no interface is formed.

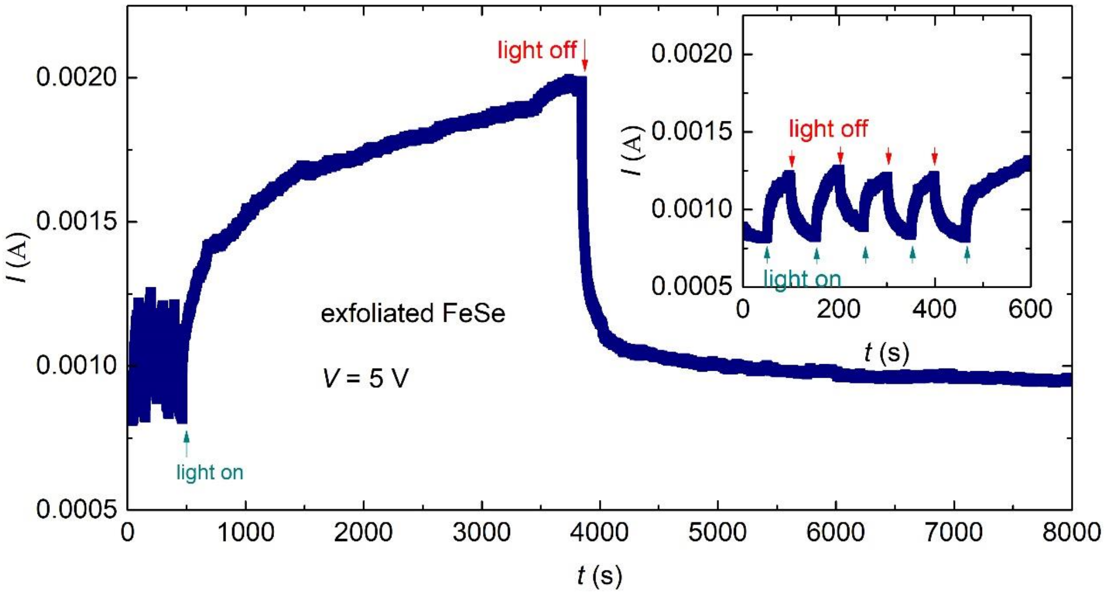

Figure S4. Light-induced current in exfoliated FeSe nanosheets under light illumination was modulated by an on-off circle period of 50 seconds in the beginning (inset). The light-induced current can be saturated when the device was illuminated for enough long time and gradually recovered to the initial state after turning off the light.

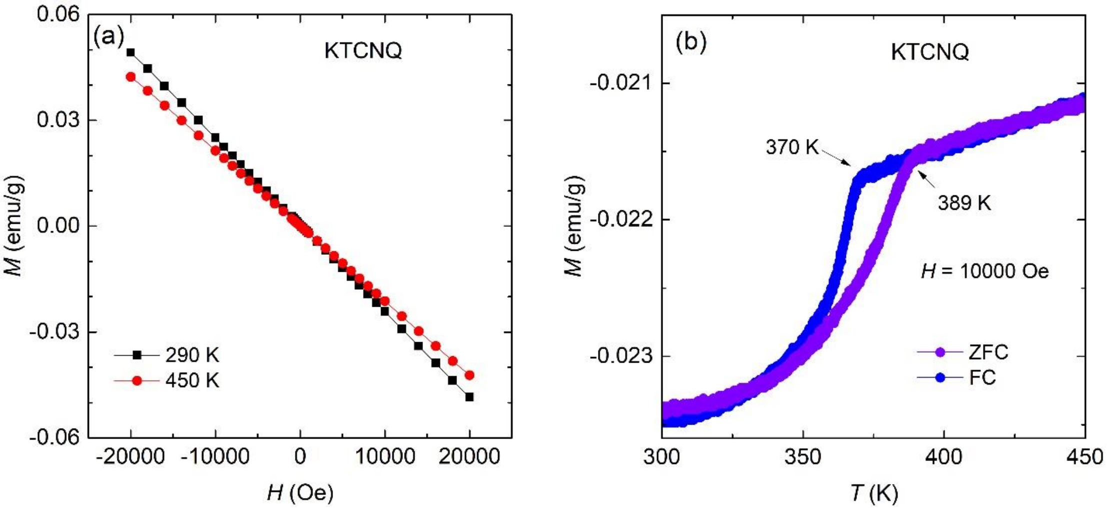

Figure S5. (a) MH loops of KTCNQ at 290 K and 450 K show the diamagnetic behaviors without magnetic hysteresis. (b) Dimerization transition of KTCNQ measured under 10000 Oe by ZFC and FC.

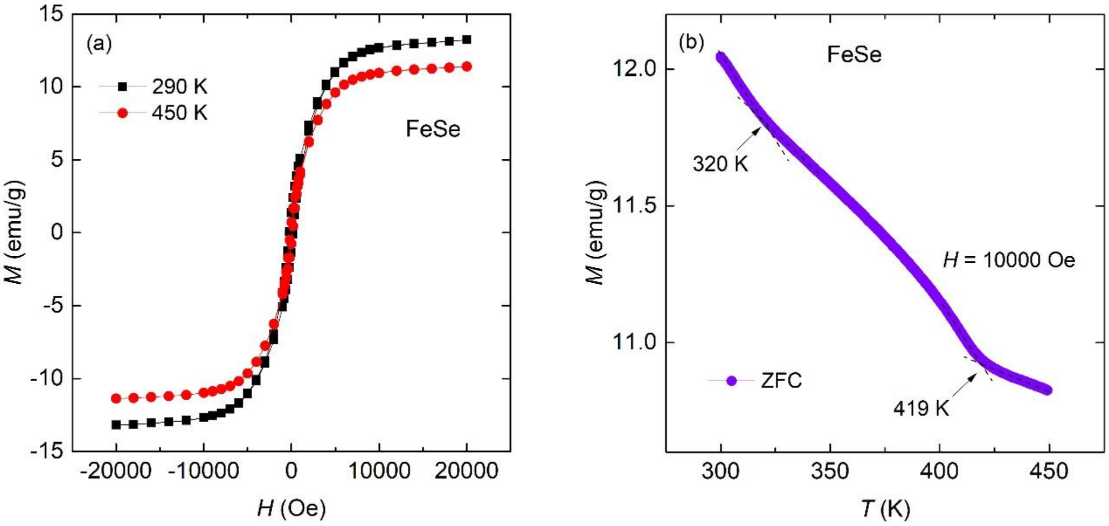

Figure S6. (a) MH loops of FeSe powder at 290 K and 450 K. (b) Temperature dependent magnetization of FeSe powder measured from 300 K to 450 K under 10000 Oe, showing two transitions at 320 K and 419 K.

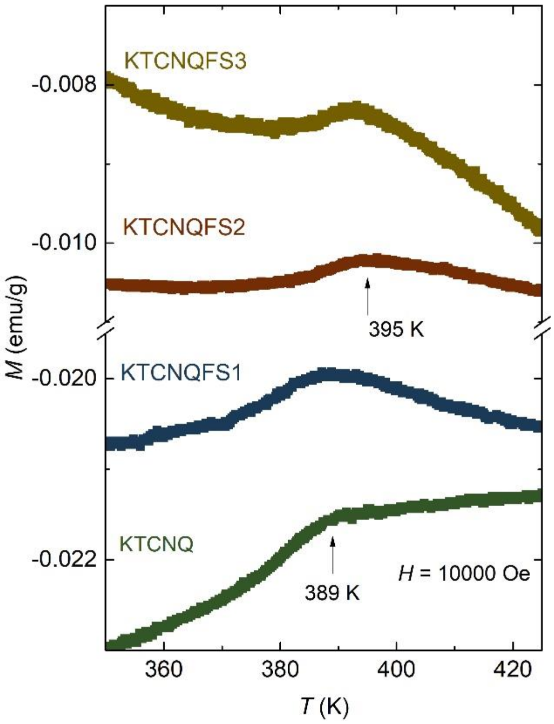

Figure S7. Temperature dependent magnetization of KTCNQ before and after mixing with 2D exfoliated FeSe nanosheets. KTCNQFS1, KTCNQFS2 and KTCNQFS3 represent the molar ratio of n(FeSe) : n(KTCNQ) = 0.0032, 0.0096 and 0.0141, respectively.

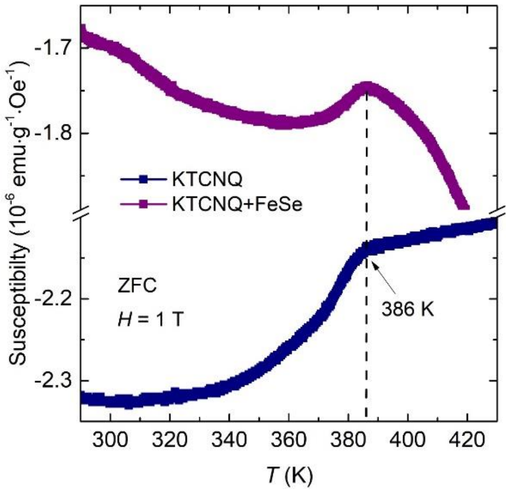

Figure S8. The comparison of magnetic susceptibilities of KTCNQ before and after mixing with FeSe powder at the molar ratio of n(FeSe) : n(KTCNQ) = 0.0096 instead of exfoliated FeSe nanosheets solution. The sample KTCNQ shows a dimerization transition at 386 K that does not changed after mixing with FeSe powder, indicating the spin coupling is not formed in the mixture of FeSe powder and KTCNQ.

References:

(1) Okamoto, H., Journal of Phase Equilibria 1991, 12 (3), 383.