EPR spectra detection by heat release using PVDF films

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The energy absorption by the sample during EPR resonance leads to a detuning of the resonator and reflection of MW power that is recorded by a crystal detector located outside the resonator. Since the absorption of energy by the sample leads to its heating, this heating can be used to record EPR spectra instead of a standard way. This method of detection is especially advantageous for recording the EPR spectra of recombining radical pairs, when the change in the heat released during resonance is determined by the difference in the recombination energy of pairs in the states with different spin multiplicity. This difference can exceed by several orders of magnitude the heat released due to spin reorientation at resonance. As very sensitive sensors to measure heat variations one can use pyroelectrics that can transform the change in heat released into a change in electric current. In this work, we investigated three types of PVDF (polyvinylidene difluoride) standard pyroelectric films with indium tin oxide (ITO), Cu/Ni, and Au coatings to determine their sensitivity for detecting EPR signals. A comparative study based on the calculation of the noise-equivalent power and specific detectivity from experimental spectra showed that the Au coated PVDF film is the most promising active element for measuring the EPR signal. Using the best achieved sensitivity, estimation is given whether this is sufficient for using a PVDF-based pyrodetector for indirectly detecting EPR spectra by recombination heat release or not. The authors gratefully acknowledge the financial support of this work by the Russian Foundation for Basic Research (Project 19-29-10020)

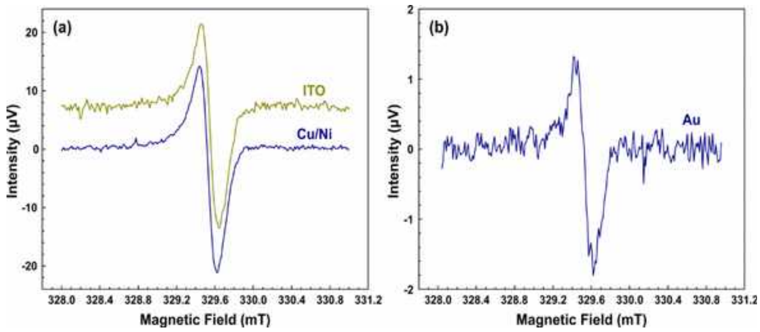

Figure 1. (a) EPR spectra of DPPH powder registered by a pyrodetector based on an active element with Cu/Ni coating (dark blue) or ITO coating (dark green, vertically shifted). The thickness of PVDF film is 28 µm. Modulation amplitude is 0.15 mT, modulation frequency is 115 Hz, time constant is 0.3 s, MW power is 200 mW, temperature is 298 K. DPPH weight is 2.2 µg (about $3 \cdot 10^{15}$ spins) and 2.8 µg (about $4 \cdot 10^{15}$ spins) for Cu/Ni and ITO coating, respectively. Spectrum recording time is 400 s (Cu/Ni coating)

and 1280 s (ITO). (b) The same as (a) for an active element with Au coating. The thickness of PVDF film is 12 μm. DPPH weight is 0.23 μg (about $3 \cdot 10^{14}$ spins). Spectrum recording time is 2000 s.