Nanostructured photoelectrochemical solar cell for nitrogen reduction using plasmon-enhanced black silicon

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Ammonia (NH₃) is one of the most widely produced chemicals worldwide. It has application in the production of many important chemicals, particularly fertilizers. It is also, potentially, an important energy storage intermediate and clean energy carrier. Ammonia production, however, mostly uses fossil fuels and currently accounts for more than 1.6% of global CO₂ emissions (0.57 Gt in 2015). Here we describe a solar-driven nanostructured photoelectrochemical cell based on plasmon-enhanced black silicon for the conversion of atmospheric N₂ to ammonia producing yields of 13.3 mg m⁻² h⁻¹ under 2 suns illumination. The yield increases with pressure; the highest observed in this work was 60 mg m⁻² h⁻¹ at 7 atm. In the presence of sulfite as a reactant, the process also offers a direct solar energy route to ammonium sulfate, a fertilizer of economic importance. Although the yields are currently not sufficient for practical application, there is much scope for improvement in the active materials in this cell.
Ammonia production is a highly energy intensive process, consuming 1–3% of the world electrical energy and ~5% of the world natural gas production. World production is around 200 million tonnes annually, reflecting the vast need for this chemical in agriculture, pharmaceutical production and many other industrial processes. Ammonia is also being considered as a carbon-free solar energy storage material, due to its useful characteristics as a chemical energy carrier. Compared with other chemicals that could be used to store solar energy (such as hydrogen), ammonia is safe, ecofriendly and, most importantly, produces no CO₂ emissions. Apart from solar energy (such as hydrogen), ammonia is safe, ecofriendly to its useful characteristics as a chemical energy carrier. Considered as a carbon-free solar energy storage material, due to many other industrial processes. Ammonia is also being used in the manufacture of fertilizers, pharmaceuticals, and other products.

Results
Fabrication of the photoelectrochemical cell. A schematic illustration of the fabrication steps and working mechanism of the photoelectrochemical cell and corresponding scanning electron micrograph and transmission electron micrographs are shown in Fig. 1 and Supplementary Figs 1 and 2. A p-type boron-doped commercial <100> silicon wafer was used as a substrate material. bSi was fabricated using a dry etching method. A GNP layer was then sputtered onto the etched surface as the photocathode. Finally, a Cr layer with thickness ~50 nm was sputtered onto the back surface of the silicon wafer as an anode.

Photoelectrochemical reduction of nitrogen. A nitrogen photo-reduction cell was constructed (Fig. 2a) with nitrogen gas bubbling over the surface of the material and artificial solar light (300 W Xe lamp) as an illumination source. The yield of...
ammonia was measured by using an ammonia/ammonium ISE and the indophenol method.\(^{27}\)

Control experiments were conducted in H\(_2\)O (18.2 MΩ cm). Yields obtained over a 24 h period are shown in Fig. 2b. Ammonia production can be observed at a low level on bSi; however, after coating with GNPs, the yield of ammonia is increased by nearly four times. To avoid silicon oxidation and enhance charge separation, a Cr layer was coated on silicon to act as the hole-sink and anode; in other words, Cr facilitates hole collection from the Si and acts in this case as a sacrificial anode. This GNP/bSi/Cr photoelectrochemical cell exhibits yield of 320 mg m\(^{-2}\) over 24 h. However, the oxidation of Cr was also observed, confirming its role as a sacrificial hole-sink in the process. To avoid the loss of Cr, sodium sulfite was added to the electrolyte used to provide an alternate electron donor to scavenge the photogenerated holes and hence protect the Cr anode. Ammonia production as a function of time with this GNP/bSi/Cr/sulfite structure is shown in Fig. 2c; the final yield of ammonia under these conditions over a 24 h period was 320 mg m\(^{-2}\) or 13.3 mg m\(^{-2}\) h\(^{-1}\). A durability test consisting of repeated 3 h runs using this sodium sulfite electrolyte also showed very reproducible and stable behaviour for up to 18 h (Supplementary Fig. 3). These results show that the GNP/bSi/Cr cell exhibits excellent activity and stability for ammonia production compared with previous reports, as summarized in Supplementary Table 1. A control experiment was also performed to confirm that the source of the nitrogen in the ammonia was the bubbled N\(_2\), by using Ar to replace N\(_2\) in the experiment; no ammonia was detected (Supplementary Fig. 4).

While a number of possible sacrificial reagents could be used in this context, sulfite was chosen on the basis that, when used in its aqueous acid form, the product of the overall reaction can be

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**Figure 2** | Photoelectrochemical nitrogen reduction. (a) Schematic diagram of the cell. (b) Yield of ammonia over 24 h obtained on different substrates: (i) P-type silicon, (ii) bSi, (iii) GNP/bSi, (iv) GNP/bSi/Cr and (v) Au/Si/Cr after illumination with two suns and (vi) GNP/bSi/Cr in dark. (c) The time-dependence of ammonia yield obtained after illumination with two suns (error bars are the s.d. of at least three replicates of independent measurement). (d) The light intensity-dependence of ammonia yield obtained after illumination for 3 h (error bars are an estimate of the combined errors of measurements).

**Figure 3** | Quantum efficiency and high-pressure yield obtained on a GNP/bSi/Cr photoelectrochemical cell. (a) Quantum efficiency of ammonia synthesis on a GNP/bSi/Cr photoelectrochemical cell as a function of wavelength (error bars are estimates of the combined errors of measurements). (b) Yield of ammonia in three hours as a function of nitrogen gas pressure at two suns illumination in a fixed volume glass reactor (error bars are the s.d. of at least three replicates of independent measurement).
ammonium sulfate: N₂ + 3H₂SO₃ + 3H₂O → 2H₂SO₄ + (NH₄)₂SO₄. Equivalent reactions can use potassium or ammonium bisulfite in this process (as described in Supplementary Note 1). The final 24 h yield in terms of ammonium sulfate as a product corresponds to 1.24 g m⁻². Since the production rate appears to be quite constant over the 24 h period of the experiments in Fig. 2c, it would appear that this yield is not limited by product buildup under these conditions (Supplementary Fig. 5). The effect of light intensity is shown in Fig. 2d, the ammonia yield increases linearly with the intensity of light up to 300 mW cm⁻² and then plateaus. This limiting rate is likely to be related to factors such as the rates of mass transport of the reactants and products at the active surfaces.

Quantum yield experiments (Fig. 3a) were carried out with 50-nm-wide bandpass filters, confirming that the nitrogen reduction can occur in whole visible range, dropping away as the band gap energy of Si is approached. A small absorption maximum that is observed in the region of the SPR region for GNP/Si (Supplementary Fig. 6) also appears in the region of 500 nm in Fig. 2a. This suggests that excitation of surface plasmons in the GNP particles is responsible for an additional photo-excitation mechanism that contributes to the overall yield in this region of the spectrum, as has been observed in other SPR-enhanced processes. To understand the relationship between the dissolved amounts of nitrogen in the solution and the generated ammonia-ammonium yield, the effect of N₂ pressure on the reaction was investigated in a closed glass pressure vessel (Fig. 3b). An approximately linear dependence of yield on pressure was observed over the range studied, and the yield was 60 mg m⁻² h⁻¹ at 7 atm, as would be expected from a Henry’s law dependence of nitrogen solubility on pressure in the aqueous medium. This suggests that the concentration of nitrogen at the reactive sites on the surface is a rate limiting factor in these experiments. On the other hand, in our ambient condition experiments, bubbling nitrogen gas generates strong agitation of the medium created near the surface as well as a dynamic gas–liquid–solid interface, which enhances reactions rates by facilitating transport to and from the reaction sites in the structure (this also explains the relatively lower yields at lower pressures in Fig. 3b). This suggests that strategies to further enhance yield in either case could seek to enhance the kinetics of these processes via further manipulation of the nanostructure of the bSi.

Discussion

The various reference experiments in Fig. 2b reveal the roles of each layer in the overall reaction process, as illustrated in Supplementary Fig. 7. When the bSi was replaced by unetched pristine silicon, the ammonia yield was only ~11% of that produced by the GNP/bSi/Cr structure. bSi effectively suppresses reflection, while simultaneously enhancing the scattering and absorption of light. bSi also provides an extremely large surface area for decoration by the GNPs. High activities of silicon nanostructures have been demonstrated previously in both photoelectrolytic and chemical water splitting. The GNP-coated bSi material shows much superior ammonia yield over bSi alone, revealing the functions of the GNPs in separating charge and as an electrocatalytic site for the N₂ reduction reaction. Meanwhile, bSi facilitates hole transfer to the anode layer (Cr) to execute the oxidation reactions. After coating with Cr on the backside, the ammonia production of the GNP/bSi/Cr cell increases to about two times that of GNP/bSi and eight times that of pure bSi. The detailed reduction mechanism of N₂ to NH₃, which involves six electrons and six protons, is not yet well-understood and is the focus of ongoing experimental and theoretical investigations by a number of groups, including ourselves. It is important to note that the overall reaction in the dark with sulfite is not spontaneous, as indicated by the free energy calculation shown in the Supplementary Note 2. This confirms that role of the cell is energy injection into the process, as opposed to photo-catalytic. It is worth noting that sulfite is a product of coal-fired power station flue gas scrubbing, while ammonium sulfate is a commonly used form of ammonia as a fertilizer. So this autonomous photoelectrochemical process may offer scope to valorize this otherwise hazardous waste product.

In summary, we describe a nanostructured photo-electrochemical cell that is capable of mimicking the nitrogen fixation and conversion process of nitrogenases in nature and producing ammonia (13.3 mg m⁻² h⁻¹, at 2 suns) and an ammonia based fertilizer in a fully solar-driven process. The photoelectrochemical cell is not inherently area limited and can be scaled up with the silicon wafer size, and the nanostructures of the cell can be further improved and optimized in term of the component, size and configuration. Hence significant potential exists for further development of this approach to ammonia generation by using standard manufacturing process. At this preliminary stage, the efficiency of our photoelectrochemical process is still too low for practical ammonia manufacture. One of the possibilities to improve the efficiency is to couple our cell with a separate PV cell (as detailed further in Supplementary Table 2), since the configuration of our cell is ready to be utilized as an electrochemical cell. Finally, the combination of black silicon-based photo-adsorber and plasmonic catalysts described here could provide a pathway toward an unassisted solar-to-chemical conversion in many applications such as CO₂ fixation and water splitting.

Methods

Preparation and characterization of black silicon (bSi) and electrodes. A p-type boron-doped 100 mm commercial <100> silicon wafer (resistivity = 10–20 ohm cm) of 525 μm thickness (Atecom Ltd, Taiwan) was used as a substrate material for black silicon formation. The wafers were used as supplied. The dry etching process was carried out using an Oxford PlasmaLab 100 ICP3800 system. The etching process was a mixed mode, wherein etching and passivation occurred at the same time. Process conditions for the black silicon formation were: SF₆ gas flow rate 65 s.c.c.m., O₃ gas flow rate 44 sccm, process pressure of 35 mTorr, 100 W reactive ion etching (RIE) power, 20°C electrode temperature and 10 Torr He backside cooling pressure. The RIE process resulted in a homogeneously distributed silicon nanowire arrays with length about 3 μm across the full wafer after 20 min etching. Nitrogen adsorption–desorption experiments were performed at 77 K with a Micromeritics Tristar II. The samples were degassed at 200°C for 5 h before measurement. The surface area of bSi calculated from nitrogen sorption results by Brunauer–Emmett–Teller method is 10.4 m² g⁻¹. After the RIE on a K550X sputter etcher at 25 mA at 1 × 10⁻¹ mbar. The discharge time was 4 min. The size of the GNPs ranges from 3 to 30 nm. The prepared bSi with GNP on its surface was back coated with chromium; the coating process was carried out using a high-resolution chemical vapor deposition system (Q150T S Quorum Technologies). The coating conditions were 40 mA current density for 120 s (2 suns). The morphology and structure of bSi were investigated by scanning electron microscopy (scanning electron micrograph, JEOL JSM-7100) and transmission electron microscopy (transmission electron micrograph, JEOL-2100F).

Photoelectrochemical nitrogen reduction. All of the chemical reagents in this study were of analytical grade and were supplied by Sigma-Aldrich (Australia). A photo-electrochemical cell to reduce nitrogen into ammonia was constructed; the cell contained 10 ml deionized water or electrolyte as specified below and the nitrogen flow rate was 10 ml min⁻¹. Nitrogen was passed through the cell for 1 h to remove oxygen. Black silicon pieces with size of 10 × 10 mm² were tested. The artificial solar light source was a 300 W Xe lamp, while the illumination intensity used was 2 suns unless otherwise specified. The experimental conditions were as follows: bSi (dark); black silicon, (reaction conditions; 10 ml deionized water, in dark). SiC pristine unetched silicon (reaction conditions; 10 ml deionized water, 2 suns). GNP/bSi: GNP-coated black silicon, (reaction conditions; 10 ml deionized water, 2 suns). GNP/bSi/Cr: GNP-coated black silicon (front) and chromium (back) (10 ml deionized water, 2 suns). GNP/bSi/Cr/Si: GNP-coated black silicon (front) and chromium (back) (10 ml deionized water, 2 suns). SiC electrode: SiC electrode (front) and chromium (back) (reaction conditions; in 10 ml 150 p.p.m. sodium sulfite electrolyte, 2 suns). GNP/bSi/Cr: GNP-coated
pristine unetched silicon (front) and chromium (back) (reaction conditions; 10 ml deionized water, 2 suns) GNP/ISi/Cr(dark): GPNs-coated black silicon (front) and chromium (back) (reaction conditions; 10 ml deionized water, in dark). The cell solution was analysed directly for its ammonia content. The exiting nitrogen gas stream was bubbled through a water filled collector vessel to trap any ammonia carried by the nitrogen for analysis; the fraction appearing in the collector vessel was typically ~12% and was included in the overall NH3 yield results of GNP/ISi/Cr cell in sodium sulphite electrolyte.

High-pressure experiments. The p-GNP/ISi/Cr was tested under high-pressure nitrogen gas using a Q-tube purging-35-SS vessel, purchased from Q Labtech. The reaction was carried out under irradiation using a 300 W Xe lamp with the intensity equivalent to 2 suns. The electrolyte was used 10 ml deionized water and the catalyst size 1 cm² (0.12 g). The electrolyte was bubbled with nitrogen for 20 min followed by addition to the reaction vessel which was purged with nitrogen gas before irradiation. Following irradiation for 3h the concentration of ammonia/ammonium was analysed.

Ammonia analysis. Ammonia products were analysed by using (i) an ammonia/ammonium ISE (YSI, 6883) and (ii) the indophenol method. The YSI probe was calibrated using standard ammonia solutions containing the sacrificial agent (at concentration lower than electrode manufacturer’s salinity limit). To ensure that the added SO₄²⁻ did not interfere with the ammonia analysis method in this work, the ISE was recalibrated using standard solutions containing the same amount of sacrificial agent (Supplementary Fig. 8). The indophenol method was used as a confirmation of the final yield of each experiment (Supplementary Fig. 9). The UV–vis absorption peak of indophenol at ~630 nm. At higher concentrations near the UV–vis spectrophotometer absorption limit, samples were diluted 1 or 2 of original concentration.

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Author contributions
D.R.M., X.Z. and M.A. conceived the experiments. M.A., F.Z., C.X and C.K. performed the use of facilities at the Monash Centre for Electron Microscopy. M.A. is on leave from the Chemistry Department, Al-Nahrain University, Baghdad, Iraq.

Additional information
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