Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for:

Electronically coupled hybrid structures by graphene oxide directed self-assembly of $Cu_{2-x}S$ nanocrystals

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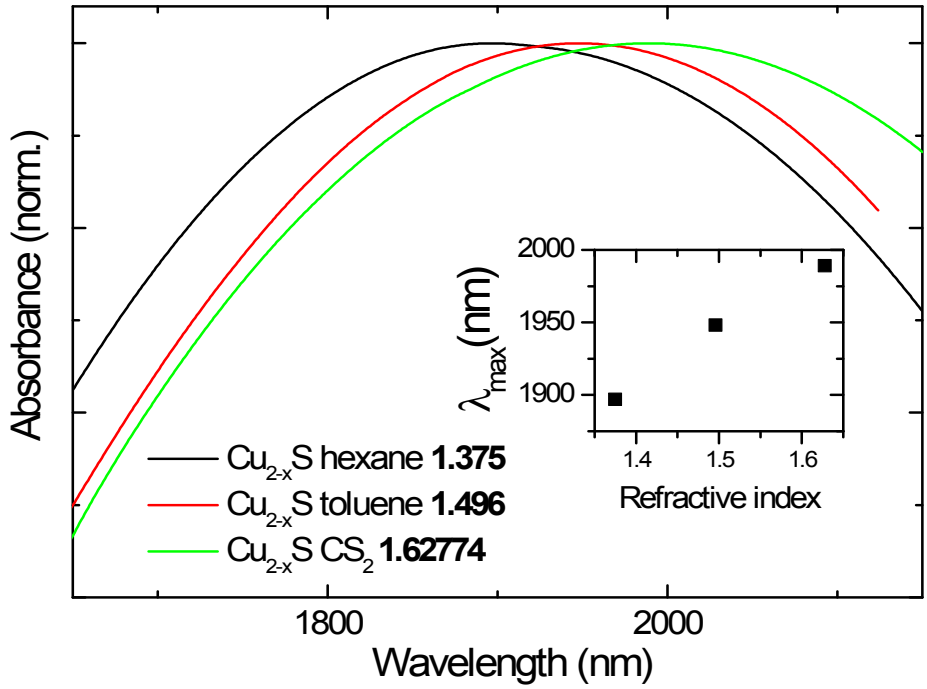

Figure S1: Dependence of the LSPR spectral position of $Cu_{2-x}S$ on various refractive index solvents, such as hexane, toluene, and CS_2. A red-shift of the maximum LSPR is observed with increasing refractive index (linear dependence, see inset).

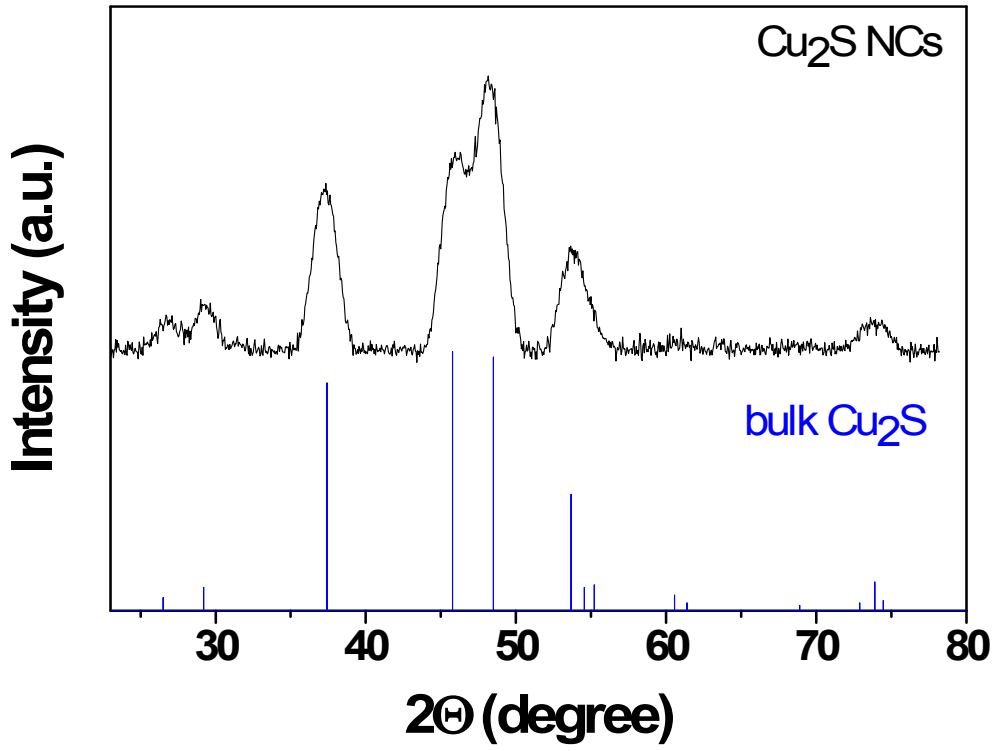

Figure S2: XRD analysis of the as-synthesized Cu_2S NCs. Synthesized under controlled air-free conditions the Cu_2S NCs show the crystal structure of stoichiometric chalcocite. Without vacancies in the structure, the NCs do not show absorption in the NIR, due to the absence of free carriers in the system.

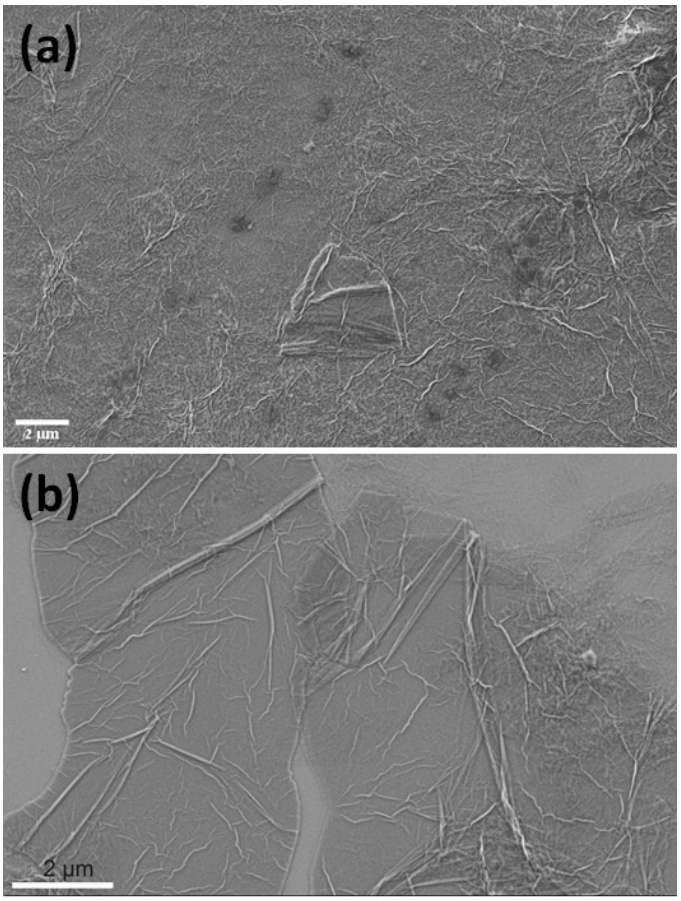

Figure S3: SEM images of a thick graphene oxide (GO) film (a) formed by the macroemulsion process, as described in the experimental section, and (b) a thin part of the film, where separate flakes are observed.

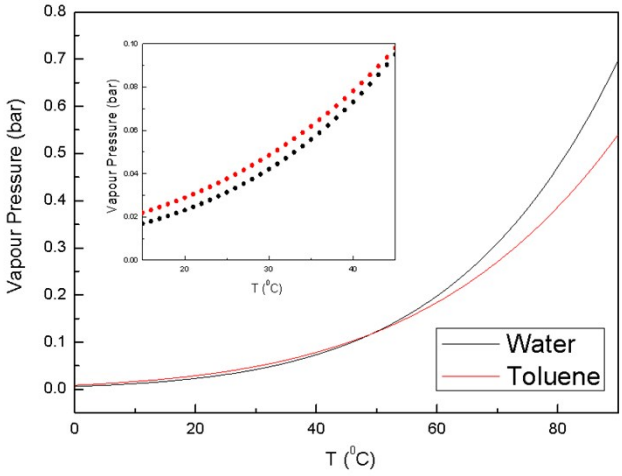

Figure S4: Vapor pressure of water and toluene as a function of temperature, based on the data taken from the NIST database.[1] The inset shows an enlargement of their vapor pressure between 15 and 45°C. The plots demonstrate that toluene should evaporate faster than water, which contributes to the self-assembly of the $Cu_{2-x}S$ nanoparticles in between the graphene oxide sheets.

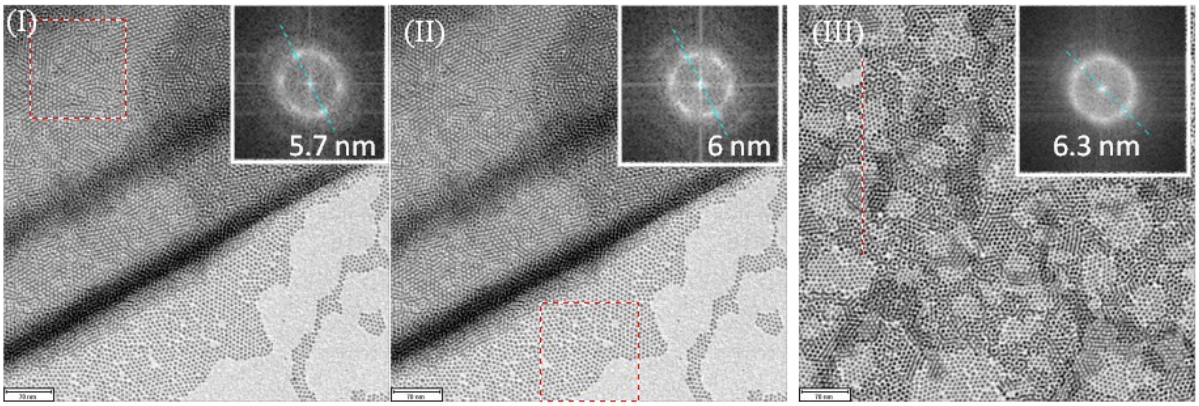

Figure S5: TEM images and corresponding FFTs as insets of three hybrid GO/$Cu_{2-x}S$ NCs films. The FFTs of GO supported NCs (I) shows a 6-fold symmetry, while the unsupported NCs (II), and (III) show only a weak long range order. The scale bar is 70 nm in all images.

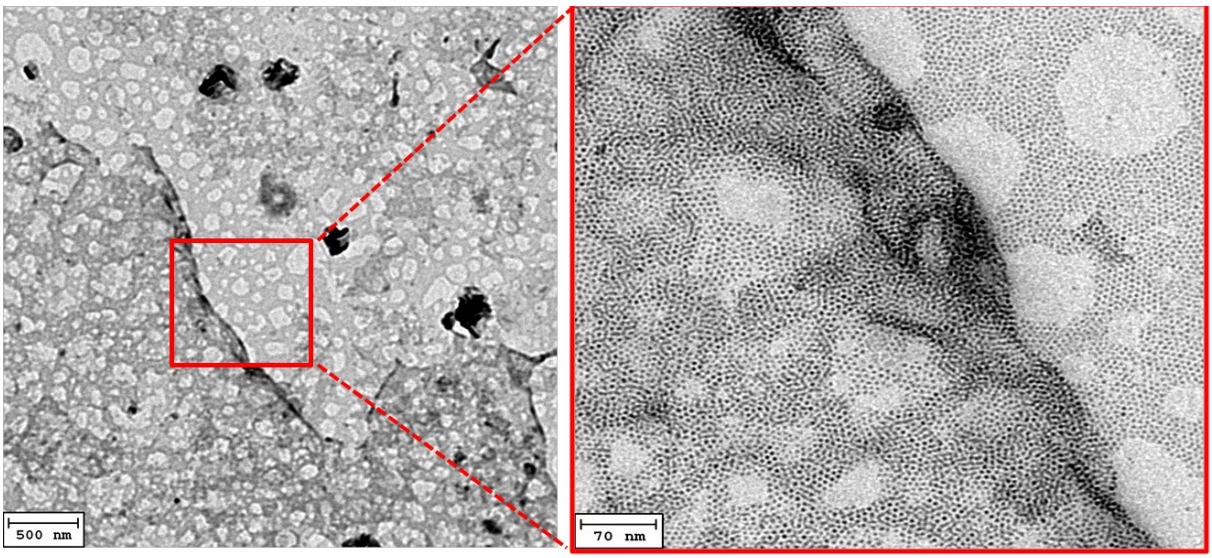

Figure S6: TEM images (small magnification – left, and high magnification - right) of a composite film based on GO and inorganic cadmium sulfide (CdS) NCs.

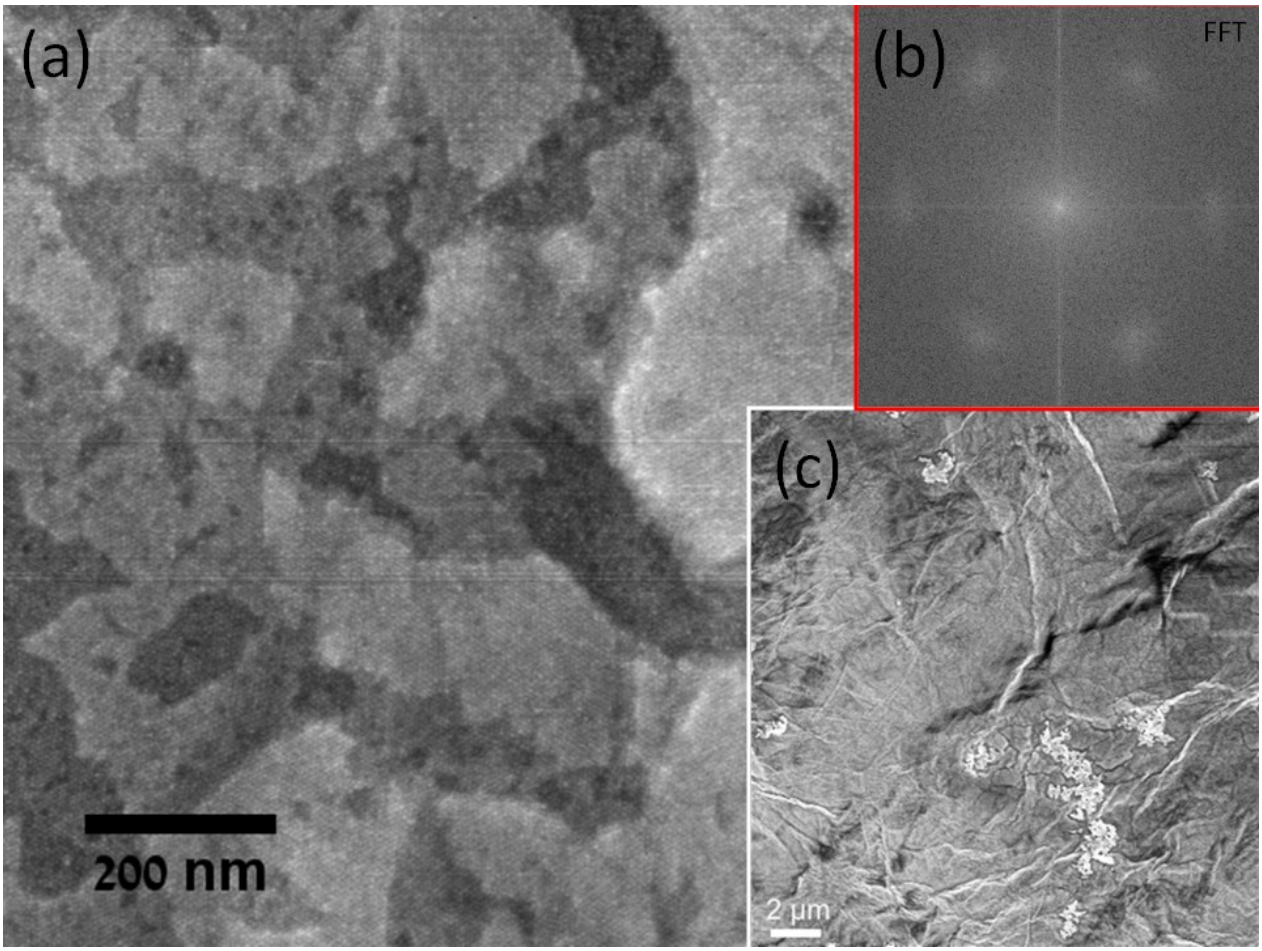

Figure S7: SEM micrograph of a GO/$Cu_{2-x}S$ NCs hybrid (top view), taken with high (a) and low (c) magnification. The six-fold arrangement of the NCs is observed in the FFT of the high resolution SEM image in (b). The observed wrinkling (Figure S5c) is characteristic for pure GO layers deposited from solution.[4] A closer examination of the sample, shown in Figure S5(a), reveals a multilayer arrangement of the $Cu_{2-x}S$ NCs. Again, the six-fold symmetry of the FFT indicates that the NCs self-assemble in a hexagonal fashion (Figure S5(b)).

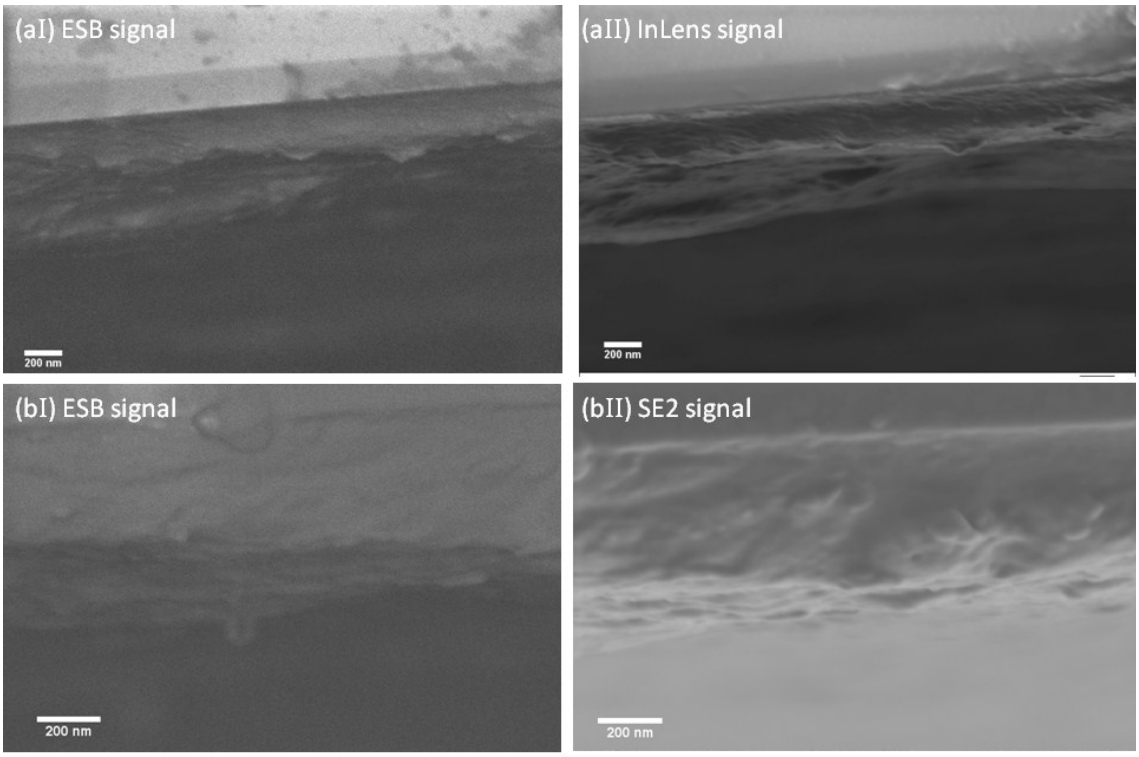

Figure S8: Cross-section images of GO/$Cu_{2-x}S$ films in two different locations (a) and (b), taken with back-scattered (I) and secondary (II) electron detectors. The cross-sectional SEM analysis of the GO/$Cu_{2-x}S$ hybrids shown in the figure indicates that there is no clear difference in intensity between the top and bottom of the films when using back scattered electron detectors (ESB). This suggests an even distribution of the $Cu_{2-x}S$ NCs throughout the film.

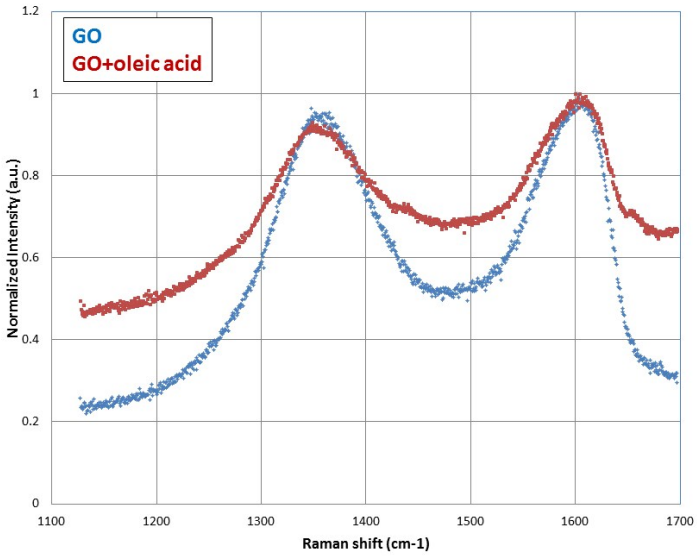

Figure S9: Raman spectrum of a GO film (blue curve) and of a film prepared from a GO macroemulsion containing oleic acid (red curve). The Raman G band of the GO does not shift due to the presence of oleic acid, indicating that no electron transfer occurs between the GO and the oleic acid.

References

1. National Institute of Standarts and Technology; Materials Measurement Laboratory, Antoine Equation Parameters for Water and for Toluene. 2011.