

Quantum dot emitters integrated with smart peptides

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Semiconductor nanocrystal quantum dots find a wide range of device applications such as solar cells [1], white LEDs [2], modulators [3] as well as life science applications such as labeling [4] and imaging [5]. Especially in device applications, specific and targeted self-assembly of quantum dot emitters is of critical importance in terms of the device efficiency and the ability to design devices at molecular scales.

While other assembly methods lack specific interactions between quantum dots and surface, using genetically engineered peptides for inorganics (GEPs) as quantum dot immobilizers offers specific interactions with high affinity between the targeted surface and GEPI integrated quantum dots. These smart peptide linkers can be designed by using innovative bioinformatics knowledge based methods [6] to specifically and selectively bind to various inorganic surfaces such as SiO₂, Au, Ag, Pd, and Pt [7-9].

In our study, we investigated the quantum dots integrated with silica binding peptides on silica surface for three different assembly approaches. We used biotinylated silica binding peptides (SBP-bio) as smart linkers to immobilize quantum dots and streptavidin functionalized CdSe/ZnS core-shell quantum dots (SA-QD) as light emitters.

In the first assembly approach, SA-QDs were immobilized on silica surface in the absence of peptide linkers. These negative control groups were used to understand the effect of using SBP-bio as a quantum dot immobilizer. The second approach was based on sequential assembly of first SBP-bio and then SA-QDs on the silica surface as a layered structure. Finally, in the nanohybrid assembly technique, quantum dots were decorated with silica binding peptides before immobilization on the silica surface. Both the sequential and nanohybrid assembly methods were based on streptavidin-biotin interaction between SBP-bio and SA-QD. All the three assembly approaches were examined with surface plasmon resonance (SPR) spectroscopy, quartz crystal microbalance (QCM), and fluorescence microscopy (FM) techniques.

From the SPR experiments, we observed increase in the adsorption equilibrium constant when SBP-bio was used as a quantum dot immobilizer as shown in Table 1. In the sequential assembly approach, 3.4 folds enhancement in the binding affinity of quantum dots was achieved compared to the negative control group prepared in the deficiency of the peptide linkers. On the other hand, 82.5 folds increase in the binding affinity on silica surface was obtained with the nanohybrid approach compared to the negative control group.

By analyzing SPR results using single Langmuir adsorption model, we investigated the surface coverage of quantum dots on silica surface in these three different assembly approaches. Similar to the binding constant results, using smart peptide linkers improved the quantum dot surface coverage. The best surface coverage was attained with nanohybrid approach as shown in Figure 1.

The change in the dissipation of the quantum dot film on silica surface was monitored with QCM as presented in Figure 2. The QCM results revealed that the change in the dissipation of quantum dots is minimum in the negative control group and maximum in the nanohybrid assembly approach. The highest change in resonance frequency in the nanohybrid approach shows that maximum amount of quantum dots was adsorbed with this method on the silica surface compared to the other approaches.

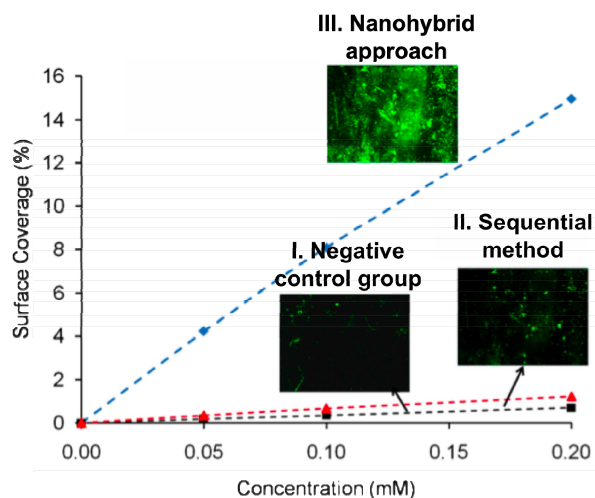


Figure 1. The surface coverage of green emitting quantum dots versus concentration of these quantum dots is given with the corresponding fluorescence microscopy images in three assembly techniques: Assembly of SA-QDs (I) in the deficiency of SBP-bio, (II) after immobilization of SBP-bio on silica surface, and (III) with decoration of SBP-bio before immobilization on the surface.

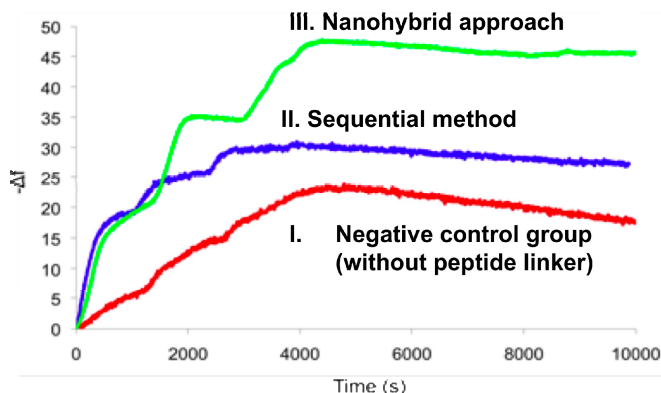


Figure 2. Time-dependent changes in the resonance frequency (note that it is negative) during QCM analysis are given in three assembly methods: (I) negative control group (without using SBP-bio as quantum dot immobilizer), (II) sequential assembly of quantum dots on top of SBP-bio layer, and (III) nanohybrid assembly in which quantum dots are decorated with SBP-bio before assembly on the surface.

	I. Negative control	II. Sequential method	III. Nanohybrid approach
$K_D (\mu\text{M})$	2.46×10^4	8.4×10^4	2.03×10^6

Table 1. The binding constants of quantum dots on silica surface for three different cases are given.

To sum up, we exhibited enhanced binding and high surface coverage of quantum dots on silica surface by decoration with smart peptides by analyzing their binding kinetics. Comprehending fundamentals of adsorption behavior of quantum dots provides us with the ability to construct more complex assemblies of quantum dots and other nanostructures resulting with innovative molecular scale hybrid devices.

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