

Supplementary Information for the paper

Graphene-protected copper and silver plasmonics

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1. ATR experimental setup.

The ATR ellipsometric spectra and ATR polarized reflection spectra of the samples were measured by the focused beam M-2000F spectroscopic ellipsometer (J. A. Woollam, Inc.). In the unfocused mode, the measurement spot was about 3.5 mm × 7 mm; in the focused mode, a measurement spot was about 30 μm × 60 μm (for an angle of incidence of 60°), see Fig. S1 for experimental setup.

We recorded a pair of ellipsometric parameters Ψ (ellipsometric reflection) and Δ (ellipsometric phase shift) in the wavelength range from 250nm to 1000nm with the wavelength step of 1nm. The parameter Ψ provides the ratio of field amplitude reflection coefficients for p and s polarizations and Δ gives the phase difference for the same coefficients so that $\tan(\Psi)\exp(i\Delta) = r_p / r_s$, where r_p and r_s are the complex field reflection coefficients for p - and s -polarizations respectively. In M-2000F phase

Δ is determined through the ratio of in-phase and out-of-phase signals generated by a rotating compensator. The typical measurement time of one ellipsometric spectra was about 5-10s (depending on acquisition time for each spectral point).

In our experiments we performed both focussed and unfocussed measurements which showed similar results. The water-glycerol mixtures were replaced in exchange chamber. The absence of air bubbles were checked by the CCD camera placed directly above the cell.

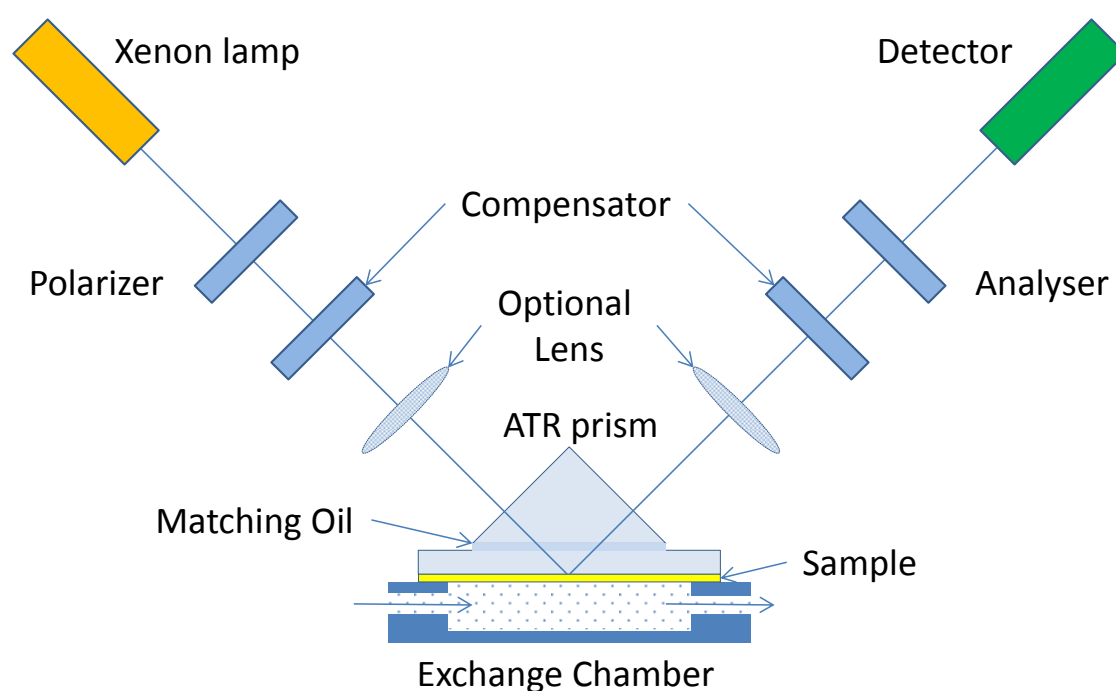


Figure S1. ATR experimental setup.

2. Raman spectra of hydrogenated graphene

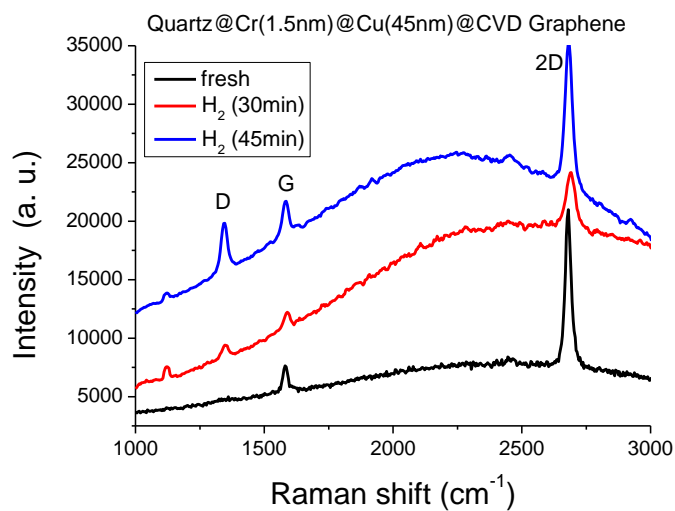
Graphene hydrogenation has been performed by cold hydrogen plasma. We used low-pressure (0.1 mbar) hydrogen-argon mixture (10% H₂) with dc plasma ignited between two aluminum electrodes. The sample was kept 30 cm away from the discharge zone in order to minimize any possible damage by energetic ions. We performed two plasma exposures of 30 and 45 mins. We found that it typically required 20-30 mins of plasma treatment to reach a detectable level of hydrogenation.

Graphene hydrogenation level was evaluated using Raman spectra. Raman spectra were measured at room temperature with a Witec alpha 300R Raman spectrometer. The spot size was $\sim 1 \mu\text{m}$ for a $\times 100$ objective, and the power was kept at $\sim 1.0 \text{ mW}$ to avoid heating. The excitation laser energy was 2.41 eV (wavelength $\lambda_L = 514.5 \text{ nm}$, Ar+ laser).

Figure S2(a) shows the Raman spectra of three CVD graphene samples exposed to hydrogen plasma for different exposure times. The Raman spectrum for fresh CVD graphene sample (black curve) displays the G peak at $\sim 1580 \text{ cm}^{-1}$ due to the in-plane vibrational E_{2G} mode at the Brillouin zone centre and the 2D peak at about 2680 cm^{-1} due to two-phonon inter-valley scattering. The ratio of intensities I_{2D}/I_G is equals to ~ 6.1 which demonstrates high quality of the CVD graphene. Raman spectra taken before hydrogenation (Fig. S2 (a)) show no detectible defect related Raman D band ($\sim 1340 \text{ cm}^{-1}$), indicating that the graphene sheet is virtually free from defects. After hydrogenation, Raman spectra show an additional sharp Raman D peak at about 1340 cm^{-1} activated by defects, see Fig. S2(a). This D peak is due to the breathing modes of six-atom rings and requires defects for its activation. Partially hydrogenated graphene (30 to 45 mins) exhibits the Raman spectra that have comparable intensities of the G and D peaks. In hydrogenated stage, the Raman spectrum evolves as follows: (a) D peak appears and ratio I_D/I_G increases; (b) all peaks broaden. For different stages of hydrogenation the 2D stays wide and starts to shift around of 2685 cm^{-1} (see Fig. S2 (b)). To determine hydrogenation level we used the D and G peak intensity ratio I_D/I_G of the Raman spectra of the hydrogenated samples. In recent Raman studies [S1], it was shown experimentally that the ratio between the intensities of the D and G bands I_D/I_G is linearly proportional to the point defect density (n_D) generated by the impact

of the ions on the graphene plane. (The background Raman signal in spectra demonstrated in Fig. S2 may be due to weak photoluminescence of the substrate).

(a)



(b)

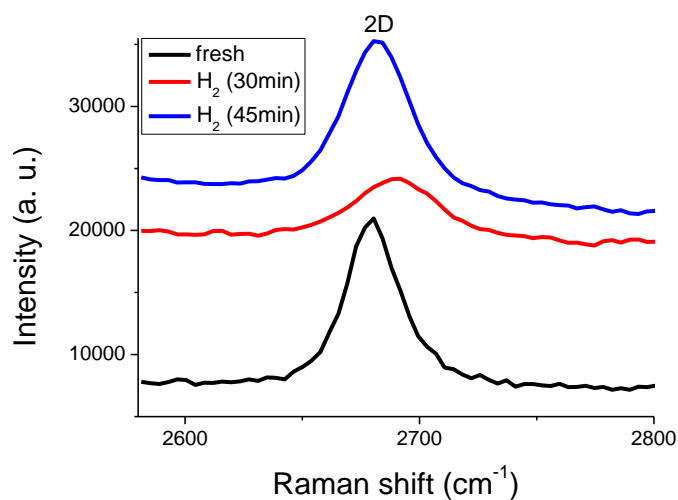


Figure S2. Raman spectra of CVD graphene on top of Cu thin film produced by hydrogenation (laser excitation wavelength $\lambda_L = 514.5$ nm). (a) Pure CVD graphene film, sample hydrogenated for 30 and 45 min. (b) The evolution of 2D peak for partially hydrogenated CVD graphene.

References:

[S1] L. G. Cancado *et al.*, Nano Lett., **11**, 3190–3196 (2011).