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Hotspot generation for unique identification with nanomaterials

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Nanoscale variations in the structure and composition of an object are an enticing basis for verifying its identity, due to the physical complexity of attempting to reproduce such a system. The biggest practical challenge for nanoscale authentication lies in producing a system that can be assessed with a facile measurement. Here, a system is presented in which InP/ZnS quantum dots (QDs) are randomly distributed on a surface of an aluminium-coated substrate with gold nanoparticles (Au NPs). Variations in the local arrangement of the QDs and NPs is shown to lead to interactions between them, which can suppress or enhance fluorescence from the QDs. This position-dependent interaction can be mapped, allowing intensity, emission dynamics, and/or wavelength variations to be used to uniquely identify a specific sample at the nanoscale with a far-field optical measurement. This demonstration could pave the way to producing robust anti-counterfeiting devices.

Physically Unclonable Functions (PUFs) are a form of hardware cryptographic primitive, that allows for the authentication and identification of physical objects[1]. When applied towards the authentication of electronic devices, this authentication usually occurs through entirely electronic channels, but when physical objects are to be verified, optical evaluation methods are typically more practical[2,3]. A valuable metric for a PUF is the number of unique challenge-response pairs (CRPs) a potential device can provide. Increasing the number of CRPs supported by a device has a variety of benefits, including the ability to concatenate the CRPs to increase the total response length. This increase in the response length enhances the level of security of a single exchange. Other benefits include reducing the error rate by introducing sacrificial bits for post-processing, or the ability to separate responses to reduce vulnerability to replay attacks[4,5].

Naturally, the number of useful extractable bits from a given device is directly related to the range of potential analogue values that a measurement can take before digitisation. Therefore, to increase the number of available CRPs, either the resolution of the measurement or the dynamic range of the measured parameter of the PUF can be increased. The former often comes with additional requirements, and so it is this second avenue of development for a quantum dot PUF (QD-PUF) that is presented in this paper.

The QD-PUF consists of colloidal quantum dots, distributed on a surface in a manner which is random and uncontrollable during the fabrication process[6]. When the sample is illuminated above the bandgap of the dots (by a laser or otherwise), they emit photoluminescence (PL), which can then be measured, digitised, and converted into a unique fingerprint whose uniqueness originates from the random spatial distribution of the QDs[7]. Typically, the smaller the type of particle to be deposited on a surface, the harder the corresponding PUF is to clone. This is due to the increase in precision needed when manipulating or emulating the individual particles; size and composition fluctuations also lead to greater variations in emission properties[8,9].

This paper seeks to probe the efficacy of adding gold plasmonic nanoparticles (Au NPs), in conjunction with a reflective sample back-coating, in the form of a thin layer of aluminium (Al), to improve the dynamic range of emission intensities of a random distribution of QDs. In this case, heavy-metal free InP/ZnS core/shell QDs are examined due to their low toxicity, low environmental cost, high adsorption coefficient and desirable emission wavelength for use with silicon-based sensors[10]. This makes them an attractive candidate for practical deployment, as part of an optical authentication device. Au NPs were transferred from solution to the substrate via a very simple dropcasting method, increasing the feasibility of including nanoparticle treatment in the fabrication process. Previous studies on the deposition of colloidal metal nanocrystals on a variety of substrates have mainly focused on electrostatic deposition, changing the chemical treatment of the substrate, spray deposition and Langmuir–Blodgett technique[11,12]. These methods are generally limited with non-uniform particle densities, changing functional groups or surface charge that need multiple preparation steps, or can only cover small areas.