
Satyam Ladva\textsuperscript{a}, William Travis\textsuperscript{a}, Raul Quesada-Cabrera\textsuperscript{a}, Martin-Rosillo Lopez\textsuperscript{a}, Abdulkareem Afandi\textsuperscript{b}, Yaomin Li\textsuperscript{a}, Richard B. Jackman\textsuperscript{b}, Joseph C. Bear\textsuperscript{a}, Ivan P. Parkin\textsuperscript{a}, Christopher Blackman\textsuperscript{a}, Christoph G. Salzmann\textsuperscript{a}, Robert G. Palgrave\textsuperscript{*}

\textsuperscript{a} Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ

\textsuperscript{b} Department of Electronic & Electrical Engineering, University College London, Torrington Place, London, WC1E 7JE

Experimental Methods

Chemicals

Dicyandiamide (DCDA) (99%), lithium bromide (99.995%) and potassium bromide (99%) were purchased from Aldrich chemical company and used without further purification.

X-ray photoelectron spectroscopy (XPS)

XPS was carried out using a Thermo Fisher Scientific K-Alpha+ spectrometer utilising a 72 W monochromated Al K\textsubscript{\alpha} x-ray source (with photon energy of 1486.6 eV). A dual beam flood gun was used to compensate for sample charging, instrument specific relative sensitivity factors were used to normalise the data and the binding energy scale was referenced by setting the C1s peak from adventitious carbon to 285.0 eV. Depth profiling was performed using both mono beam argon etching and argon cluster source etching under a vacuum of \(<5 \times 10^{-8}\) mBar. Depth profiles were performed with a mono beam at 1000eV, and cluster etching was performed at 8 keV energy.

Infra-red (IR) spectroscopy

IR spectra were obtained using a Bruker Alpha FT-IR spectrometer, equipped with ALPHA’s Platinum ATR single reflection diamond ATR module. Measurements were performed in the range of 400 cm\textsuperscript{-1} to 4000 cm\textsuperscript{-1}. Films were placed directly onto the ATR surface with the probe pressed into direct contact with the material.
X-ray diffraction (XRD)

X-Ray Diffraction (XRD) was performed using a Siemens Bruker D500 and Cu-Kα radiation source (0.15418 Å). The sample was scanned between 5°-60° 2Θ in Bragg-Brentano geometry, at a step size of 0.05° at 50 second per step. The Carbon Nitride was coated onto silicon dioxide substrate, cut into a 20mm x 20mm grid and then placed onto a plastic holder, fixed with blu-tack, as parallel to the base of the holder as possible. This holder was then encased into the traditional D500 steel sample holder.

Raman

Raman Spectroscopy was performed using a Renishaw Invia Raman Spectroscope with a 325 nm laser excitation. 20 iterations of the scans were performed between the ranges of 200cm⁻¹ to 1500cm⁻¹ at 20 second acquisition time per scan in air, under ambient conditions.

UV-vis

UV-visible Spectroscopy was performed with a Perkin-Elmer Lambda 950 spectrophotometer. Samples were prepared for reflectance and transmittance tests, with uncoated substrate used as the blank test for transmittance measurements. Reflectance and transmittance were both performed between 200cm⁻¹ and 1500cm⁻¹ at steps of 5cm⁻¹ with absorbance information interpolated from these.

Scanning Electron Microscopy (SEM)

SEM images were recorded using a Jeol 7500F Field Emission SEM. Samples were placed onto carbon tape and then secured onto a grid. Films were then made conductive by connecting the plate through use of a copper tape. Carbon coating or Gold coating was avoided to prevent sample from being covered.

Transmission Electron Microscopy (TEM)

GCN coating was directly coated onto a holey-carbon by placing the grid into the coating chamber. Deposition was carried out for 30 minutes. The coated grid was then inserted into the Jeol 200kv 2100-F TEM system, with images recorded on a Gatan Orius Charge-coupled device (CCD). Energy dispersive X-Ray spectra (EDS) were recorded on an Oxford Instruments XMAX EDS detector running AZTEC software.

Profilometry

Profilometry of the films was performed through application of the DektakXT Surface Profiler, using a 5µm stylus radius at a force of 5mg and scan range of 6µm. The films, GCN coated onto glass, were suspended on 2 additional glass slides, to prevent film damage to opposite side film. The scan duration per film was 40 seconds with a scan length of 2000 µm and resolution of 0.17 µm.
**Figure S1.** Photographs of coating apparatus before and after heating the reaction mixture. The coating chamber contains the substrate and is held at room temperature. The reaction mixture (dicyandiamide, KBr, LiBr) is contained in a quartz tube inside the furnace. After heating the reaction mixture to 600°C, a black coating forms on all cold parts of the apparatus, including the substrates contained in the coating chamber.
Additional Results

Transmission Electron Microscopy

Figure S2. Additional TEM images of GCN coated TEM grid, showing lattice fringes throughout.
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Figure S3. TEM EDS analysis on GCN film grown directly onto a copper TEM grid.
Figure S4. Scanning electron microscopy images of GCN films coated on quartz, showing a smooth and featureless film on the micron scale with some cracking.
Figure S5. a) Powder X-ray diffraction pattern of GCN film on glass. b) Infra red absorption spectrum of a GCN film on glass. c) Raman spectrum of a GCN film on quartz. d) Optical absorption spectrum of a GCN film on glass.
Figure S6. X-ray photoelectron survey spectrum of GCN film on quartz. Core and Auger lines assigned to C, N, O are observed.
Mass Spectrometry

Dicynandiamide was combined with a KBr/LiBr eutectic salt mixture and was initally heated from room temperature to 180°C at 10°C min⁻¹ under vacuum (~5 x 10⁻³ mbar), and held at this temperature for 20 h. The material was then heated to 600°C at 10°C min⁻¹ under high vacuum conditions (~5 x 10⁻⁶ mbar) and held at this temperature for a further 2 h. The desorbing gaseous species produced after the initial annealing to 180°C were analyzed by mass spectrometry every 5°C within the 1 to 200 a.m.u mass range.

**Figure S7.** Time resolved mass spectroscopy of DCDA heated in a LiBr/KBr eutectic mixture. The mixture was dried at 180°C for 20 h before heating to 600°C at 10°C min⁻¹ and held at this temperature for 120 mins.
WO$_{3-x}$ nanorod films synthesis

WO$_{3-x}$ nanorod films were synthesized by aerosol assisted chemical vapour deposition (AACVD). The precursor for the deposition of WO$_{3-x}$ thin films was prepared by adding 60 mg tungsten hexacarbonyl (Sigma-Aldrich, 97%) into 10 mL acetone (Emplura, 99%) and 5 mL methanol (Emplura, 99.5%). An ultrasonic humidifier (Liquifog, Johnson Matthey operating at 2 MHz) was used to generate aerosol droplets. The aerosol droplets were transported to the heated substrate using a nitrogen gas flow (300 sccm) by a mass flow controller (MFC, Brooks). The deposition temperature and deposition time were 375 °C and 45 min respectively.

XRD (Figure S8) shows that the as-deposited WO$_{3-x}$ film is monoclinic $W_{24}O_{68}$ (WO$_{2.83}$) (JCPDS data card No. 36-0103). And the SEM and TEM images show that the film is comprise of well crystallized WO$_{3-x}$ nanorods, with the diameter around 100 nm and 2.5 μm.
Figure S8. a) Powder XRD pattern of WO$_3$$_x$ film. b) SEM image of WO$_3$$_x$ film. c) TEM image of WO$_3$$_x$ nanorods d) HRTEM image of WO$_3$$_x$ nanorods
Hydrogen evolution studies were carried out following a well-established method for photocatalytic water reduction, using ethanol as hole scavenger. The reaction took place at 15 °C in a 50:50 water:ethanol solution (20 ml) in acidic conditions (0.1 M HCl) under strong stirring conditions. A standard dispersion of 1 g/L of photocatalyst was used in all these experiments. Gas samples (250 µL) were taken from the headspace above the solution using a gas-tight syringe and the fractions of hydrogen in the aliquots were monitored upon irradiation time using a Varian CP-3800 gas chromatograph equipped with a packed molecular sieve column (80-100 mesh). The instrument was calibrated from several dilutions of 5% H₂: 95% N₂ gas mixtures, establishing a linear correlation between H₂ fraction (%) and volume (µV) in the gas aliquots. The light source used was a LED board with a single emission band at $\lambda_{\text{MAX}} = 450$ nm (bandwidth, $\Delta \lambda = 25$ nm) (Figure S9, inset). Under these conditions, production of hydrogen was observed from a platinised GCN-coated TiO$_2$ sample. The TiO$_2$ sample used was the ubiquitous commercial standard Evonik P25. The platinisation of the GCN-coated sample was performed by precipitation from a Pt-citrate sol, as described in the literature.$^1$ After 18 h of irradiation the rate of hydrogen was estimated as $1.85 \times 10^{-2}$ µmol h$^{-1}$ g$^{-1}$ (Figure S9). This value is comparatively low compared with the leading GCN materials reported in the literature (of 2-3 orders of magnitude higher for bulk and mesoporous materials)$^2$. However, it is notable that none of the individual components, namely platinised TiO$_2$ or GCN and non-platinised GCN-coated TiO$_2$—resulted in any hydrogen being produced under visible-light irradiation (Figure S9). This is also the case for the corresponding experiments carried out in the dark. The evidence suggests that this GCN coating acts as a photosensitiser on the TiO$_2$ surface, encouraging absorption of the system in the visible range.

Figure S9. Hydrogen evolution upon visible-light irradiation of platinised gCN-coated Evonik TiO$_2$ P25 powder. No hydrogen production was observed from the individual components of this system under the same conditions. The inset shows the emission spectrum of the LEDs board used in the experiments ($\lambda_{\text{MAX}} = 450$ nm).
References
