

## Supporting Information

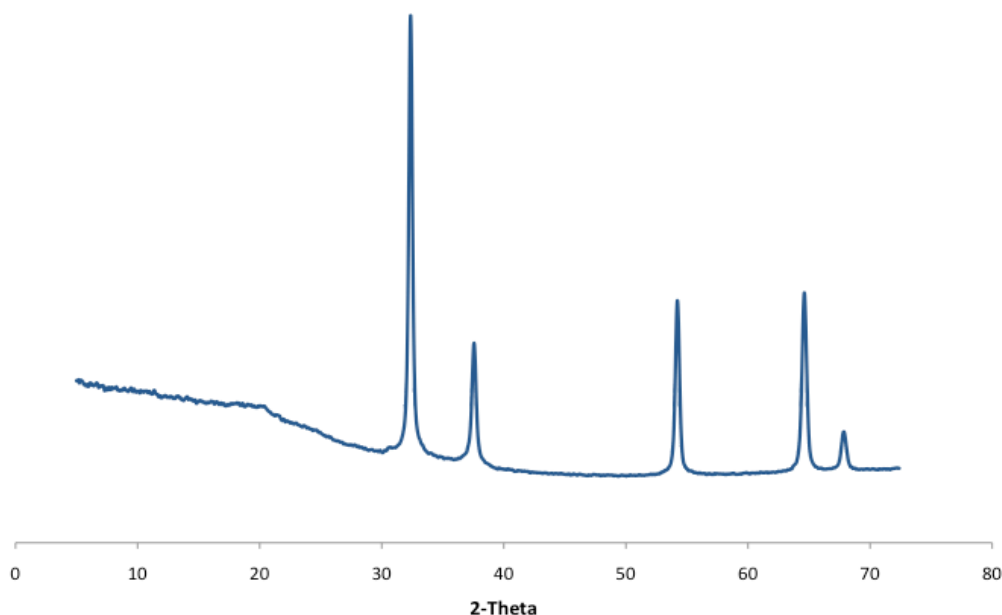
### Synthesis and Characterization of a p-type Boron Arsenide Photoelectrode

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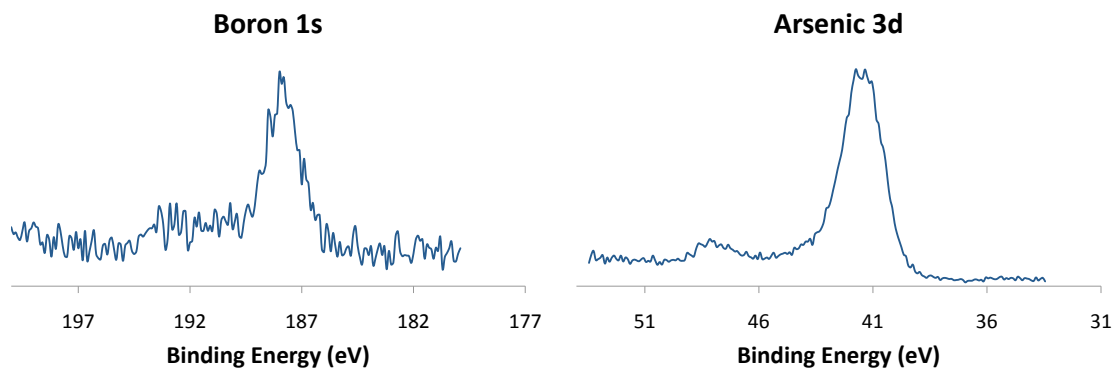
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**Preparation of BAs from boron powder.** Elemental boron (Alfa Aesar, powder, amorphous and crystalline, -325 mesh, 99%, 0.0218 g, 2.02 mmol) and elemental arsenic (Alfa Aesar, polycrystalline lump, 2-8 mm, puratronic, 99.9999%, 0.2864 g, 3.82 mmol) were ground together in a mortar and pestle and then loaded into a quartz tube of approximately 4 mL volume. The tube was evacuated and sealed and subsequently heated to 800 °C for 12 h. Subsequent to the heat treatment, the excess arsenic was removed manually.



**Figure S1.** XRD data for the BAs prepared from boron powder.



**Figure S2.** XPS data for the BAs prepared from boron powder. The experimental boron-to-arsenic ratio was 1 to 0.993, after correction for the atomic sensitivity.

**Table S1.** XPS quantification data for the BAs material prepared from boron powder.

Peak	Position (eV)	FWHM (eV)	R.S.F.	Area	% Conc.	Start (eV)	End (eV)	Centroid (eV)	Peak To Peak
B 1s	187.91	1.501	0.159	891.89	50.18	189.86	185.429	187.66	410.7
As 3d	41.26	2.091	0.677	3770.46	49.82	46.353	36.7051	41.39	1072

**Preparation of BAs from granular boron.** Elemental boron (Alfa Aesar, powder, crystalline, -4+40 mesh, 99.999%, 0.0588 g, 5.44 mmol) and elemental arsenic (Alfa Aesar, polycrystalline lump, 2-8 mm, puratronic, 99.9999%, 0.8000 g, 10.68 mmol) were loaded into a quartz tube of approximately 4 mL volume. The tube was evacuated and sealed and subsequently heated to 800 °C for 3 days. At the conclusion of the heat treatment, the excess arsenic was removed manually.

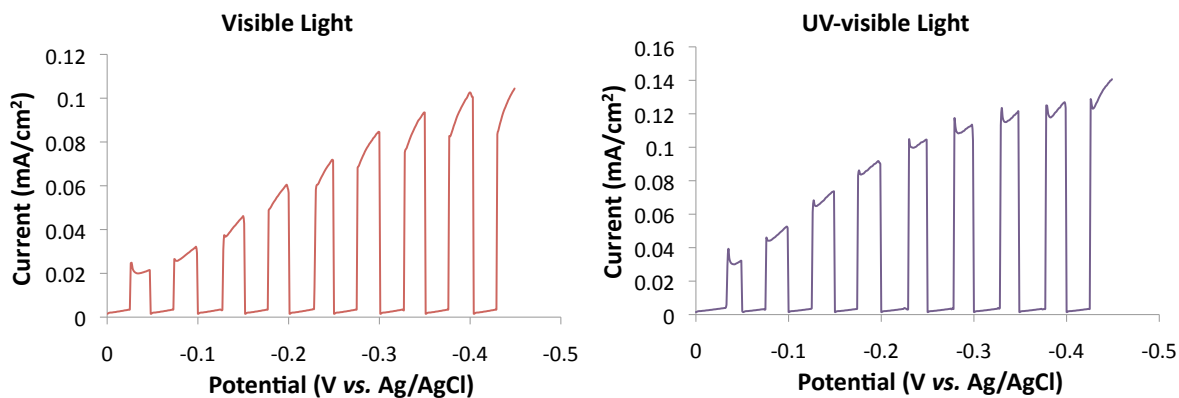
**Table S2.** XPS quantification data for the BAs material prepared from granular boron. The experimental boron-to-arsenic ratio was 1 to 0.989, after correction for the atomic sensitivity.

Peak	Position (eV)	FWHM (eV)	R.S.F.	Area	% Conc.	Start (eV)	End (eV)	Centroid (eV)	Peak To Peak
B 1s	188.51	0.745	0.159	929.62	50.27	190.112	186.438	188.46	749.3
As 3d	41.76	1.256	0.677	3915.91	49.73	43.7121	40.0149	41.97	2056

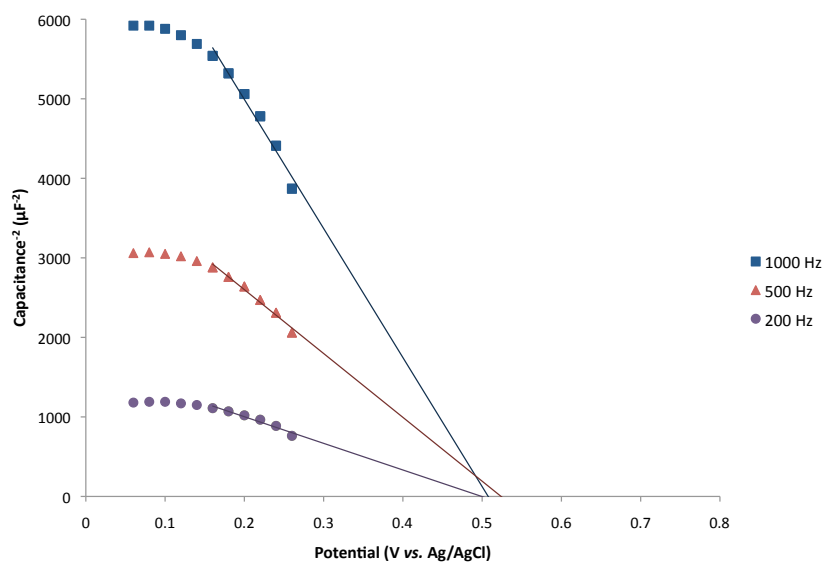
**Preparation of As-doped boron.** Elemental boron (Alfa Aesar, powder, crystalline, -4+40 mesh, 99.999%, 0.0583 g, 5.39 mmol) and elemental arsenic (Alfa Aesar, polycrystalline lump, 2-8 mm, puratronic, 99.9999%, 0.0240 g, 0.32 mmol) were loaded into a quartz tube of approximately 4 mL volume. The tube was evacuated, sealed and subsequently heated to 800 °C for 2 h.



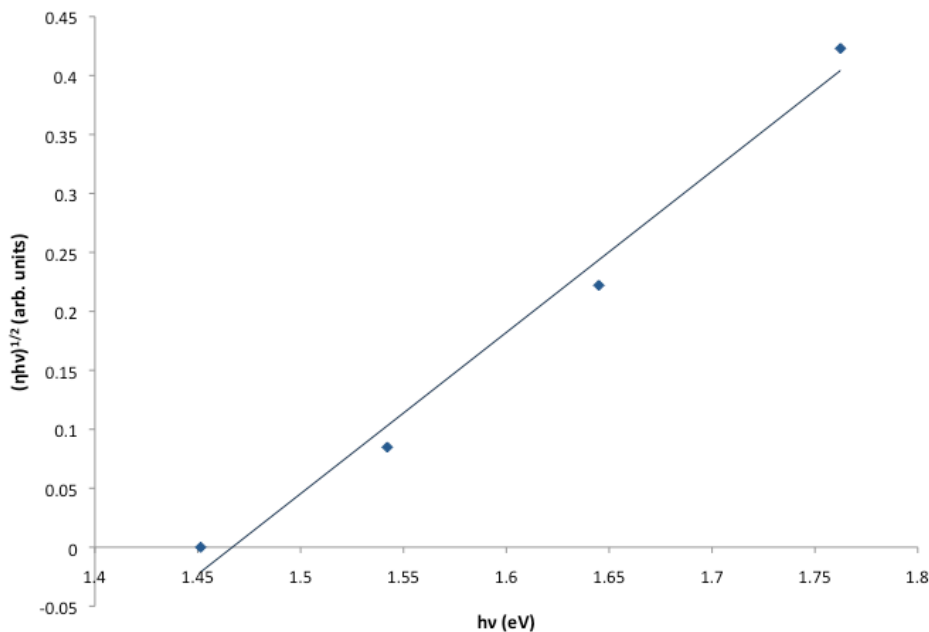
**Figure S3.** A typical boron arsenide electrode.



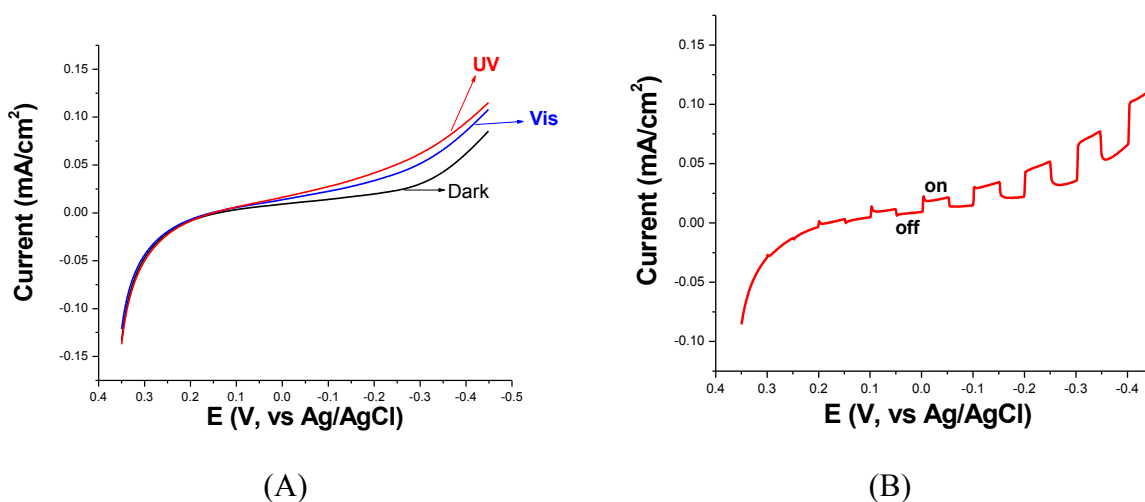
**Figure S4.** Linear sweep voltammograms in a 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution containing 0.01 M methyl viologen. The potential was swept from 0.0 V to -0.5 V vs. Ag/AgCl at a scan rate of 20 mV/s. The incident light intensity at the electrode surface was 100 mW/cm<sup>2</sup>. (Left frame) Net photocurrent after subtraction of the dark current for the BAS material under chopped visible light irradiation. (Right frame) Net photocurrent after subtraction of the dark current for the BAS material under chopped UV-visible light irradiation.



**Figure S5.** Mott-Schottky plots at three different frequencies (purple circles: 200 Hz; red triangles: 500 Hz; blue squares: 1000 Hz) of a BAS electrode in the dark immersed in a 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution containing 0.01 M methyl viologen. The AC modulation amplitude was 10 mV peak-to-peak.



**Figure S6.**  $(\eta h\nu)^{1/2}$  vs.  $h\nu$  for a p-type BAs electrode in a 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution containing 0.01 M methyl viologen. Here,  $\eta$  represents the external quantum efficiency (or IPCE) and  $h\nu$  is the photon energy. The electrode is biased at -0.25 V vs. Ag/AgCl.



**Figure S7.** Linear sweep voltammograms in a 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution. The potential was swept from 0.35 V to -0.45 V vs. Ag/AgCl at a scan rate of 20 mV/s. The incident light intensity at the electrode surface was 100 mW/cm<sup>2</sup>. (A) Current flow for the new BAs material in the dark, under visible and UV-visible light irradiation. (B) Current flow for the BAs material under chopped UV-visible light irradiation.

**X-ray Powder Diffraction.** The data were collected on a Rigaku R-Axis Spider diffractometer with an image plate detector using a graphite monochromator and Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). The instrument was controlled using Rapid/XRD Version 2.3.8 diffractometer control software from Rigaku Americas Corporation, The Woodlands, TX. The integration of the two dimensional data into a one dimensional pattern was accomplished using 2DP Version 1.0 from Rigaku Americas Corporation, The Woodlands, TX.

**X-ray Photoelectron Spectroscopy.** The XPS spectra were recorded on a Kratos Axis Ultra X-ray photoelectron spectrometer utilizing a monochromated Al K $\alpha$  X-ray source. All spectra were collected with a pass energy of 20 eV. CasaXPS software version 2.3.16 was used to determine the stoichiometries of the samples from the corrected peak areas by applying the relative sensitivity factors of 0.159 and 0.677 for B 1s and As 3d, respectively.

**Scanning Electron Microscopy.** The SEM images were acquired on a Quanta FEG 650 instrument.

<sup>†</sup> These authors contributed equally to the work.