Polydopamine coated CdSe@CdS dot-in-rod heterostructures with Rhodium-based catalysts for stable photocatalytic NAD+ reduction

Marcel Boecker,[a] Mathias Micheel,[b] Alexander K. Mengele,[c] Christof Neumann,[d] Tilmann Herberger,[a] Tommaso Marchesi D'Alvise,[a] Bei Liu,[b,d] Andreas Undisz,[f,g] Sven Rau,[c] Andrey Turchanin,[d,e] Christopher V. Synatschke,[a] Maria Wächtler *[b,d,e] and Tanja Weil*[a]

[a]Department for Synthesis of Macromolecules, Max Planck Institute for Polymer Research, 55128 Mainz, Germany

[b]Department of Functional Interfaces, Leibniz Institute of Photonic Technology, 07745 Jena, Germany

[c]Institute of Inorganic Chemistry I, Ulm University, 89081 Ulm, Germany

[d]Institute of Physical Chemistry, Friedrich Schiller University Jena, 07743 Jena, Germany

[e]Abbe Center of Photonics (ACP), Albert-Einstein-Straße 6, 07745 Jena, Germany

[f]Institute of Materials Science and Engineering, Chemnitz University of Technology, 09125 Chemnitz, Germany

[g]Otto Schott Institute of Materials Research, Friedrich Schiller University Jena, 07743 Jena,

Germany

Abstract

We report on a photocatalytic system consisting of CdSe@CdS nanorods, coated with a polydopamine (PDA) shell functionalized with molecular rhodium catalysts. The PDA shell was implemented to enhance photostability of the photosensitizer, to improve charge carrier separation and to offer multiple options for stable covalent functionalization, allowing for spatial proximity and efficient shuttling of charges between sensitizer and reaction center. The activity of the photocatalytic system was demonstrated by light-driven reduction of nicotinamide adenine dinucleotide (NAD$^+$) to its reduced form NADH. This work shows that PDA coated nanostructures present an attractive platform for covalent attachment of reduction and oxidation reaction centers for photocatalytic applications.

Maintext

In recent decades, the field of photocatalysis has greatly expanded to meet increasing energy demands.[1] Inspired by nature's photosynthesis, photocatalysis uses photons as energy source to

fuel chemical reactions and therefore, making use of the ultimate renewable energy source, the sun.[2] These photocatalytic reactions transform chemicals into more useful, high-value compounds or create molecules with higher energy density for energy storage.[1, 2]

Semiconductor nanostructures based on cadmium chalcogenides have been explored as efficient photosensitizers for performing a range of photocatalytic reactions.[3-6] In particular, CdSe@CdS dot-in-rod nanostructures have shown high activity, for example, hydrogen generation in aqueous solution when connected to reaction centers such as platinum[7] or nickel[8] nanoparticles, redox-active enzymes[9] or transition metal complexes[10, 11]. In these structures, charge-separation is very efficient as the photo-generated hole localizes in the CdSe core, and the electron is transferred to the catalytic center, supporting charge accumulation at the reaction center driving multi-electron reactions.[7] Unfortunately, these photosensitizers easily undergo photooxidation if the holes remaining in the semiconductor nanostructure are not efficiently quenched, which limits their longer term usage.[12] Therefore, the addition of sacrificial electron donors is necessary to stabilize catalytic systems. The choice of the quencher determines the rate and efficiency of hole quenching and thus preventing recombination, whereby catalytic efficiency and long term stability are increased.[13]

The highly cross-linked melanin-like biopolymer polydopamine (PDA)[14] has been applied in several photocatalytic systems to improve their efficiency. It forms universal multifunctional coatings through a simple autoxidation process of dopamine, which forms a highly adhesive polycatechol-based polymer.[15] Moreover, PDA films reveal broad band absorption, electron donating properties[16-19] and hence can act as protective layer reducing photooxidation,[18] but also support electron transport towards, *e.g.*, a reaction centers, similar to natural photosystem II, either mediated via electron accepting groups[20] or in the case of very thin layers direct tunneling.[18]

Previously, CdS/PDA/TiO$_2$ core/shell nanoparticles have been achieved, where the PDA layer improved photocurrent and photocatalytic performance due to enhanced light absorption and charge carrier mobility.[21] Furthermore, PDA coatings increased the photostability of CdS semiconductors, which facilitated the transfer of electrons to quench holes and prevent oxidation by forming a strong coordination bond.[21, 22] Reported PDA coatings for photocatalytic systems make use of the interaction of PDA and semiconductor or metal nanoparticles.[23] Additionally, the presence of multiple functional groups in PDA also allows for straight-forward surface functionalization, *e.g.*, by reacting the quinones of PDA with amines in Michael addition or Schiff base reactions[24, 25] and therefore offers the opportunity to functionalize PDA also with molecular catalysts via various functional groups. This stands in contrast to the functionalization of bare CdSe@Cds nanorods, which is only possible with limited anchoring groups, *e.g.*, thiols or dithiocarbamates.[10, 11]

Motivated by these promising photocatalysis results of nanorods and PDA, we designed a photocatalytic system consisting of CdSe@CdS nanorods as a photosensitizer coated by a highly cross-linked, protective and functionalizable PDA biopolymer layer and equipped the system with a rhodium-based molecular catalyst [(ipphCOOH)Rh(Cp*)(Cl)]Cl (Cp* is pentamethylcyclopentadienyl and ipphCOOH is a functionalized 1*H*-imidazo[4,5-*f*][1,10]phenanthroline).

The newly established photocatalytic system was characterized for the photocatalytic reduction of nicotinamide adenine dinucleotide (oxidized form, NAD$^+$) to NADH.[26] nicotinamide adenine dinucleotide is a key redox compound in all living cells responsible for energy transduction, genomic integrity, life-span extension, and neuromodulation[27] and it plays a key role in enzymatic reductions. Given the high cost, stoichiometric usage, and physical instability of NADH, there is

substantial interest in NADH regeneration.[28] Recently, several systems comprising a Rh-based catalyst have been proposed for the purposes of light-driven reduction of NAD$^+$ in combination with either molecular chromophores in a homogenous catalytic approach[26, 29] or quantum dots as light-absorber.[30, 31]

By combining the photosensitizer and the catalytic reaction center in close contact in a nanoparticlate assembly by linking them to the PDA matrix, the system presented herein serves as a suspended heterogeneous catalytic system. In contrast to the many reported homogeneous systems for photocatalytic reduction of NAD$^+$, our approach offers the advantage to recover the photoactive nanomaterial from the reaction solution by centrifugation. In addition, different types of catalyst could be attached by simply functionalizing the PDA shell.

The CdSe@CdS nanorods (NR, length = 43.8 ± 5.8 nm, width = 4.8 ± 0.4 nm, Figure S7) were synthesized by the seeded growth approach[32] followed by transfer into aqueous medium *via* ligand exchange with mercaptoundecanoic acid (for details see SI).[33] For the synthesis of the molecular catalyst, 1,10-phenanthroline-5,6-diones were first prepared according to the literature[34] and then reacted with 4-formyl-benzoic acid and ammonium acetate to afford the carboxylic acid-functionalized phenanthroline ligand 4-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)-benzoic acid (ipphCOOH, for details see SI). The molecular catalyst was generated by ligand exchange mixing ipphCOOH with [Rh(Cp*)Cl$_2$]$_2$ (for details see SI). Subsequently, the multicomponent photocatalytic system was generated in a two-step procedure as shown in Scheme 1. First, the prepared nanorods were coated with PDA by autoxidation of dopamine in alkaline Tris-buffer (0.1 M, pH = 8.5) for 24 h. Then, the PDA coated nanorods (cNR) were purified by centrifuge filtration (cut off 100 kDa) and redispersed in MilliQ water, which was repeated three times.
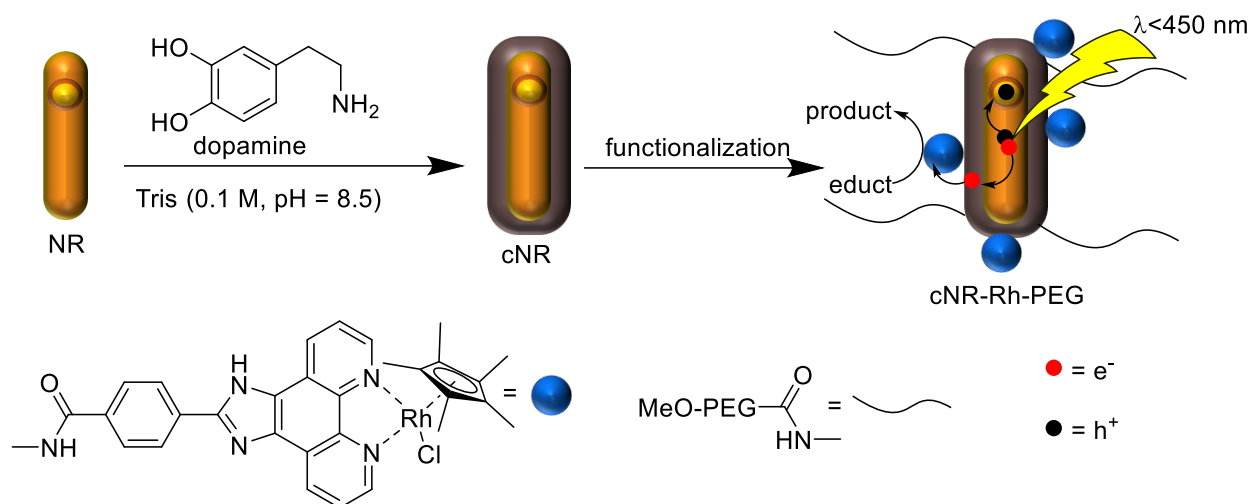
Scheme 1: Generation of the photocatalytic system based on CdSe@CdS nanorods (NR) coated by PDA yielding cNR, followed by functionalization with Rh-catalysts and PEG (5 kDa) yielding cNR-Rh-PEG.

A very thin PDA coating of 1 to 2 nm was generated covering the NRs as imaged in transmission electron microscopy (TEM, Figure 1B) and could therefore also allow tunneling of the electron to the catalyst.[18] This surface coating strongly affected the physico-chemical properties of the cNRs. Compared to the uncoated NRs, which mostly absorb below 460 nm (Figure 1C), cNRs revealed an extended absorbance over the entire visible spectrum. The characteristic reduction abilities of the new PDA layer on the cNRs for $HAuCl_4$ to elemental gold nanoparticles based on a published procedure[35] was tested and the formation of gold nanoparticles was only observed on cNRs, but not on the untreated CdSe@CdS NRs (Figure S8).

Moreover, the photoluminescence (PL) quantum yield (QY) of cNR indicates a very significant quenching effect of the QY induced by the PDA layer. The PL of NRs (QY of 0.14) was reduced after coating about 200-fold, with an estimated QY in the order of 0.001 (Figure 1D). This indicates

a strong interaction between photoexcited nanorods and the PDA shell and charge transfer processes between the PDA matrix and nanorods efficiently competing with radiative exciton recombination.
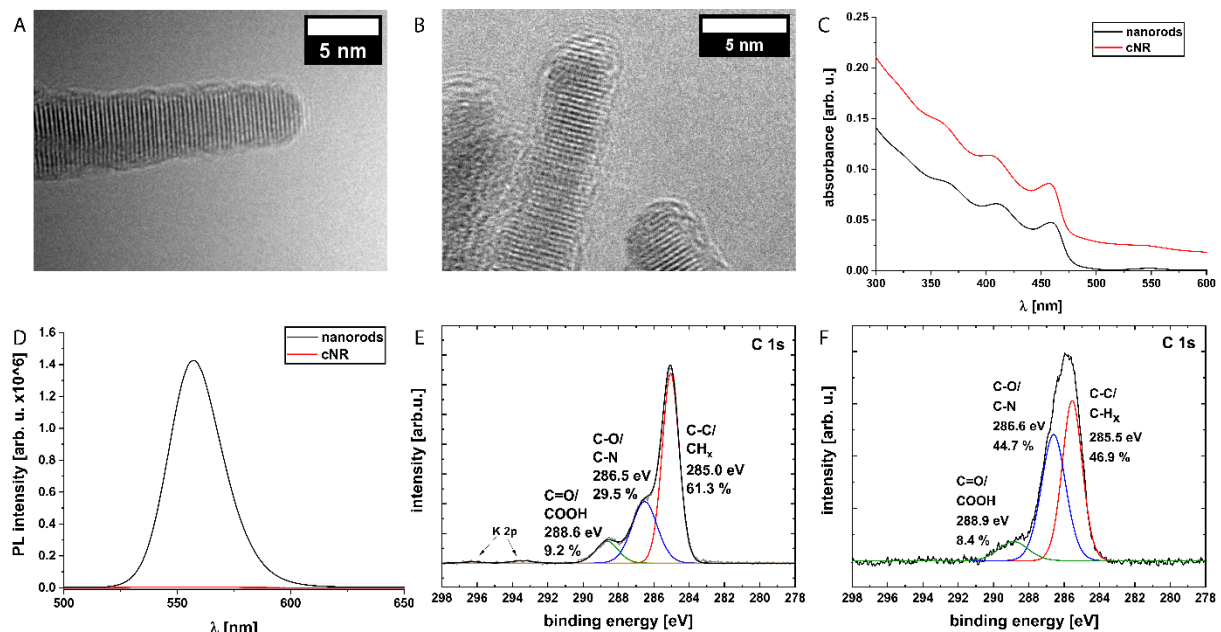

Figure 1: TEM images of the pure nanorods (A) and cNR (B), absorption spectrum of the bare nanorods and cNR functionalized with PEG (C), photoluminescence spectra ($\lambda_{ex} = 450$ nm) of bare and coated nanorods (grafted with PEG for better colloidal stability) in water (D), High-resolution C 1s XP spectrum of the cNR (E) and the cNR-Rh-PEG (F).

Next, the photocatalytic system was assembled by attaching several Rh-catalysts as well as stabilizing polyethylene glycol (PEG, MW: 5 kDa) chains in a one pot reaction by the formation of amide bonds between PDA and the carboxylic acid group of the catalyst or the PEG chains. Grafting of PEG chains onto the cNR was essential to achieve sufficient colloidal stability in buffer solutions and to prevent precipitation (see Figure S10). In the following, the PDA coated nanorods functionalized with PEG and Rh-catalysts is referred as cNR-Rh-PEG.

The assembled cNR-Rh-PEG was then characterized by energy-dispersive X-ray spectroscopy (EDX, Figure S11), which shows signals of the NR elements cadmium (3.1 keV), selenium (1.4 keV) and sulfur (2.3 keV). Additionally, signals for oxygen (0.5 keV) were assigned to the PDA coating, as well as carbon (0.3 keV) and nitrogen (0.4 keV) were found, which are present in both the PDA coating and the ligand of the catalyst. The Rh signal at 2.7 keV indicates the successful functionalization of the cNR with the Rh-catalyst.

In addition, X-ray photoelectron spectroscopy (XPS) measurements were carried out to validate the EDX results and to assess whether the catalyst and PDA matrix were covalently conjugated. The XP survey and high-resolution Rh 3d spectra (Figure S12) of the cNR-Rh-PEG reveal the rhodium signal at 310.5 eV, indicating the successful covalent surface functionalization with the Rh-catalyst. Furthermore, in the C 1s spectrum (Figure 1D and E), the shoulder at 286.6 eV was assigned to C-N/C-O bonds, which appears more intense for the cNR-Rh-PEG compared to cNR owing to the addition of the PEG chains and the Rh-catalyst.

By utilizing a commonly applied thermal NAD^+ reduction test,[36] we further evaluated whether the successful immobilization procedure of [(ipphCOOH)Rh(Cp*)Cl]Cl afforded a catalytically active cNR-Rh-PEG system. Whereas for cNR-Rh-PEG formate-driven NADH-formation is clearly observed, no NAD^+-reduction was observed for the Rh-free system (see Figure S13). This clearly indicated, that i) the catalytic activity of the Rh-complex is preserved following material integration and ii) that the Rh-center is spatially accessible by NAD^+ as well as $NaHCO_2$.

As proof of principle for the light-driven activity of the system, the photocatalytic reduction of NAD^+ was tested as well. Therefore, 10 µg/mL of the cNR-Rh-PEG and 250 µM NAD^+ were dissolved in demineralized water and irradiated with blue light (466 nm, 45-50 mW/cm^2) at room temperature and under argon atmosphere. At this excitation wavelength, both the CdS rod and the

PDA are photoexcited. The photocatalytic reduction of NAD$^+$ to NADH was monitored by following the emission peak of NADH at 462 nm in the emission spectrum (λ_{exc} = 340 nm). The NADH concentration produced in the reaction medium was determined by calibration and the efficiency of our photocatalytic system was analyzed by converting the produced NADH quantity per quantity of the cNR-Rh-PEG (Figure 2B, for calculation see SI).
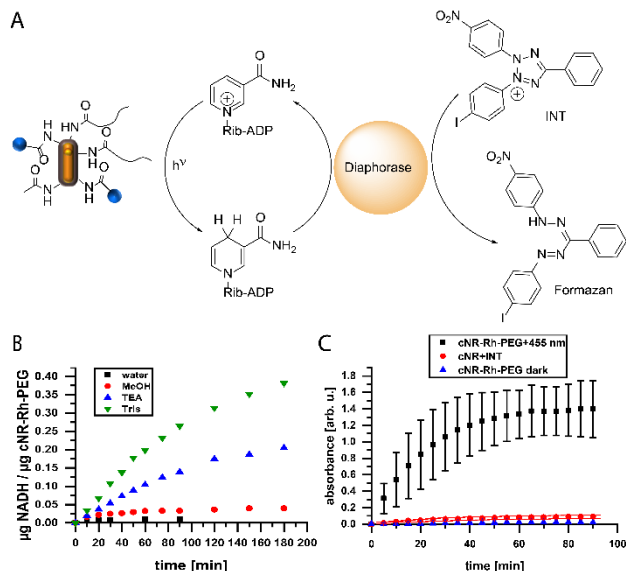

Figure 2: (A) Reaction scheme of the photocatalytic reduction of NAD$^+$ with the coupled reduction of 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium (INT) in the presence of diaphorase enzyme. (B) Produced mass of NADH per mass of the photocatalytic system (cNR-Rh-PEG) over time without or with MeOH, TEA or Tris as sacrificial agents determined from emission spectroscopy measurements. (C) Time evolution of the absorbance at 492 nm during the enzyme assay under irradiation and in the dark and for cNR with INT under irradiation.

Irradiation of the cNR-Rh-PEG in the presence of NAD$^+$ afforded a minute increase in the emission detected at 462 nm, indicating the formation of NADH. To improve the photocatalyic efficiency, three different sacrificial agents were used (methanol (MeOH), triethylamine (TEA)

and 2-amino-2-(hydroxymethyl)propan-1,3-diol (Tris)). A MeOH:water mixture (1:1 vol), water containing both TEA (0.12 M) and sodium phosphate (NaH_2PO_4, 0.1 M), or Tris-HCl buffer (25 mM, pH= 7.5) were used as reaction media. In case of TEA as sacrificial agent the addition of sodium phosphate was necessary to keep the pH acidic enough to guarantee stability of the cofactors. The addition of MeOH leads to a slight increase of NADH emission, in contrast, a mixture of non-functionalized cNR and NAD^+ did not produce any NADH under identical conditions (Figure S14). The addition of TEA and Tris drastically enhanced NADH production with cNR-Rh-PEG, in accordance with TEA being a well-known sacrificial reducing agent.[26] Surprisingly, with Tris as electron donor, 0.26 µg NADH was produced per µg of the cNR-Rh-PEG, which is about 26 times higher than without any sacrificial agent and still two times higher than using TEA as sacrificial agent. The fact that Tris outperforms all other tested sacrificial agents could be related to an increased interaction of Tris with the PDA shell based on the findings of strong interactions of Tris with PDA during PDA synthesis.[37] Consequently, the amine and hydroxyl groups in Tris and the surface groups of PDA could in principle interact resulting in co-assembly and faster hole quenching, which is known to be the rate limiting step in CdS-based photocatalysis.[13] The corresponding signal of the time-dependent NADH production in the presence of Tris showed a linear increase for the first hour of irradiation and then gradually slowed down. This process could be due to deactivation of the catalyst or degradation and aggregation of the CdSe@CdS nanorods upon prolonged irradiation.

Next, we evaluated if the produced NADH could be used as a high-value chemical in further downstream chemical conversion. In biocatalysis, which is of emerging interest in industry as the usage of enzymes facilitates low-energy, sustainable methods of producing high-value chemicals and pharmaceuticals potentially at lower costs, NADH is an important cofactor for these enzymatic

reactions.[28] Furthermore, the enzymatic reoxidation of NAD$^+$ can lead to higher activity of the light-sensitive system as the reoxidation of NADH by its role as electron donor can be avoided.[26]

Therefore, the optimized cNR-Rh-PEG, was used for the regeneration of NADH that serves as cofactor in a downstream chemical transformation reaction with the enzyme diaphorase as biocatalyst. Diaphorases transfer a hydride from NADH to another substrate molecule, such as 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium (INT). The transformation of INT as the substrate to the respective formazan can be monitored by absorption spectroscopy at 492 nm, as confirmed in a model reaction with added NADH (Figure S16). In a one-pot reaction, the cNR-Rh-PEG successfully reduced NAD$^+$ to NADH, which subsequently transfers the hydride to INT in the presence of diaphorase. All reactions were performed in a quartz cuvette under nitrogen atmosphere and irradiation with a blue LED (455 nm, 45 mW/cm^2).

As shown in Figure 2C, a continuous increase in the absorption spectrum at 492 nm was observed when the reaction solution was irradiated with blue light (455 nm), but not in the dark. As control, cNRs without the catalyst were combined with INT in Tris-HCl and irradiated under the same reaction conditions used for the enzyme assay (for details see SI). Under these conditions, no absorbance increase at 492 nm was observed (Figure 2C) indicating the importance of the entire photocatalytic system for the successful downstream reaction.

In summary, we report for the first time on a system consisting of inorganic semiconductor nanostructured photosensitizer with covalently attached molecular catalysts for NADH production. We designed a photocatalytic system consisting of CdSe@CdS nanorods coated with PDA and functionalized with Rh-catalysts was prepared and characterized by applying state of the art surface characterization techniques. By applying a PDA shell, a molecular catalyst was successfully conjugated to the CdSe@CdS nanorods without the need of a thiol group, which is i)

usually required for such surface chemistry and ii) may potentially act as poison for *e.g.* the herein utilized Rh-catalyst.[38] The assembly of a suspendable heterogenous system was achieved merging all photocatalytic entities within one nanosystem. Efficient photocatalytic activity was confirmed by the light-driven reduction of NAD^+ to NADH and this product was then used in a downstream chemical transformation, namely the reduction of INT to the respective formazan by diaphorase with NADH as cofactor. A direct comparison of the performance of this nanosystem with literature-known systems is not easily possible as in most cases, the photosensitizer and catalyst is homogenously dissolved,[26, 29] leading to different reaction kinetics. Also in the few examples that exist for heterocatalytic systems,[30] the catalysts are not attached to the photosensitizer, but they remain molecularly dissolved, again resulting in important changes of the reaction kinetics compared to our system. It was not possible to calculate a turn over number (TON) for our system, due to the detection limit for quantifying the amount of attached catalyst.

In the herein designed system combining photosensitizers, a redox-active polymer matrix and molecular catalysts into a photocatalytic system capable of producing functional chemicals, the PDA coating of CdSe@CdS nanorods serves as an adhesive, functional layer with great prospects for integration in future photocatalytic systems as it allows straight-forward functionalization with different catalysts able to catalyze various reactions. In this way, one could envision attaching two catalyst each for one half reaction and therefore combining reduction and oxidation reaction centers within one system, which could afford photocatalytic systems functioning without the need of additional sacrificial agents.

ASSOCIATED CONTENT

Additional experimental details, materials, methods and characterization

AUTHOR INFORMATION

Corresponding Author

Tanja Weil – Department for Synthesis of Macromolecules, Max Planck Institute for polymer research, 55128 Mainz, Germany; Email: weil@mpip-mainz.mpg.de

Maria Wächtler – Department of Functional Interfaces, Leibniz Institute of photonic technology, 07745 Jena, Germany; Email: maria.waechtler@leibniz-ipht.de

Notes

The authors declare no competing financial interest.

ABBREVIATIONS

NAD$^+$, β-Nicotinamide adenine dinucleotide hydride , oxidized form; NADH, β-Nicotinamide

adenine dinucleotide hydride , reduced form; PDA, Polydopamine; NR, CdSe@CdS dot-in rod

nanostructures; cNR, polydopamine coated CdSe@CdS dot-in rod nanostructures; cNR-Rh-PEG,

polydopamine coated CdSe@CdS dot-in-rod nanostructures functionalized with Rh catalyst and

PEG; TEM, Transmission electron microscopy; PEG, polyethylene glycol; EDX, Energy-

dispersicve X-ray spectroscopy; XPS, X-ray photoelectron spectroscopy; TEA, triethylamine;

Tris, 2-Amino-2-(hydroxymethyl)propan-1,3-diol; INT, 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-

phenyl-2H-tetrazolium; PL, photoluminescence

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