

# An Effective Dialysis Method for Surface Functionalization of Nanoparticles in Liquid Phase - Sample: Porphyrine derivatives @ ZnO-Nanorods

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## ABSTRACT

In order to optimize electron transfer and optoelectronic properties in nanoparticulate thin films for electronics we show the surface functionalization of ZnO nanorods by exchanging the stabilizing 2-[2-(2-Methoxyethoxy)ethoxy]acetic acid at the ZnO surface with redoxactive organic molecules. Surface functionalization is undertaken by an efficient dialysis method. Emission- and absorption-spectroscopy indicate an effective electronic interaction between the ZnO nanorods and the porphyrine derivatives. In addition, we discuss on the binding mechanism and the ligand exchange kinetics of the porphyrine molecules. Our experiments suggest a better and faster binding to the ZnO nanorod surface for porphyrine A than for porphyrine B. This can be explained by steric effects. Moreover we claim a fourfold anchored binding for porphyrine A and we shed light on entropic effects during ligand exchange.

**Keywords:** provide up to five comma separated, keywords for indexing, don't capitalize

## 1 INTRODUCTION

In past we demonstrated control of the electronic properties of ZnO nanorods by means of surface functionalization with a variety of C<sub>60</sub> phosphonic acid derivatives [1]. We showed that the C<sub>60</sub> molecule acts as an acceptor system for electrons and becomes a radical anion. Since porphyrine is known to be an efficient donor system for electrons and to advance the understanding on the binding mechanism and the adsorption behavior of molecules on nanoparticles, in our actual work we use two porphyrine derivative molecules that differ in the number of carboxylic acid anchor groups to functionalize ZnO nanorods with novel porphyrine systems.

## 2 EXPERIMENTAL SECTION

For the efficient and fast method for surface functionalizing semiconducting metal oxide nanoparticles in liquid phase

we used a specific dialysis route with a molecular weight cut off membrane 100-500 Da. The dialysis process leads to a successful surface functionalization of nanoparticles with complex organic molecules. In our case we took ZnO nanorods from a precipitation route described in [3]. After ZnO synthesis the rods were surface modified by stabilizing 2-[2-(2-Methoxyethoxy)ethoxy]acetic acid (TODS). Syntheses of the porphyrines will be reported soon. Porphyrine A features 4 carboxylate groups per 4 arms (linked to the porphyrin ring) whereas porphyrine B offers 12 carboxylates per 4 arms (see Fig 1).

## 3 RESULTS AND DISCUSSION

Faster and more homogenous binding we detect from the porphyrine A at ZnO nanorods system. We suppose a displacement of four TODS molecules by one porphyrine A molecule. So the driving force for the molecular exchange would be entropic nature. Porphyrine B shows a less homogenous binding to the ZnO surface and slower binding kinetics. The latter results we obtain from HRTEM and time resolved spectroscopy studies (absorption and emission). Porphyrine B offers 12 anchor groups and a more complex structure compared to porphyrine A. Therefore we assume that porphyrine B exhibits an intrinsic steric hindrance because of the additional generation within its structure. High resolution transmission electron (HRTEM) images verify the successful bonding of the molecules to the surface of the ZnO nanorods (see Fig 1)

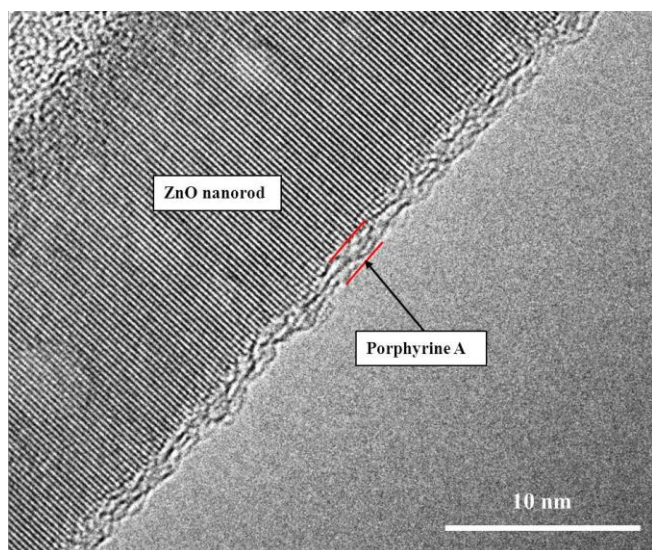


Figure 1: HRTEM image of a surface functionalized ZnO nanorod. Distinct amorphous coating of the nanocrystal can be derived from that pattern.

The thickness of the amorphous coating in Figure 1 (~1.5 nm) gives a strong hint on the binding geometry of the porphyrine A: all 4 arms bind to the surface. The latter result is derived from theoretical calculations on the binding geometry face to face / parallel [4].

Absorption and emission spectra from both systems porphyrin A at ZnO and porphyrin B at ZnO reveal an efficient electronic coupling between the delocalized pi electron system of porphyrine and the semiconducting ZnO. Q-bands and Soret-bands from the porphyrine system are changing in consequence of the surface functionalizing of the ZnO. Figure 2 depicts absorption and emission spectra from the surface functionalized ZnO nanorods.

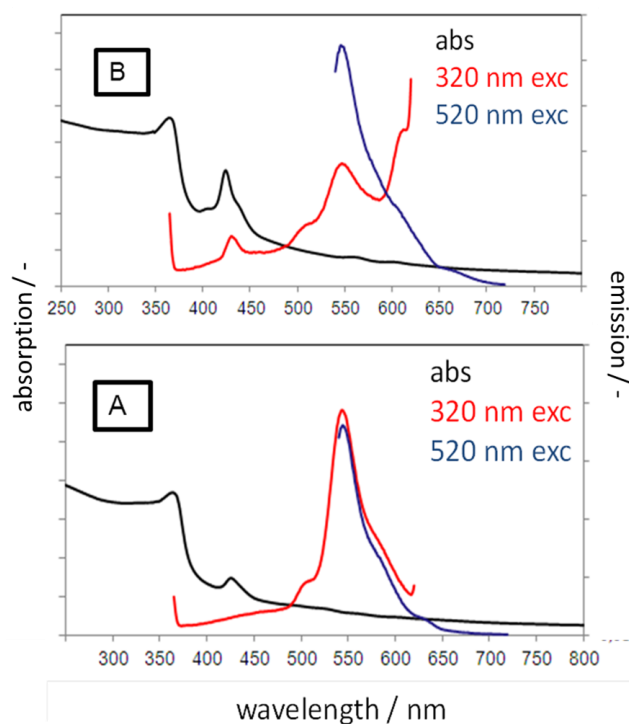


Figure 2: absorption and emission spectra of the surface functionalized ZnO nanorods. Porphyrine B reveals 12 carbocylate anchor groups and A reveals 4 carboxylate anchor groups. Blue and red lines showing the emission spectra from 320 nm and 520 nm excitation respectively.

## 4 CONCLUSIONS

In this work we specify and characterize an efficient method for surface functionalizing nanoparticles. As a sample we bind novel porphyrine molecules to the surface of ZnO nanorods. The successful binding is evidenced by microscopy and spectroscopy techniques.

## REFERENCES

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