Calligraphed plasmonic lines on paper operating as a miniaturized portable biosensing device

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Paper-based biosensors are emerging as promising devices for point-of-care applications due to their low-cost, easy fabrication and high flexibility providing rapid and accurate detection of diseases in resource-limited environments [1]. The quality of paper-based platforms can be improved by integrating the unique optical properties of nanomaterials, such as optical response tunability and local enhancement of the electromagnetic field, for multiple target analyte via Localized Surface Plasmon Resonance (LSPR), Surface Enhanced Raman Spectroscopy (SERS), and Metal Enhanced Fluorescence (MEF) [2].

Herein, we introduce a cost effective, easy-to-use method of integrating Gold Nanorods (GNRs) with different LSPR responses of the longitudinal band (603, 680, 813 nm) onto inexpensive Whatman® filter paper via plasmonic calligraphy using a commercial ball-point pen and nanoparticles in colloidal suspension as ink. This approach counteracts any complex and time-consuming process to ensure multiple test domains on the same paper substrate. The successful deposition of GNRs on the cellulose fibers was confirmed by both LSPR measurement and SEM images. The optical efficiency of our nanoplatforms was enhanced by re-tracing new lines with plasmonic ink in the same position resulting in a higher optical density of nanoparticles. For the biosensing protocol, we grafted our plasmonic lines with a para-aminothiophenol@Biotin (p-ATP@Biotin) Raman label as a recognition element with high affinity for target Streptavidin@Alexa (Strep@Alexa) detection. We chose to use two fluorophores complexes (Strep@Alexa514 and strep@Alexa680) added on the same line to prove the multidetection capabilities and analytical performance of our nanoplatforms. The UV-Vis extinction spectra confirm the presence of each analyte through successive red-shifts of the longitudinal plasmonic band, while the ultrasensitive SERS technique identifies the Raman fingerprint of p-ATP activated biotin and the vibrational bands of Streptavidin protein. Finally, the fluorescence capabilitys of our plasmonic nanoplatforms were enhanced in the case of GNRs@680nm by employing the biotin-streptavidin complex as a spacer leading to an optimal interface between the gold surface and the Alexa fluorophores. As a result, a 2.91 and 1.67-fold emission enhancements of Streptavidin@Alexa were obtained compared to the emission of Alexa 514 and Alexa 680 on paper. In summary, by employing a simple and inexpensive calligraphy approach, our flexible and portable plasmonic paper-based nanoplatforms poses excellent multimodal capabilities which makes them suitable for sensing applications such as disease diagnosis and biological analysis.

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