ADVANCED MATERIALS

Supporting Information

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Actively Tunable Visible Surface Plasmons in Bi_2Te_3 and their Energy-Harvesting Applications

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Experimental Section

Materials and synthesis. Bismuth oxide (Bi_2O_3, 99.999%), tellurium dioxide (TeO_2, 99.995%) and selenium dioxide (SeO_2, 99.995%) were purchased from Alfa Aesar. Ethylene glycol (EG), isopropanol (IPA), glycerol, sodium hydroxide (NaOH), and polyvinylpyrrolidone (PVP, molecular weight 55000) were purchased from Sigma-Aldrich. Highly conductive PEDOT:PSS (Clevios PH1000) was purchased from Heraeus Precious Metals GmbH & Co. KG, in which the PEDOT:PSS weight ratio is 1 : 2.5 and the specific conductivity is 850 S/cm. All the chemicals were analytical grade and directly used as received without further purification.

In a typical process of synthesizing Bi_2Te_3 nanoplates, 0.4 g PVP was dissolved in ethylene glycol (18 mL) to form a clear solution, followed by the addition of Bi_2O_3 (0.2298 g, 0.5 mmol), TeO_2 (0.2394 g, 1.5 mmol) and 2 mL of NaOH solution (5 mol/L). The resulting precursor suspension was stirred vigorously for 30 min, and then sealed in the autoclave, which was then heated to 220 °C, maintaining for 4 h. The products were washed several times with distilled water and absolute ethanol, and then collected by centrifugation. The final product with uniform morphology was collected by centrifuging at 1000 rpm for 5min. To synthesize the Se doped samples, certain amount of SeO_2 was added to replace TeO2, while the other parameters were kept the same.

Characterizations. The synthesized samples were characterized with AFM (Bruher Dimension FastScan), SEM (JEOL 6701 FESEM), TEM (JEOL JEM-3010) and Raman (Alpha 300 R). UV-Vis spectra were collected by dispersing samples in IPA. Single particle dark field scattering spectra were collected by drop casting Bi_2Te_3 nanoplates on glass substrates, and used the same instrument configuration with previous study. EELS were performed in STEM mode of FEI Titan TEM, with the same parameters used as our previous

study.[2] The Bi_2Te_3 samples used for EELS measurements were drop cased onto a 30 nm silicon nitride membrane.

Preparation of silicon substrates. The n-type Si (100) wafer (300 µm, resistivity of 5 Ω/cm) was sequentially cleaned in acetone, ethanol and deionized (DI) water for 20 minutes at room temperature, this is followed by cleaning in the mixture of concentrated H_2SO_4 and H_2O_2 for 1 hour at 110 ℃. The chemical passivation of silicon substrate was carried out in the following ways. First, the substrate was chlorinated by immersing it in an aqueous solution of HF (4.8 M) for 30 minutes at room temperature and then dipped into the saturated solution of PCl_5 in chlorobenzene (CB) at 120 ℃ under inert atmosphere for 1 h, after which the Si–H bond became Si–Cl bond. The substrate was then rinsed sequentially with CB and tetrahydrofuran (THF). Second, the substrate was immersed in the solution of CH_3MgCl (1 M) in THF for at least 5 h at 80 ℃ to complete methylation process, then rinsed with THF. Finally, the substrate was immersed into diluted hydrochloric acid for 1 h and rinsed with DI water. To enhance the charge carrier separation, the n-Si substrate is pre-treated to form a surface passivation layer by methyl termination. The covalent bonding between methyl group and silicon means the dangling bonds on the surface of silicon are dramatically reduced, resulting in efficient suppressing of the surface charge recombination.[3],[4]

Device fabrication and characterizations. PEDOT:PSS solution was filtered through a 0.45 um PVDF filter, and then mixed with a certain amount of Bi_2Te_3 nanoplates as well as a wetting agent of 1wt% Trion X-100 and 5 wt% DMSO, which help to decrease the surface energy of hydrophilic PEDOT:PSS on hydrophobic silicon substrate and increase the conductivity of the film. After stirring at room temperature and under inert atmosphere for half an hour, the Bi_2Te_3/PEDOT:PSS blend film (80 nm) was deposited on planar silicon substrate by spin-coating process with a spin speed of 1800 rpm per minute. The substrate

was annealed at 115 ℃ for 15 minutes in ambient atmosphere. 200-nm-thick silver top grid contacts were deposited by electron beam evaporation. The metal covered part consists of 10% of the whole area of top surface. Aluminum back electrode was deposited by thermal evaporation.

The characterizations of the devices were performed in ambient atmosphere. Simulated solar spectrum irradiation source was generated by Newport 91160 solar simulator with a 300 W Xenon lamp and an air mass (AM) 1.5 filter. The irradiation intensity was 100 mW/cm^2, and calibrated by a Newport standard Si solar cell 91150. Incident photon to charge carrier efficiency (IPCE) measurements were performed by Newport monochromator 74125 and power meter 1918 with Si detector 918D. The data were recorded by Keithley 2612.

PL measurements. Dispersed Bi_2Te_3 nanoplates were drop-casted onto a quartz substrate, on top of which a thin Al_2O_3 film was deposited by atomic layer deposition with various thicknesses as the spacing layer. CdSe/ZnS QDs then self-assembled on the surface to form a uniform monolayer. Photoluminescence of quantum dots supported by individual Bi_2Te_3 nanoplates with an excitation source of 410 nm laser was measured. All spectra were normalised to the reference sample. Time-resolved PL decay spectra were collected and fitted to the bi-exponential function to derive the PL lifetime.[5]

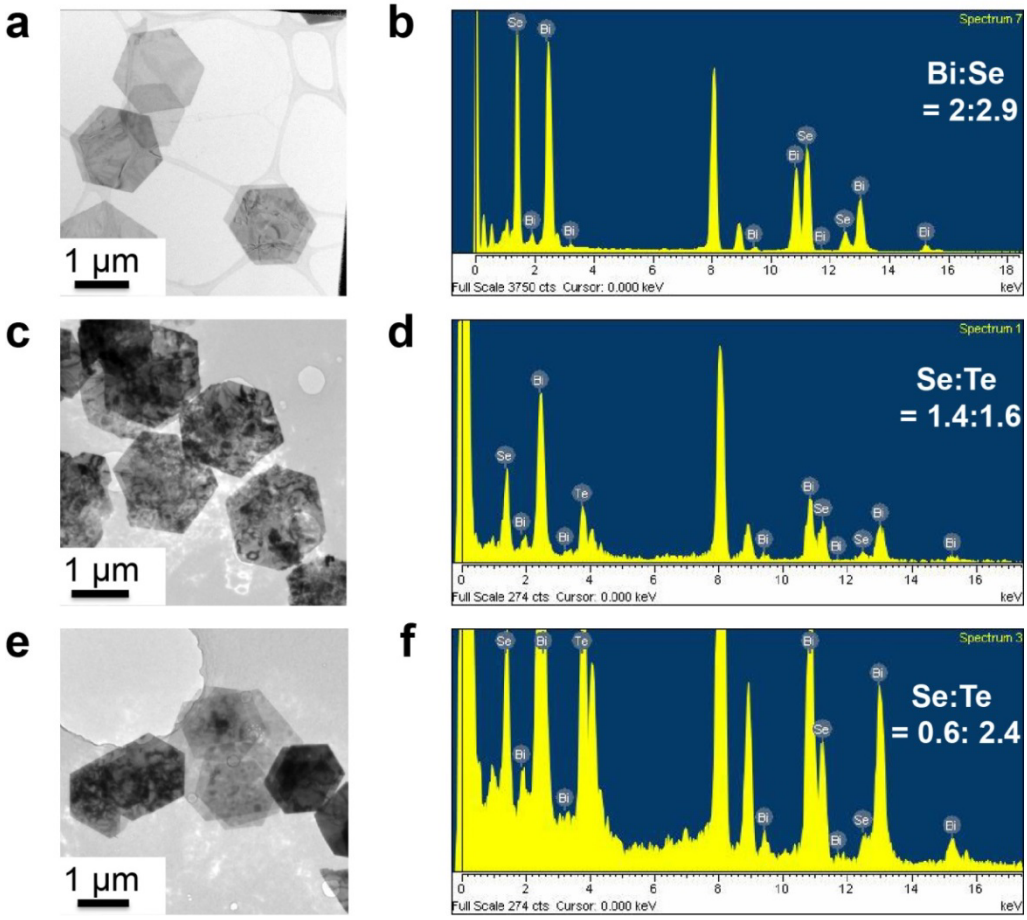

Figure S1. (a), (c), (e) TEM images and (b) (d) (f) EDX spectra of the doped samples with the ratio indicated in EDX.

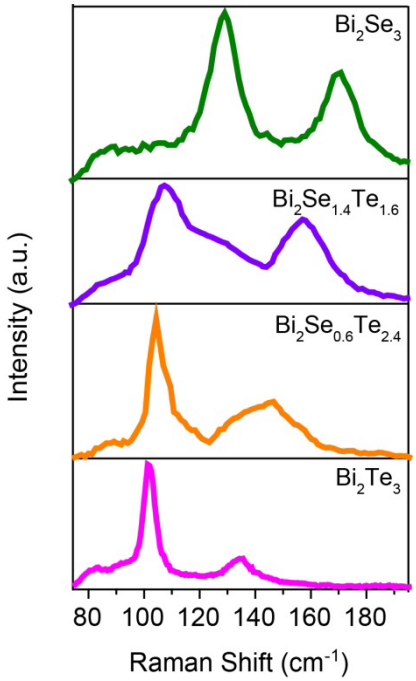

Figure S2. Raman spectra of as-synthesized nanoplates with different Se doping level.

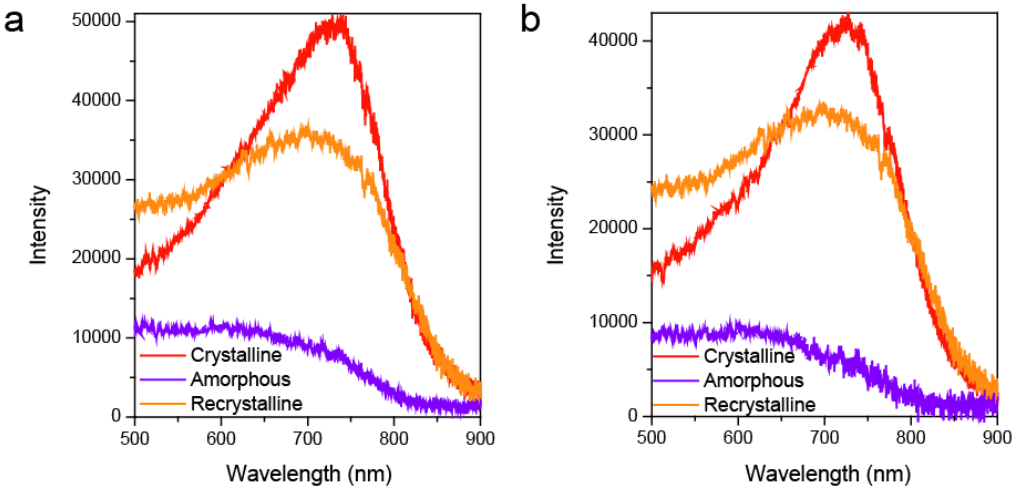

Figure S3. Dark field scattering spectra of other two typical Bi_2Te_3 nanoplates.

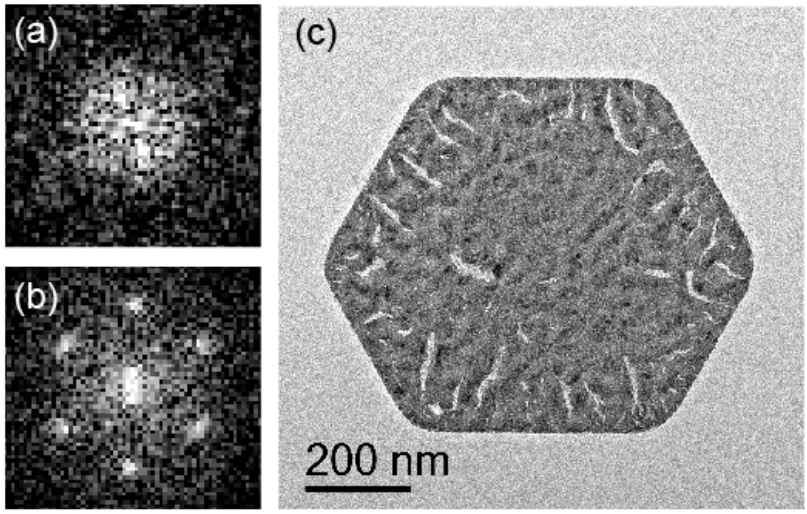

Figure S4. FFT TEM images of (a) right amorphous corner and (b) left crystal corner of the nanoplate shown in Figure 2c. (c) TEM image of a fully amorphous Bi_2Te_3 nanoplate.

Schottky barrier height. The barrier height of Schottky junction is determined using the following equation[6]

$$J = J_0[\exp(\frac{eV}{nkT}) - 1] = A^* A T^2 \exp(-\frac{\phi_{SBH}}{kT})[\exp(\frac{eV}{nkT}) - 1]$$

Where A is the contact area, A^* is the effective Richardson constant (252 A cm^{-2} K^{-2} for n-Si) , e is the electronic charge, n is the diode ideality factor, ϕ_{SBH} is the barrier height, V is the applied potential, J_0 is the reverse leakage current density, J is the current density. Figure S4a shows the energy diagram of Schottky junction formed between interface of metal and n-type semiconductor. The ϕ_{SBH} of reference solar cell and Bi_2Te_3 enhanced solar cell was calculated as 0.79 eV and 0.85 eV, respectively, as determined from the dark current-voltage characteristics shown in Fig. S4b.

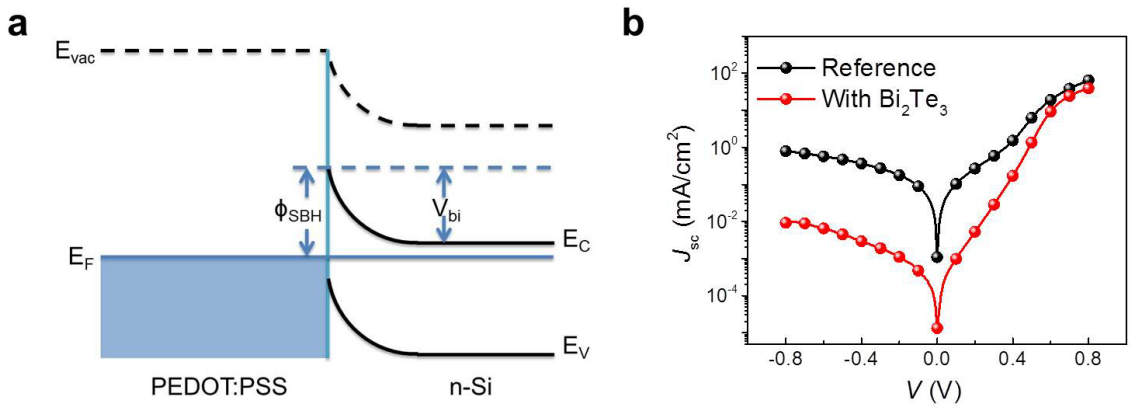

Figure S4. (a) Energy diagram of Schottky junction formed between interface of metal and n-type semiconductor. (b) Dark current-voltage characteristics of reference cell and solar cell with Bi_2Te_3 nanoplates incorporated.

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