Supporting Information

Observing Charge Transfer Interaction in CuI and MoS$_2$

Heterojunction for Photoresponsive Device Application

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1.1 Scanning electron microscope (SEM) of γ-CuI film deposited on MoS$_2$ crystals

As discussed in the main manuscript γ-CuI film was thermally evaporated on a continuous MoS$_2$ film to analyze the heterostructure and photoresponsivity. Further, the γ-CuI was thermally evaporated on individual MoS$_2$ crystals as shown in the figure S1a. The continuous γ-CuI film was obtained on the MoS$_2$ crystals, where small voids (black spots in the figure S1b) were observed in the grain boundaries of the crystals.
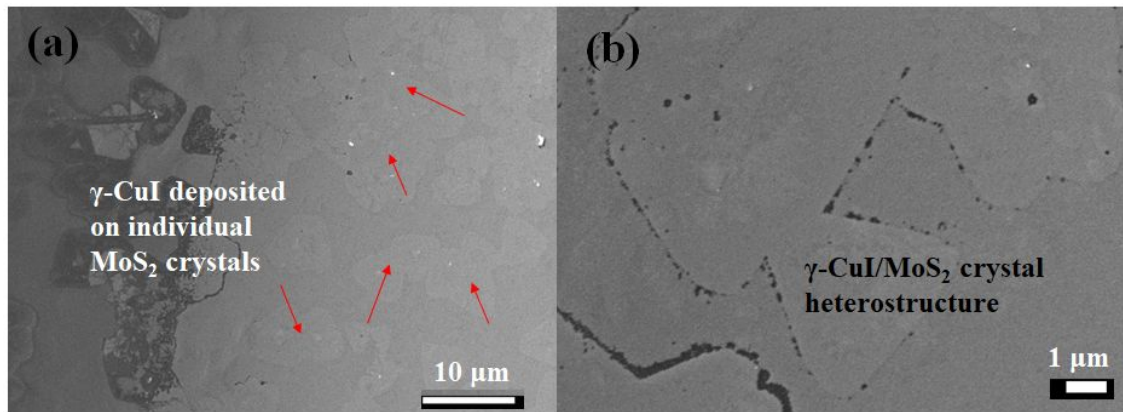

Figure S1 (a) Thermally evaporated γ-CuI on individual MoS$_2$ crystals (b) higher resolution of triangular MoS$_2$ crystal with top γ-CuI film.

1.2 Transmission electron microscope (TEM) study of the continuous MoS$_2$ film

The TEM analysis of the continuous MoS$_2$ film deposited on a SiO$_2$/Si substrate was analyzed by transferring on the TEM grid. The large-area CVD synthesized MoS$_2$ film mostly contains single and bilayer at the edge of the SiO$_2$/Si substrate (figure S2), whereas few-layers were formed at the center part of the substrate. The sample with monolayer and bilayer MoS$_2$ was used for deposition of γ-CuI film and device fabrication.
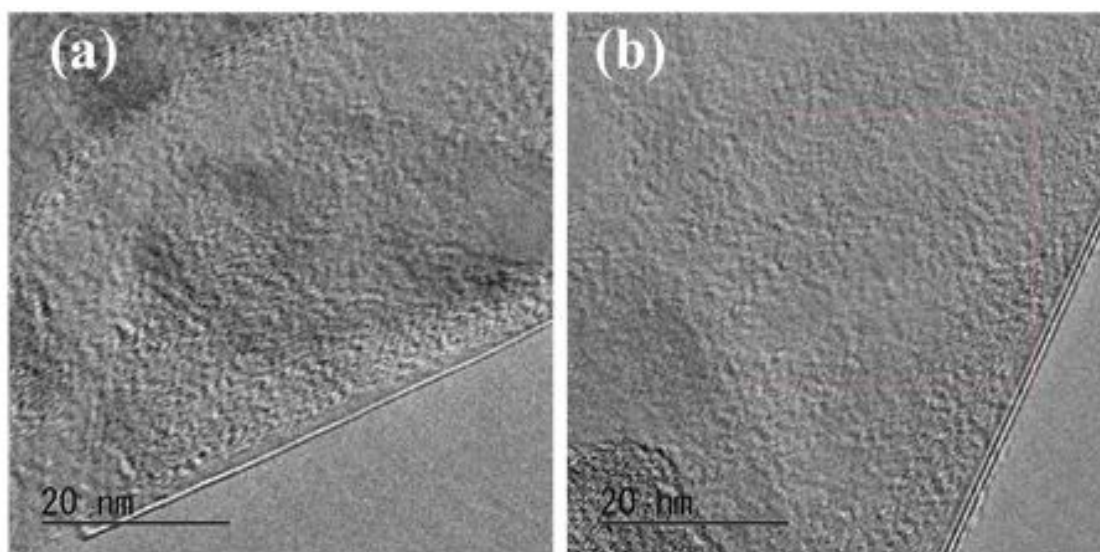
Figure S2 (a) Monolayer and (b) bilayer MoS_2 synthesized by the CVD process, where γ-CuI film was deposited for device fabrication.

1.3 Stoichiometry analysis of γ-CuI film

Stoichiometry analysis of the thermally evaporated γ-CuI film was performed by fitting spectra for Cu3p and I3d as shown in figure S3a-b. The area of fitting spectra for both Cu and I peaks were analyzed to obtain the quantities of Cu and I atoms. The fitting spectra showed almost 1:1 ratio (Cu ~51 and I~49%) of the Cu and I atoms in the highly crystalline γ-CuI film.
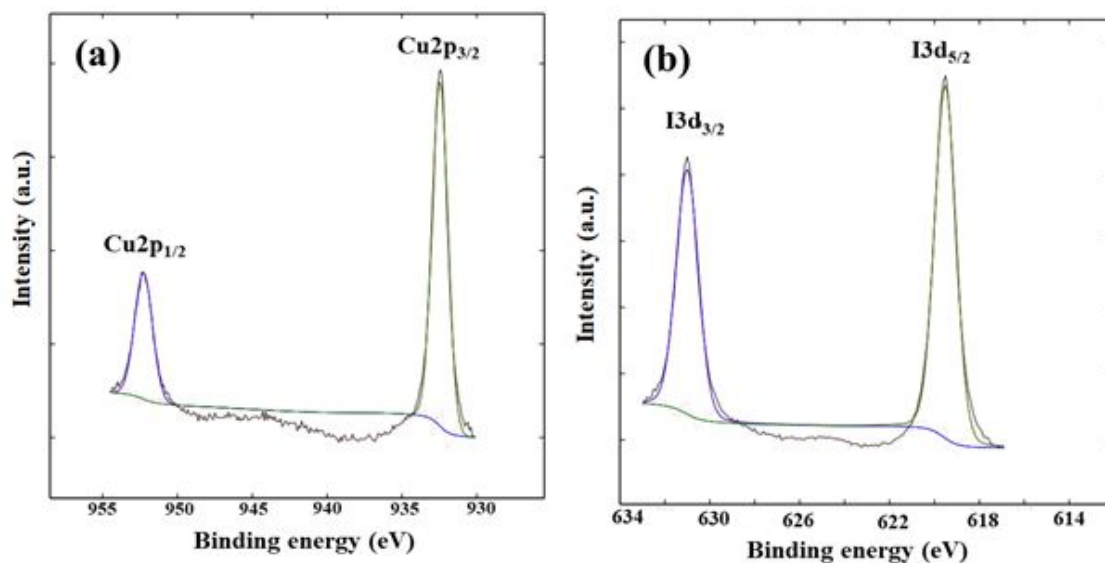
Figure S3 Fitting spectra for (a) Cu3p and (b) I3d spectra of the thermally evaporated γ-CuI film.

1.4 SEM micrograph of the Au/γ-CuI/MoS₂/Al heterojunction device
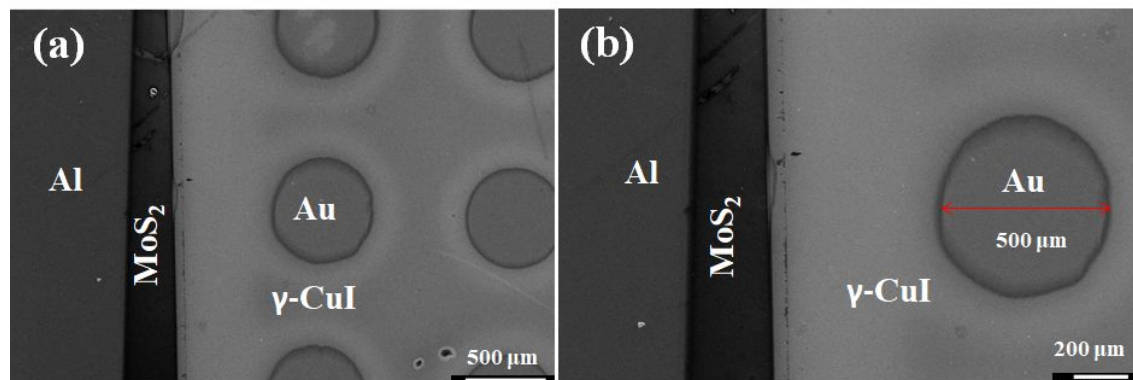

Figure S4 (a) and (b) SEM images of the Au/CuI/MoS₂/Al heterojunction device presenting the Au contact on γ-CuI and Al contact on MoS₂.

Figure S4a-b shows the SEM images of the fabricated Au/γ-CuI/MoS₂/Al heterojunction device. Al electrode was thermally evaporated on MoS₂ layer around 200 μm apart from

the γ-CuI film. The high work function Au round electrodes (radius 250 μm) were

deposited by thermal evaporation at a high vacuum condition.

1.5 Comparison of XRD data with standard JCPDS (Card No. 06-0246) for cubic CuI (γ-CuI)
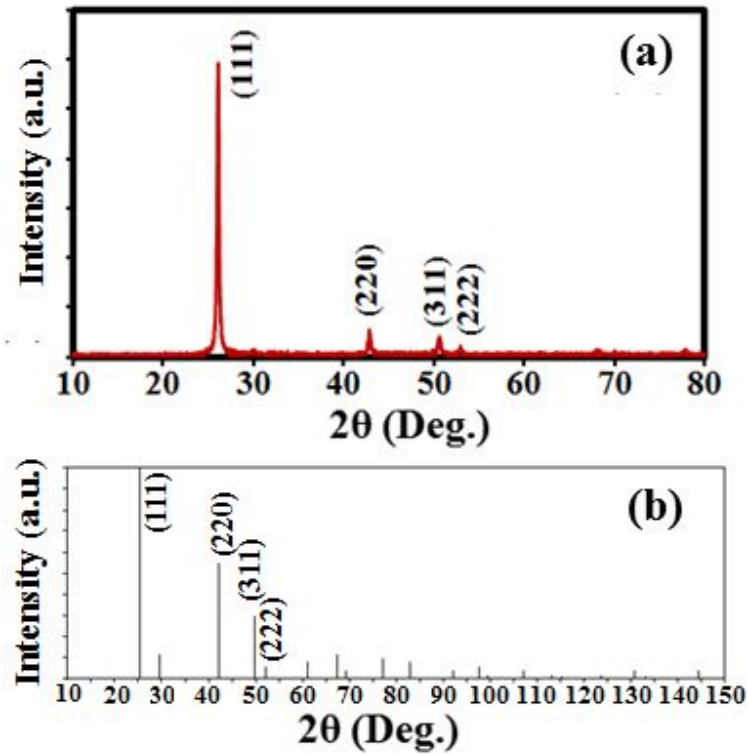

Figure S5 (a) XRD diffraction pattern of thermally evaporated CuI film on glass substrate

(b) Standard JCPDS Card No. 06-0246 for cubic CuI (γ-CuI).

The XRD spectra for thermally evaporated CuI film (figure S5a) show a strong

diffraction peak corresponding to the (111) plane and the synchronicity of (220), (331)

and (222) facets show that CuI crystal growth preferably oriented along the (111)

direction which is in coordination with standard JCPDS (Card no. 06-0246, figure S5b)

for cubic CuI (γ-CuI).

1.6 Determination of band alignment for the γ-CuI/MoS₂ heterostructure

The bandgap offset values of semiconductor materials are very critical for developing heterojunction based electronic and optoelectronic devices [1-3]. The valence band offset of the fabricated γ-CuI/MoS₂ heterostructure was investigated from the XPS analysis as also discussed in the paper. The top deposited γ-CuI film was very thin, allowing to obtain XPS signal for both the γ-CuI and MoS₂ layer. The desired area is located by measuring the intensity of Cu3p and Mo3d core-levels for the γ-CuI and MoS₂ layer. The method allows us to calculate the precise values of valence band offset for the γ-CuI/MoS₂ heterojunction using the following equation (1).

$$\Delta E_v = \left(E_{Mo3d}^{MoS2} - E_{Cu3p}^{CuI}\right) + \left(E_{Cu3p}^{CuI} - E_{VBM}^{CuI}\right) - \left(E_{Mo3d}^{MoS2} - E_{VBM}^{MoS2}\right) \quad (1)$$

Where, the first term is the separation in binding energy for Cu3p and Mo3d core levels of the γ-CuI/MoS₂ interface. The second and third terms of the equation are the binding energy difference between the core level and valence band maximum (VBM) of MoS₂ and γ-CuI, respectively. The VBM positions are calculated by extrapolating the leading edge of VBM spectra as shown in figure 6e and 6f in the paper. The VBM values for the MoS₂ and p-type γ-CuI film are 0.25 eV and -0.27 eV, respectively. The difference between the Cu3p and Mo3d$_{5/2}$ core-levels is measured to be 153.5 eV at the interface. Now, from the values of Cu3p, Mo3d and respective VBM values the valence band offset

(ΔE_v) is calculated to be 0.52 eV by using Eq. (1).

Again, the conduction band offset can be calculated as the following equation (2) for the

γ-CuI/MoS$_2$ heterojunction.

$$\Delta E_C = \Delta E_v + E_g^{CuI} - E_g^{MoS2} \quad (2)$$

Where, ΔE_v is the valence band offset as obtained from above equation (1). The band

gap of CuI as 2.98 eV, and MoS$_2$ as 1.81 eV are used for determining the conduction band

offset, which is calculated to be 1.69 eV.

1.7. Device characteristic for γ-CuI synthesized by solid-phase iodization on MoS$_2$
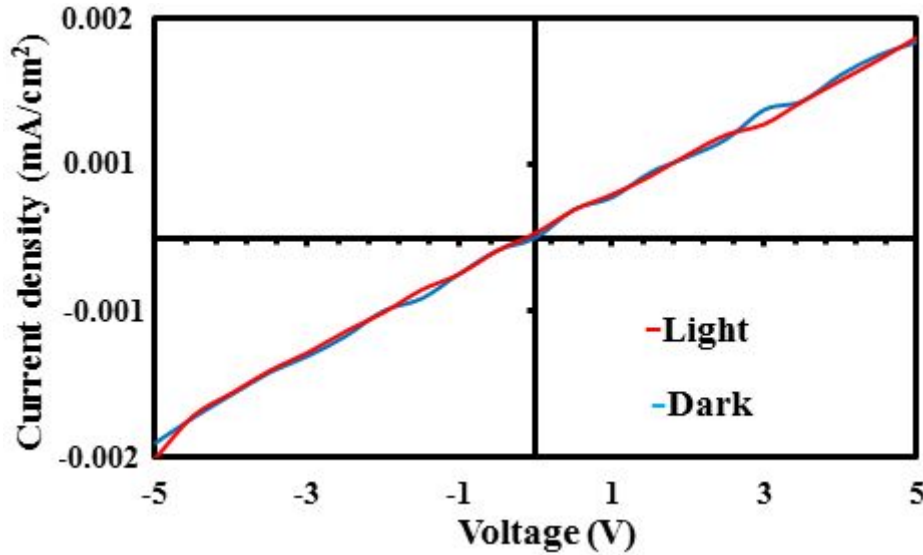
layer (γ-CuI/MoS$_2$)

Figure S6. *J-V* characteristics under dark and light illumination for the γ-CuI synthesized

by solid-phase iodization on MoS$_2$ layer with a device structure of Au/γ-CuI/MoS$_2$/Al.

The *J-V* measurement for the device with **γ-CuI** synthesized by solid-phase iodization on MoS$_2$ layer is represented in figure S6. The **γ-CuI** film obtained by solid-phase iodization showed particle-like structures with high surface roughness on MoS$_2$ layer as explained in figure 2b. It is difficult to deposit a continuous gold electrode for contact on the highly rough CuI. Whereas, a thicker gold contact is opaque to incident light for photoresponse, due to which a photoresponsivity was not observed in the fabricated device. We believe that better morphology, crystalline structure and the selection of electrode material are important aspects for the device with γ-CuI synthesized by solid-phase iodization on MoS$_2$ layer to obtain photoresponsivity. Thus, the thermally evaporated γ-CuI on MoS$_2$ layer has been used for fabrication of high performance photoresponsive device.

References:

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