Electronic Supporting Information

Arsenene Nanosheets and Nanodots

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EXPERIMENTAL SECTION

Preparation of few-layer arsenene nanosheets. Arsenene was prepared by liquid exfoliation of grey arsenic (99.99%, Smart-Elements) in NMP. Anhydrous NMP was purchased from Spectrochem, India. All the manipulations were carried out under a dry nitrogen atmosphere. In brief, 20 mg of ground grey arsenic was taken in a screw cap vessel of 50 mL capacity. NMP was taken in a Schlenk flask and de-gassed by gentle bubbling of N\textsubscript{2} gas for 5 h. Subsequently, 20 mL of de-gassed NMP was added to the vessel charged with arsenic under a nitrogen atmosphere. The vessel was closed with the cap fitted with a tapered tip of 6 mm tip-diameter and 142 mm length. The interfaces between vessel, cap and probe were sealed with silicon grease, Teflon and Parafilm to avoid exposure to ambient during sonication. The probe was then connected to the probe-sonicator (Sonics Vibra cell™ VCX 750; 750 Watt power and 20 kHz frequency). The sonicator was operated in a pulse mode (4 sec on and 4 sec off pulses) with an input power intensity of 200 W for 12 h. The sealed vessel was immersed in a cold water bath. During sonication process, the temperature of the water bath was maintained below 10 °C by continuous circulation of a mixture of ethylene glycol-water using a Julabo thermostatic bath. The black dispersion obtained after 12 h of sonication, was transferred to another screw cap vessel and centrifuged at 1000 rpm (100 rcf) for 30 minutes in a REMI PR-24 centrifuge equipped with an angular R-242 rotor head (REMI Instruments, India). The supernatant containing few-layer arsenene was collected in a Schlenk flask under nitrogen atmosphere and was used as-such for characterization.

Preparation of arsenene nanodots. Arsenene nanodots were prepared by probe sonicating 20 mg of ground grey arsenic in 20 mL of toluene. Anhydrous toluene was purchased from Sigma-Aldrich and de-gassed for 5 h by bubbling of N\textsubscript{2} gas. The mixture
of grey arsenic in toluene was subjected to sonication and centrifugation in the same way as have been described above in the case of nanosheets.

**Synthesis of arsenene-4-NB.** 50 mg of 4-nitrobenzenediazonium tetrafluoroborate (4-NBD) was added to NMP dispersion (20 mL) of arsenene nanosheets. The mixture was stirred for 24 h in dark at room temperature and centrifuged at 1000 rpm (100rcf) for 1 h. The supernatants were collected in another vessel under nitrogen atmosphere and centrifuged at 10000 rpm for 1 h. The sediments were collected and washed with dry and de-gassed acetonitrile to remove unreacted 4-NBD and dried under vacuum at room temperature. The functionalized sample was dispersed in acetonitrile to prepare samples for characterization.

**Atomic force microscope (AFM) imaging.** The AFM images were obtained in tapping mode with a Bruker Innova Microscope. The samples were prepared by drop casting arsenene dispersions on Si/SiO₂ substrates and dried under vacuum in a desiccator for overnight.

**Transmission electron microscope (TEM) imaging.** TEM images were collected with a JEOL-3010 and FEI Titan3 microscopes operating at accelerating voltage 300 kV respectively. The samples were prepared by drop-casting the arsenene dispersion on Lacey carbon grid and dried under vacuum in a desiccator.

**Raman spectroscopy.** As prepared arsenene dispersions were drop-casted on glass slides and dried under vacuum in a desiccator. The Raman spectra were collected with a LabRAM HR high-resolution Raman spectrometer (Horiba-Jobin Yvon) by using an Ar laser of 514.5 nm.

**X-ray photoelectron spectroscopy.** Exfoliated arsenene sheets in NMP were collected by centrifugation at 12000 rpm for 1 h. The sediments were collected and dispersed in dry and degassed acetonitrile. The acetonitrile dispersion was drop-casted on a Si-substrate and dried under vacuum in a desiccator. Similarly, the arsenene-4-NB sample was dispersed in acetonitrile, drop-casted on a Si-substrate and dried under vacuum. The XPS data were collected with an Omicron Nanotechnology spectrometer employing a
monochromatic Al Kα X-ray source (1486.72 eV). All XP spectra were charge corrected to the C 1s at 284.6 eV (due to adventitious carbon).

**Inductively coupled plasma optical emission spectrometry (ICP OES).** Four As standard solutions of 42, 83, 167 and 250 mg/L concentrations were prepared by digesting elemental As in aqua regia followed by dilution with distilled water. As-exfoliated NMP dispersion of arsenene was centrifuged at 1000 rpm (100 rcf) for half an hour to obtain a stable dispersion. The top 10 mL of the supernatants were further centrifuged at 12000 rpm (14490 rcf) for one hour to sediment the exfoliated materials. The black sediment was digested with 1.0 mL of aqua regia and diluted to 10 mL with distilled water. The concentration was determined by PerkinElmer Optima 7000 DV ICP OES.

**Optical absorption and emission spectroscopy.** Absorption and photoluminescence spectra of the arsenene dispersions were recorded with a PerkinElmer UV/VIS/NIR lambda-750 spectrophotometer and Horiba-Jobin-Yvon FluoroLog spectrofluorometer respectively. The excitation and emission slit widths were set at 1.0 and 3.0 mm. The excitation source is a 450 W xenon lamp.

**Fourier-transform infrared (FTIR) spectroscopy.** FT-IR spectra were recorded with a Bruker IFS 66v/S spectrometer as KBr pellets. The KBr pellets were prepared by mixing the compound and KBr in a 1:100 ratio and pressing the pallet in a hydraulic pressure machine.

**First-principles calculations.** Density functional theory as implemented in Quantum Espresso 6.0 Package, was used to study arsenene nanosheets comprised of 32 atoms (4 x 4 supercell), with plane wave basis set for all atoms in consideration. Exchange correlations were treated using PBE, functional under GGA (Generalized Gradient Approximation). An energy cutoff of 300 eV was used to represent valence electrons. Norm Conserving Troullier-Martin pseudopotentials were chosen to approximate the interactions between core electrons and the atomic nucleus. To avoid spurious interactions, a vacuum of 30 Angstrom was created in the non-periodic z-direction and a distance of 15 Angstroms was maintained between the molecules under the supercell consideration. The Brillouin Zone was sampled using a Monkhorst Pack grid of 4 x 4 x 1.
For electronic calculations, a 21 x 21 x 1 grid was considered. All systems were optimized until the total force reduced to 0.02 eV/atom. Time-dependent density functional theory (TD-DFT) calculations were carried out in Gaussian16,\textsuperscript{S6} set of codes to estimate the optical response of arsenene, under the Tamm-Dancoff approximation.\textsuperscript{S7,S8} CAM-B3LYP hybrid exchange correlation functional was used to treat long range interactions in the system.\textsuperscript{S9} All geometric structures were visualized by using XCRYSDEN software.\textsuperscript{S10}

The optical properties are described by the complex dielectric function\textsuperscript{S11}: \(\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)\), which can be further extrapolated to give the absorption coefficient \(\alpha(\omega)\) by using Equation 1.

\[
\alpha(\omega) = \frac{\sqrt{2\varepsilon_0}}{c} \left\{ \left[ \varepsilon_1(\omega) + \varepsilon_2^2(\omega) \right]^{1/2} - \varepsilon_1(\omega) \right\}^{1/2}
\]

Calculations on the imaginary part of the dielectric function yield the absorption coefficient as a function of energy, from where we can deduce the maximum wavelength of absorption. TD-DFT calculations enable us to study the lowest excitations from the ground state. The dipole strength function \(S(\omega)\) measures the excitation induced in a system by a particular frequency, as the fast Fourier transform of the dynamic polarizability.

\[
S(\omega) = \frac{4m_e}{\varepsilon_0^2 \hbar} \omega \Im \alpha(\omega)
\]

where \(\alpha\) is the dynamic polarizability. From the Equation 2, we find an absorption maximum at a wavelength of 354 nm, and an emission band at 431 nm.

**Dynamic Light Scattering (DLS).** The DLS measurements were carried out by using a Zetasizer Nano ZS (Malvern UK) instrument at 25 °C.
Fig. S1. (a-c) TEM images of arbitrarily selected arsenene nanosheets, showing different lateral dimensions. The insets show corresponding SAED patterns. (d) HR-TEM, showing $d$-spacing (3.57 Å) corresponding to the interlayer separation of arsenic.

Fig. S2. (a) Scanning transmission electron microscope (STEM) image, (b) EDX elemental mapping of As and (c) EDX spectrum of the arsenene nanosheet.
Fig. S3. AFM images and the corresponding height profiles of few-layer arsenene sheets.

Fig. S4. Particle size distribution of As nanosheets in NMP obtained from Dynamic Light Scattering (DLS). The average particle size is 204 nm and polydispersity index (pdi) is 0.35.
**Fig. S5.** XPS survey spectrum of few-layer arsenene.

**Tauc plot.** Bandgap was calculated Tauc plot by using equation, \((\varepsilon E)^{1/2} = C(E - E_g)\), where \(\varepsilon\) is the absorption coefficient calculated from Beer’s law, \(E\) is the energy (eV), \(C\) is a constant and \(E_g\) is the band gap.

**Fig. S6.** Absorption spectrum of NMP dispersion of arsenene. Inset shows the corresponding Tauc plot and the band gap.
**Fig. S7.** UV-visible absorption spectrum of arsenene nanodots prepared in toluene.

**Fig. S8.** Photoluminescence spectra of arsenene nanodots prepared in toluene.

**Fig. S9.** FT-IR spectrum of few layer arsenene functionalised with 4-NBD. FT-IR spectra of bulk arsenic and 4-NBD have also been given.
**Fig. S10.** Raman spectra of arsenene-4-NBD and grey (bulk) arsenic.

**Fig. S11.** STEM mage and elemental (As, O, C and N) mapping of arsenene-4-NBD sheets.
Fig. S12. X-ray photoelectron spectra (XPS) of few layer arsenene functionalized with 4-NBD. (a) Survey spectrum, (b) C 1s spectrum, (c) N 1s spectrum, and (d) As 3d spectrum.

Fig. S13. Optimized structure of arsenene (4 × 4 supercell), (a) top view and (b) side view.

References


