BROADBAND PHOTO RESPONSE OF GRAPHENE/COFE2O4 NANOPARTICLE PHOTODETECTORS UNDER AC AND DC DRIVING CONDITIONS

DOI: 10.66951/HTZA1753; https://doi.org/10.66951/HTZA1753

Oleksandr Volochanskyi, oleksandr.volochanskyi@heu.cas.cz
Heyrovský Institute, Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Prague, Czech Republic

Department of Physical Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prag ue, Czech Republic

Golam Haider, g.haider@ifw-dresden.de
Heyrovský Institute, Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Prague, Czech Republic

Martin Mergl, martin.mergl@heu.cas.cz
Heyrovský Institute, Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Prague, Czech Republic

Stefania Sandoval Rojano, ssandoval@icmab.es
Heyrovský Institute, Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Prague, Czech Republic

Martin Kalbáč, martin.kalbac@heu.cas.cz
Heyrovský Institute, Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Prague, Czech Republic

Abstract

For hybrid photodetectors with electrically complex interfaces, the choice of measurement scheme determines the quality and meaning of the obtained photoresponse. Hybrid graphene photodetectors combine the high carrier mobility and broadband optical response of graphene with light-sensitive materials that modify the electrical properties of the graphene channel, yet their response is commonly evaluated under a constant source–drain bias that also records transient current changes developing during continuous bias and illumination. Here, we compare direct current (DC) and alternating current (AC) measurement scheme of graphene devices functionalized with oleic-acid-capped $CoFe_2O_4$ nanoparticles. Under a constant 2 V bias, illumination produces a measurable broadband response together with pronounced current transients after light switching. In contrast, a 100 kHz sinusoidal bias with small amplitude produces stable and reproducible illumination-dependent AC current. Frequency-resolved impedance measurements show that the device evolves from predominantly resistive behavior at low frequency to a mixed resistive–reactive response near 100 kHz, with illumination modifying both components of the complex admittance. This frequency-selective measurement enables clear detection across 500–1100 nm, including weak response at 1100 nm that is difficult to resolve reliably in the DC traces. These results show that AC driving conditions can improve the practical detectability of weak optical signals in interface-dominated hybrid photodetectors.

1 Introduction

Graphene provides a high-mobility transport channel with optical sensitivity over a broad spectral range, but its weak absorption limits the photoresponse of simple graphene devices [1,2]. Hybrid architectures address this by coupling graphene to an additional light-sensitive material whose photoexcitation modifies the carrier density, conductivity, or electrostatic environment of the graphene channel [1,3]. In colloidal nanoparticle systems, the interface enabling this coupling can also impede charge transport. Long-chain surface ligands provide colloidal stability but act as barriers to electronic coupling and carrier transport in nanocrystal solids [4,5]. Oleic acid is widely used in the synthesis and stabilization of $CoFe_2O_4$ nanoparticles and binds directly to the ferrite surface [6]. Consequently, an oleic-acid-capped $CoFe_2O_4$/graphene interface contains an electronically resistive organic layer in the potential charge-transfer pathway. The extent to which this interface contributes resistive or capacitive components to the device response must therefore be determined experimentally.

Hybrid graphene photodetectors are commonly characterized under a constant DC source–drain bias, where illumination-induced changes in device conductance are recorded directly as changes in current [1,3], $I_{\mathrm{ph,DC}} = I_{\mathrm{light}} - I_{\mathrm{dark}}$. Time-dependent measurements performed under such conditions collect both the steady illuminated–dark current difference and transient current evolution following changes in illumination [7]. In hybrid devices with interface-limited charge transport, such transients can arise from charge accumulation and delayed release at the sensitizer/graphene interface and may obscure weak optical signals when their magnitude becomes comparable to the steady photoresponse. AC driving conditions provide a complementary measurement scheme. A sinusoidal voltage periodically reverses the source–drain electric field, and frequency-selective detection scheme measures the electrical response at the applied frequency. Contributions that vary much more slowly than this driving conditions appear less directly in the measured AC-driven measurements. At higher frequencies where the device exhibits a non-negligible reactive component, the measured AC current depends on the full complex admittance, $Y = G + jB$. Frequency-resolved impedance measurements are therefore required to interpret the AC photoresponse [8].

Here, we compare DC and AC electrical test schemes of graphene devices functionalized with oleic-acid-capped $CoFe_2O_4$ nanoparticles. Frequency-dependent impedance measurements are combined with time-dependent and wavelength-dependent optical measurements to establish how the electrical AC/DC test scheme affects the measured response. The purpose of this study is to determine whether frequency-selective AC readout can improve the stability and practical detectability of the broadband photoresponse in an interface-dominated graphene/nanoparticle photodetector.

2 Main Section

Oleic-acid-capped $CoFe_2O_4$ nanoparticles were synthesized following the procedure reported in Ref. [9] and deposited onto the graphene devices by spin coating. The graphene/$CoFe_2O_4$ nanoparticle device and representative DC and AC responses are shown in **Figure 1**. Under DC operation, a constant source–drain bias of 2 V produces a measurable current change when the illumination is switched on, together with pronounced transient features at the illumination transitions (**Figure 1c**). Similar transients are observed when the illumination is removed. Comparable transients were absent in pristine graphene devices measured before $CoFe_2O_4$ deposition, identifying the nanoparticle layer or the newly formed nanoparticle/graphene interface as their likely origin. The oleic-acid ligand shell provides a plausible contribution because long-chain aliphatic ligands impede electronic coupling and charge transport in colloidal nanoparticle systems [4–6], while surface modification or partial decomposition of the nanoparticles may introduce additional localized states. Both effects can promote charge

accumulation and delayed release at the interface, consistent with the transient current spikes observed under DC bias.

For AC measurements, a sinusoidal source–drain voltage of V_{pp} = 50 mV was applied. At 100 kHz the electrical period is 10 µs, and the polarity of the applied field reverses every 5 µs (**Figure 1B**). The measured I_{AC} represents the RMS current at the applied test frequency. Under these experimental conditions, illumination instead produces stable changes in the measured AC current, ΔI_{AC}, without the pronounced switching transients observed under DC bias (**Figure 1D**).

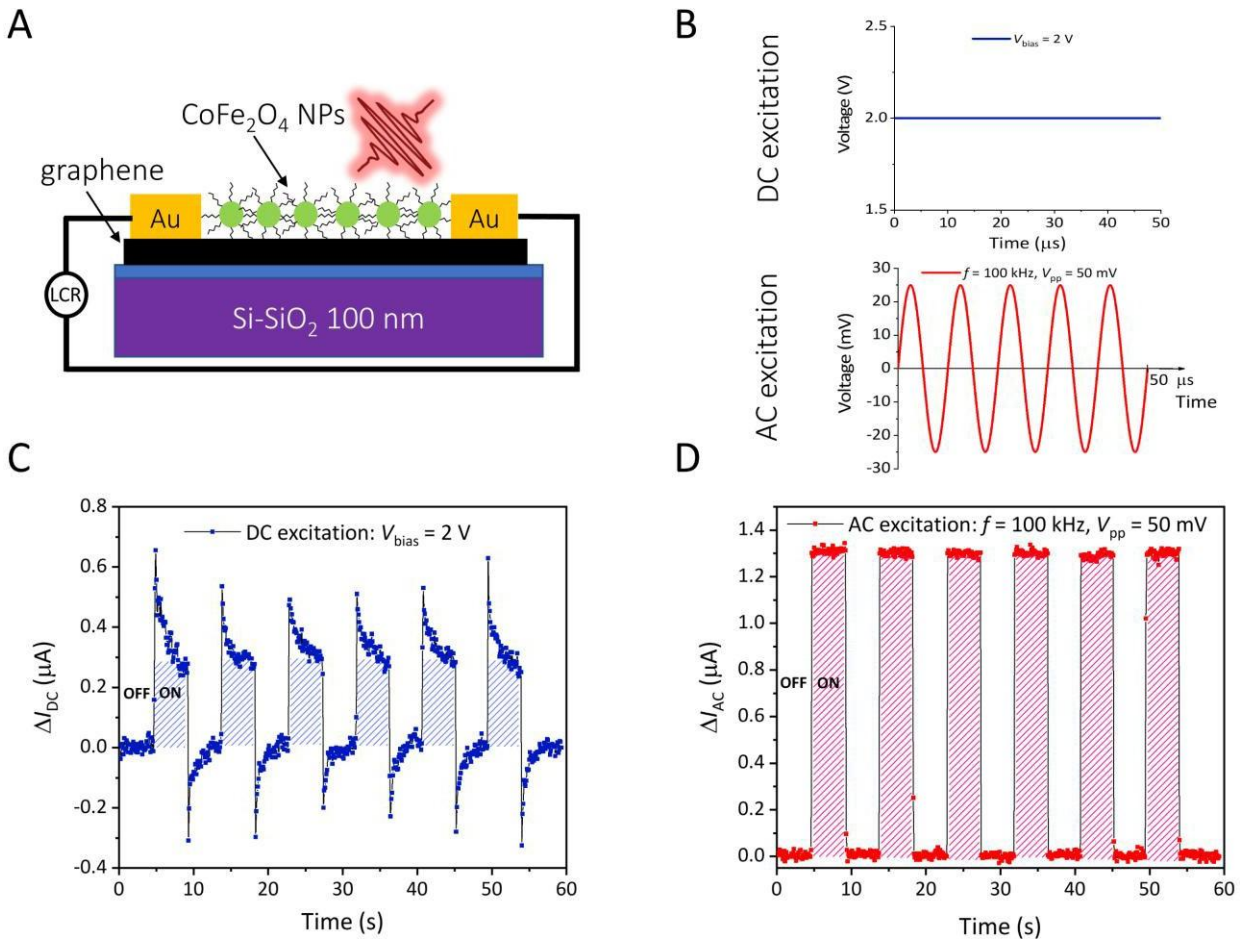


Figure 1. Device architecture and comparison of DC and AC electrical response. (A) Schematic of the graphene device functionalized with oleic-acid-capped $CoFe_2O_4$ nanoparticles and contacted by Cr/Au electrodes on a Si-SiO_2 substrate. Electrical measurements were performed using an LCR meter. (B) Applied voltage in the two measurement modes: a constant bias of V_{bias} = 2 V for DC measurements and a sinusoidal voltage at f = 100 kHz and V_{pp} = 50 mV for AC measurements. (C) Representative DC photoresponse under repeated illumination, showing pronounced transient current spikes after switching the light on and off, followed by relaxation toward the illuminated or dark level. (D) Corresponding AC photoresponse measured at 100 kHz, showing stable and reproducible light-on and light-off levels with strongly suppressed transient features. Hatched regions indicate illumination ON. AC and DC data were collected using Hioki Im3533-01 LCR meter.

Frequency-resolved impedance measurements were used to determine the electrical character of the AC response (**Figure 2A**). The complex impedance $Z = R_S + jX$ is predominantly resistive at low frequency, where reactance X approaches zero. With increasing frequency, the negative reactance becomes substantial and is comparable in magnitude to R_S near the 100 kHz operating condition, demonstrating a mixed resistive–capacitive response. To isolate the illumination-induced contribution, the impedance was converted to admittance, $Y = G + jB = 1/Z$, and the corresponding dark levels were subtracted (**Figure 2B**). Both conductance ΔG, i.e. the in-phase/dissipative contribution, and susceptance ΔB, i.e. the reactive contribution, increase with frequency and optical power density,

showing that illumination modifies both the conductive and reactive components of the device response. Thus, the measured AC photoresponse represents a light-induced change in complex admittance, $I_{AC} = V_{AC,rms}|Y|$. The increasing AC photoresponse with frequency is therefore associated with the frequency-dependent light-induced modulation of the complex admittance, with contributions from both conductance and susceptance.

The practical advantage of AC regime is most apparent in the wavelength-dependent measurements (**Figure 2C, D**). Both DC and AC measurements detect a broadband response from 500 to 1100 nm. Under a constant DC bias, however, illumination switching is accompanied by pronounced current transients and relaxation, which increasingly complicates extraction of the weak response at longer wavelengths. At 100 kHz and V_{pp} = 50 mV, stable and reproducible AC current changes are obtained across the complete spectral range, allowing the response at 1100 nm to remain clearly resolved. Frequency- selective AC measurement therefore improves the practical visibility of weak optical signals in this interface-dominated device, while detailed impedance analysis is required to establish the electrical meaning of the measured AC response.

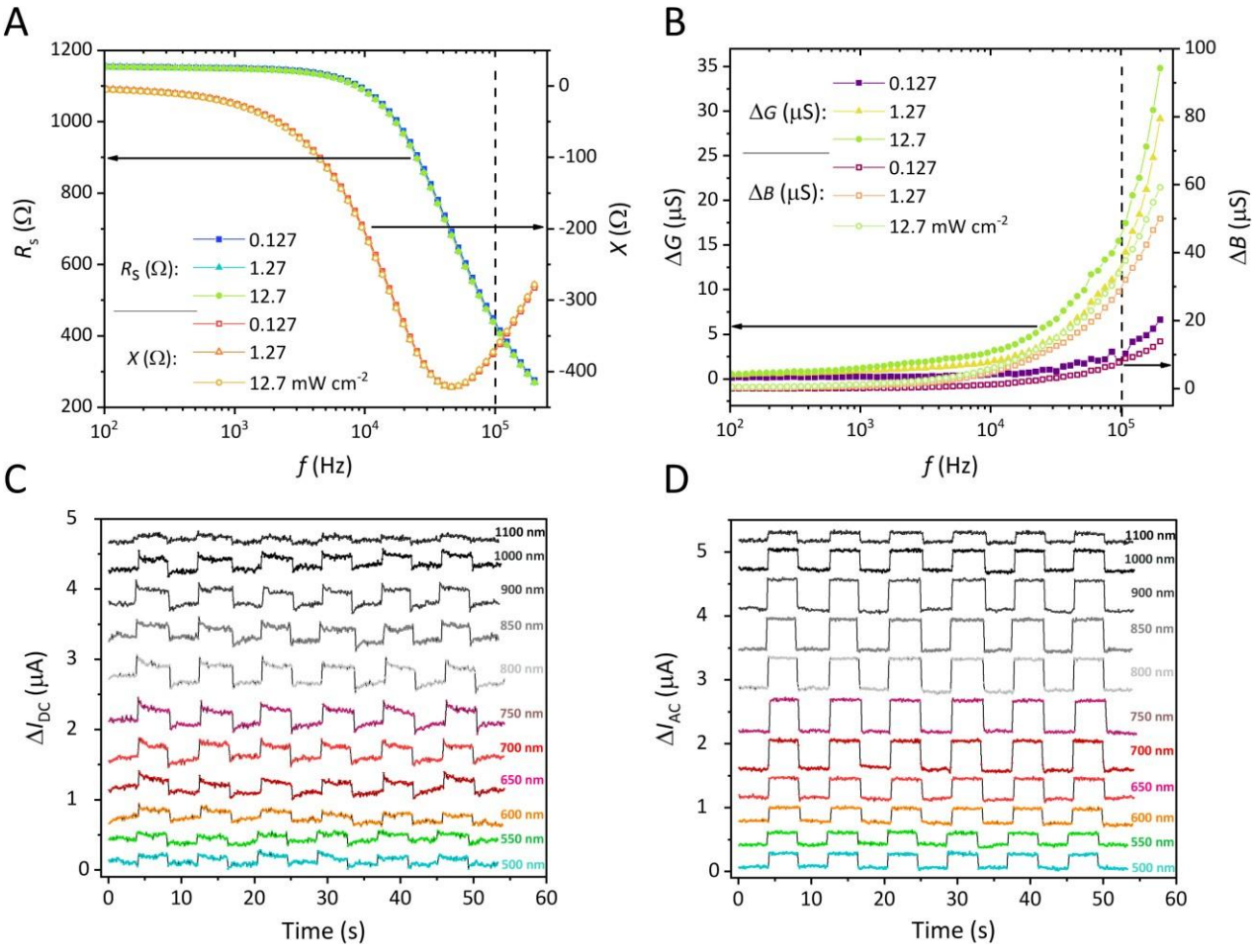


Figure 2. Frequency-dependent electrical response and wavelength-dependent response under DC and AC conditions. (A) Series-equivalent resistance R_s and reactance X of the graphene/$CoFe_2O_4$ nanoparticle device as a function of frequency under 700 nm illumination. The increasingly negative reactance indicates the development of a capacitive contribution with increasing frequency. The dashed line marks 100 kHz, used for the AC photoresponse measurements. (B) Light-induced changes in conductance, $\Delta G = G_{light} - G_{dark}$, and susceptance, $\Delta B = B_{light} - B_{dark}$, calculated from the complex impedance at the same optical powers. Both components increase with frequency and optical power, demonstrating that illumination modifies both the conductive and reactive response of the device. (C,D) Wavelength-dependent photoresponse measured from 500 to 1100 nm under (C) a constant 2 V DC bias and (D) a 100 kHz, V_{pp} = 50 mV of AC driving conditions. Traces are vertically offset for clarity. The AC readout provides reproducible light-on and light-off levels throughout the measured spectral range, including the weak response at 1100 nm. AC and DC data were collected using Hioki Im3533-01 LCR meter.

3 Conclusions

DC and AC measurements reveal complementary aspects of the photoresponse in graphene/$CoFe_2O_4$ nanoparticle devices. Continuous DC bias exposes pronounced transient behavior and is consistent with interface-limited charge redistribution. AC measurements at 100 kHz provide a substantially more stable response, enabling weak broadband signals to be resolved reproducibly up to 1100 nm. Frequency-dependent impedance measurements show that illumination modifies both conductance and susceptance at the selected AC frequency, confirming contributions from both conductive and reactive components. These results demonstrate that the electrical test scheme is an important design parameter for hybrid photodetectors with electrically complex interfaces.

4 Acknowledgement

This work has been funded by a grant from the Programme Johannes Amos Comenius under the Ministry of Education, Youth and Sports of the Czech Republic CZ.02.01.01/00/22_008/0004558 Advanced MUltiscaLe materials for key EnablingTechnologies.

5 References

[1] F. H. L. Koppens, T. Mueller, Ph. Avouris, A. C. Ferrari, M. S. Vitiello, M. Polini, *Nat. Nanotechnol.* **9** (2014) 780–793. DOI: 10.1038/nnano.2014.215.

[2] R. R. Nair, P. Blake, A. N. Grigorenko, *et al.*, *Sci.* **320** (2008) 1308. DOI: 10.1126/science.1156965.

[3] G. Konstantatos, M. Badioli, L. Gaudreau, *et al.*, *Nat. Nanotechnol.* **7** (2012) 363–368. DOI: 10.1038/nnano.2012.60.

[4] D. V. Talapin, J.-S. Lee, M. V. Kovalenko, E. V. Shevchenko, *Chem. Rev.* **110** (2010) 389– 458. DOI: 10.1021/cr900137k.

[5] X. Liang, S. Bai, X. Wang, *et al.*, *Chem. Soc. Rev.* **46** (2017) 1730–1759. DOI: 10.1039/C6CS00122J.

[6] S. M. Ansari, B. B. Sinha, D. Phase, *et al.*, *ACS Appl. Nano Mater.* **2** (2019) 1828–1843. DOI: 10.1021/acsanm.8b02009.

[7] C. O. Kim, S. W. Hwang, S. Kim, *et al.*, *Sci. Rep.* **4** (2014) 5603. DOI: 10.1038/srep05603.

[8] E. von Hauff, *J. Phys. Chem. C* **123** (2019) 11329–11346. DOI: 10.1021/acs.jpcc.9b00892.

[9] S. A. Kadam, S. Sandoval, Z. Bastl, *et al.*, *ACS Catal.* **13** (2023) 13484–13505. DOI: 10.1021/acscatal.3c02592.