Supporting Information

Photosystem I on Graphene as a Highly Transparent, Photoactive Electrode

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Synthesis and Characterization

Graphene films were grown by chemical vapor deposition on 25-μm thick Cu foils cut into thin strips and placed inside a fused silica tube where they were heated using a hot wall furnace. The Cu foil was first heated at 1000 °C under 2 sccm flow of hydrogen while being evacuated and filled by H₂ (g). This was done under ~25 mTorr to remove contaminants and oxides from the Cu surface. Subsequently, 35 sccm of CH₄ (g) was introduced along with the 2 sccm of H₂ for 30 min, while pressure was maintained at ~250 mTorr. Then the furnace was allowed to cool to room temperature. PMMA (A7) resist was spin-coated onto the samples at 4000 rpm for 45 s, making a PMMA/graphene/Cu sandwich. The Cu was then etched away (APS-100 copper etchant) and the resulting PMMA/graphene stack was placed into a DI water bath where it was transferred onto designated Si/SiO₂, Au and glass substrates. After drying, the PMMA was removed using acetone. Each sample was cut to 1 cm x 1 cm squares with electrical contact made via Cu tape. Raman spectra taken for verification of the graphene film is shown in Figure S1. The ratio of G:2D peaks was 0.53 with a small D-peak at 1343 cm⁻¹, which is attributed to minor defects in pristine graphene.¹,²

Figure S1. Raman Spectra with G peak intensity of 1240, 2D peak intensity of 2333.
PSI was extracted from organic baby spinach purchased at a local grocery store according to Reeves and Hall\cite{reaves2013} with modification.\cite{hall2013} Briefly, ~60 g of leaves were deveined and homogenized in a blender. After maceration, the mixture was filtered through 2 layers of cheesecloth followed by 8 layers, keeping the receptacle on ice. This results in ~200 mL of a green solution, which is subsequently centrifuged in two steps: i) centrifugation at 8000 RCF for 5 seconds and the supernatant poured off. The pellet is resuspended in buffer and ii) centrifugation at 20000 RCF for 15 minutes producing a dark green supernatant. The protein is purified using a chilled hydroxylapatite column previously described by Shiozawa et al.\cite{shiozawa2013} The PSI suspension was stored at -80 °C prior to deposition. Two separate extractions of PSI were used in these experiments. The P700 concentration for each extraction was determined by UV-vis spectral analysis described by Baba et al.\cite{baba2013} revealing a concentration of $3.2 \times 10^{-6}$ mM/mL of P700 in the first batch with a chl $a$:P700 ratio of ~200, while the second extraction had P700 concentration of $1.7 \times 10^{-6}$ mM/mL with chl $a$:P700 ratio of 145.

In order to study surface composition, polarized modulation infrared reflectance-absorption spectroscopy (PM-IRRAS) was performed on graphene electrodes that were transferred to an infrared reflective surface (Au) prior to deposition of PSI. The peaks at ~1662 cm$^{-1}$ and ~1540 cm$^{-1}$ in Figure 2A are indicative of Amide I and Amide II peaks, respectively of the protein complex.\cite{seven} The presence of these peaks demonstrates that a protein is present on the surface of the graphene electrode.

Further study of the composition was conducted by collecting the UV-vis spectrum of a PSI film deposited on a UV-vis-transparent graphene/glass substrate. Figure 2B demonstrates the absorption of the graphene before (black) and after (red) protein
deposition. After deposition of PSI, distinct peaks can be observed at ~680 nm and ~440 nm, consistent with the chlorophylls of PSI, indicating a protein-modified graphene surface. The low absorption values seen for the PSI-modified graphene samples can be attributed to the path length of a few nm for the PSI monolayer.

Figure S2. Spectroscopic analysis of PSI-modified graphene electrodes. a) PM-IRRAS spectrum of a PSI film deposited onto a graphene/Au electrode. The absorbance values at 1662 cm\(^{-1}\) and 1540 cm\(^{-1}\) correspond to the Amide I and II stretches respectively.\(^3\) b) UV-vis absorbance spectrum of an unmodified graphene electrode (black) and PSI film deposited on graphene/glass electrode (red). The absorbance of the glass was subtracted from the measurements, and the value for the absorbance at 750 nm was set to zero in order to easily observe the absorbance change between the unmodified and PSI-modified graphene. The two distinct peaks at ~680 nm and ~440 nm are consistent with the chlorophylls of PSI.\(^6\)

Spectroscopic Ellipsometry (SE) measurements were obtained on a J. A. Woolham Co. M-2000DI variable angle spectroscopic ellipsometer with CompleteEase™ software for modeling. Measurements were taken at three independent locations per sample at incident angles of 70, 75, and 80 degrees from surface normal and modeled using wavelengths of
400-700 nm. Optical constants were simultaneously measured and verified. For graphene on Si/SiO$_2$ substrates, the bare Si/SiO$_2$ was measured and modeled using SI JAW substrate with INTR JAW set at 10.00 Å followed by SIO2 JAW, fitting the thickness. The final average thickness was 3004.30 Å in good agreement with the manufacturer’s specifications. Graphene measurements were taken and modeled using a Cauchy film as the starting material, parameterized to a B-spline with n = 1.5, k = 0 at a resolution of 0.3 eV resulting in 18 points. Graphene thickness models varied from the interlayer distance of graphite, which is in agreement with Kravets et al.$^8$ experience and possibly results from residuals on the surface. The Raman data were verified for each graphene sample, confirming a monolayer on the surface of both the Si/SiO$_2$ and glass substrates. There have been several optical ellipsometric studies on graphene, including Gray et al.$^9$ (3.7 Å), and Weber et al.$^{10}$ (3.4 Å). Therefore, a graphene thickness of 3.4 Å was assumed for subsequent PSI measurements. The PSI was modeled using a Cauchy layer, where A = 1.422, B = 0.002, and C = 0. The refractive index was 1.459 at 632.8 nm.

References:


