Nanohybrids composed of quantum dots and enzyme as photocatalysts induced by radiation

Changhyun Roh

Division of Biotechnology, Advanced Radiation Technology Institute (ARTI),
Korea Atomic Energy Research Institute (KAERI), Republic of Korea
E-mail: chroh@kaeri.re.kr (Changhyun Roh, Ph.D.), TEL: +82-63-570-3133, FAX: +82-63-570-3139

Abstract

Semiconductor nanomaterials, such as quantum dots (Qdots), quantum rods (QRs), and nanotubes, have potential in a wide variety of fields ranging from nanoelectronics and nanophotonics to the broad area of nanosensing and bioimaging. Currently, nanotechnology and biotechnology are being joined to develop novel materials and devices, leading to the establishment of the new field of nanobiotechnology. In this study, we elucidate on a photoactivated organic transformation catalyzed by hybrid devices composed of semiconductor nanoparticles and the enzyme cytochrome P450. Cytochrome P450 belongs to a broad class of monooxygenase enzymes which are well known to catalyze a range of stereospecific and regioselective oxygen-insertion reactions into organic compounds. In general, the ionizing radiation-induced triggering of enzyme activity confers explicit advantages over chemical initiation with respect to the control of enzymatic reactions. Moreover, the P450/CdS nanohybrids should also enable convenient recycling of the catalyst in organic transformations. In addition to the investigation of other semiconductor Qdots for improving the catalytic activity of such nanohybrids, which is currently under way, we are also aiming toward applications as photocatalysts in synthetic organic chemistry and as photosensitizers for intracellular reactions.

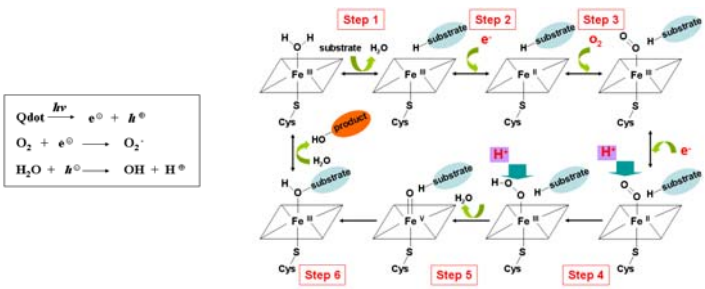
Keywords **Nanostrucutures, Photochemistry, Quantum dots, Radicals, radiation**

Backgrounds

Potential catalytic mechanism of P450-CdS photocatalysis

In general the catalytic cycle of cytochrome P450 enzymes, involves substrate binding, reduction of the ferric heme (FeIII) to the ferrous state (FeII) by electron transfer from the heme iron-center, binding of molecular oxygen to the ferrous iron, and transfer of a second electron to the resulting ferrous dioxy complex to form a ferric peroxy anion. The ferric peroxy anion is then protonated, giving rise to a ferric hydroperoxy complex.

Heterolysis of the oxygen-oxygen bond in this intermediate, results in elimination of a molecule of water and formation of a ferryl species (FeIV=O), which is thought to be responsible for most of the oxidations catalyzed by the enzyme. A possible alternative mechanism to circumvent the stepwise activation of molecular oxygen requires H2O2 or organic peroxides as the co-substrate, which can "shunt" the oxidation mechanism. Hence, activated oxygen is crucial for the generation of ferryl species, which is responsible for the various oxidation reactions initiated by P450.



Results & Discussion

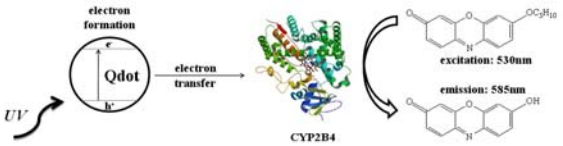


Figure 1 7-Pentoxyresorufin is dealkylated by cytochrome P450 (CYP2B4)

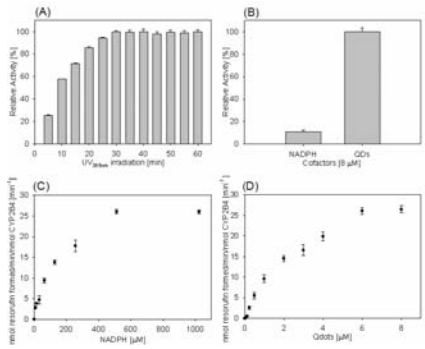


Figure 2 The CYP2B4 reaction mediated by UV-irradiation-induced Qdots. (A) Effect of the irradiation time of Qdots; CYP2B4 showed no activity when the UV-irradiation time of Qdots was zero. (B) Comparison of the efficiencies of NADPH and Qdots-mediation on CYP2B4 activity. The concentration of cofactors was 8 μM. (C) CYP2B4 activity with NADPH-dependent electron donor. (D) CYP2B4 activity with Qdots-dependent electron donor. The data are the mean values of at least three independent measurements.

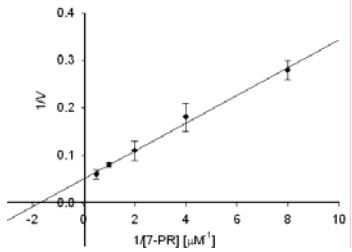


Figure 3 Kinetics of substrate quantification in enzyme reactions with Qdots as the electron donor. The y-axis is expressed as the reciprocal of the rates (nmol product/min/nmol P450). The data are the mean values of at least three independent measurements.

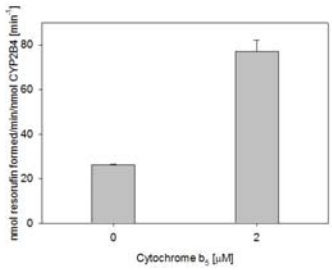


Figure 4 The effect of electron donor protein on CYP2B4 activity under the mediation of photoactivated Qdots. The activity was measured in the supporting system containing 2 μM cytb5 enzyme. The data are the mean values of at least three independent measurements.

Conclusions

In this study, we elucidated the effect of electron formation which was effectively triggered by UV-induced Qdots. The Qdots depend on the local time interval of UV irradiation for electron donors that can be considered for developing qualitative and quantitative assays of the enzymatic activity of cytochrome P450. Importantly, the UV-irradiation-induced nature of electron formation from Qdots offers an attractive feature. The approach for utilizing Qdots in sensing applications would be to create an "on/off" control system for applications that employ Qdots as promising donors. This on/off control system under the regulation of UV irradiation is sure to open up new developments and opportunities for using the novel Qdots technique. In addition, the significant potential of photocatalysts in applications such as cytochrome P450 reaction assays will motivate researchers to find methods to develop newer portable devices. To the best of our knowledge, this is the first report on quantification analysis of P450 reactions by using a Qdots-based strategy. Therefore, the P450-Qdots approach can be expected to be a significant method for characterization as well as quantification analysis of reactions amenable to Qdots-induced electron formation and transfer.

Acknowledgements

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