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Colloidal 2D Semiconductor Nanocrystals: Towards Innovative Photonics

Colloidal two-dimensional (2D) semiconductor nanocrystals, so-called nanoplatelets (NPLs) are only a few atomic layers thick and exhibit highly interesting photophysics and optoelectronic properties, including bright photoluminescence, which can be tuned between UV-Vis- and technologically relevant infrared-/telecommunication wavelengths [1-5]. The typically robust ensemble emission makes colloidal 2D semiconductor nanocrystals perfect candidates for an integration into (optical) fibers and controlled light-redirection or light emitting applications with high color purity and even lasing.

Highly photoluminescent 2D semiconductor NPLs with a quantum yields of 75-95 % at UV-Vis wavelengths are often CdSe/CdS-based and typically require a safe encapsulation, ideally inside a certain matrix, for their application [6]. Preserving the optoelectronic properties of the NPLs in the solid-state together with their efficient incorporation in the matrix is a challenge, especially when trying to achieve high-quality thin films with a defined optical density and low surface roughness. We apply different approaches including photoluminescent polymer-

encapsulated inorganic-organic nanocomposite coatings of 2D CdSe/CdS NPLs in poly(diallyldimethylammonium chloride) (PDDA) and poly(ethylenimine) (PEI), which are prepared by sequential layer-by-layer (LbL) deposition (see Figure 1) [6]. The electrostatic interaction between the positively charged polyelectrolytes and aqueous phase-transferred NPLs with negatively charged surface ligands is used as a driving force to achieve self-assembled nanocomposite coatings with a well-controlled layer thickness and surface roughness. Increasing the repulsive forces between the NPLs by increasing the pH value of the dispersion leads to the formation of nanocomposites with all NPLs arranging flat on the substrate, while the surface roughness of the 165 nm (50 bilayers) thick coating decreases to $R_a = 14 \text{ nm}$. The photoluminescence properties of the nanocomposites are determined by the atomic layer thickness of the NPLs and the 11-mercaptoundecanoic acid ligand used for their phase transfer. Both, the full width at half-maximum (20.5 nm) and the position (548 nm) of the nanocomposite photoluminescence are retained in comparison to the colloidal CdSe/CdS NPLs in aqueous dispersion, while the measured

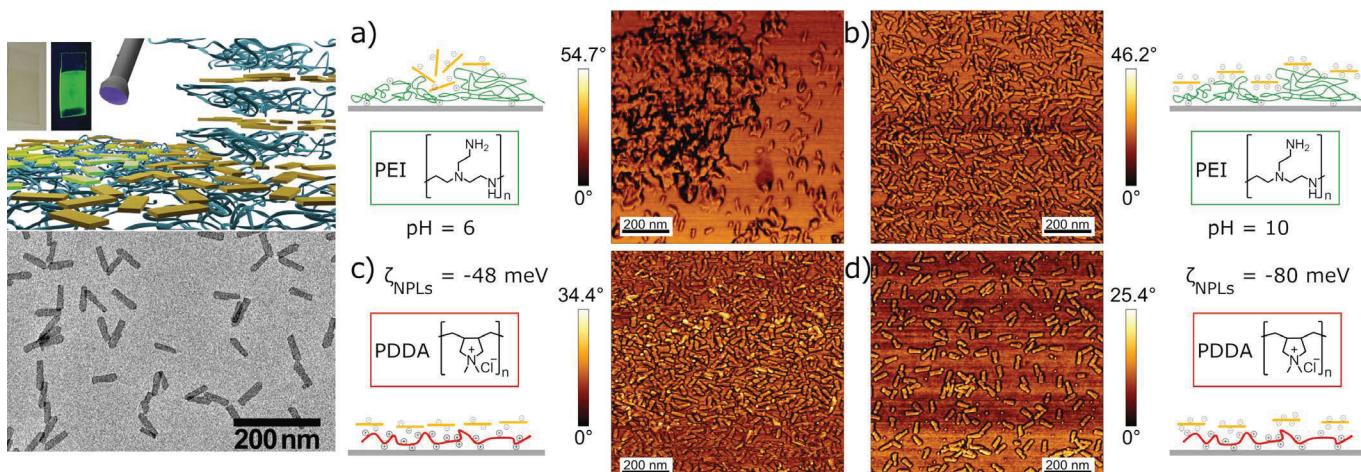


Fig. 1: Upper left: Photograph and scheme of the polyelectrolyte and NPL smooth thin films, lower left: Transmission electron micrograph of CdSe/CdS NPLs, right: The polyelectrolyte and NPL pH value influence on the LbL coating process with AFM phase images of a single bilayer taken in an area of $1 \times 1 \mu\text{m}^2$ and schemes of the formed surface coating. The combination of (a, b) PEI with NPLs at pH values 6 and 10, respectively. (c, d) PDDA with NPLs at pH values 6 and 10, respectively. By controlling the pH value of the NPL dispersion, we can control the number of charges per NPL, as shown by the ζ -potential values. The AFM phase image correlates with the softness and hardness of the measured materials. A sub-monolayer thin film thickness as well as films with a thickness of up to $\sim 150 \text{ nm}$ are accessible.

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photoluminescence quantum yield of 5 % is competitive to state-of-the-art nanomaterial coatings. This approach yields stable polymer-encapsulated CdSe/CdS NPLs in smooth coatings with controllable film thickness, rendering the LbL deposition technique a powerful tool for the fabrication of solid-state photoluminescent nanocomposites [6].

Another efficient encapsulation technique for CdSe/CdS-based colloidal 2D NPL emitters is stable jet electrospinning (SJES). SJES is a special form of optical fiber generation that prevents chaotic fiber whipping typical for conventional electrospinning procedures. Incorporation of photoluminescent semiconductor NPLs in these fibers has high potential in optical data transmission, optological circuits, fiber lasers and solar light concentrators. This is because CdSe/CdS NPLs not only show bright photoluminescence, they also exhibit strongly directed emission from their surface plane due to various in-plane transition dipole moments. Up to now, potential orientation control of NPLs in SJES was entirely unknown as electric fields and various mechanical forces contribute in a complex manner simultaneously. We report on the observation of counter-intuitive, yet very beneficial orientation of rectangular CdSe/CdS NPLs in SJES perpendicular to the fiber drawing axis. Scanning electron microscopy, 3D-single particle excitation polarization microscopy, 3D-photogoniometry, polarized emission spectroscopy and small angle X-ray scattering (SAXS) demonstrate aggregation free perpendicular alignment of the NPLs in poly(methyl methacrylate) (PMMA) fibers, resulting in dominant emission in directions parallel to the fiber. We suggest that the observed vertical alignment is due to normal forces resulting from viscoelastic expansion when the polymer solution leaves the cannula (Barus effect) and that using such perpendicular nano-emitter alignment forces allows for the generation of innovative photonic materials also beyond fibers [7].

In a third innovative approach which we have presented at the Bunsen-Tagung 2023, we show the first efficient encapsulation of colloidal 2D CdSe/CdS NPLs by zeolitic imidazolate frameworks (ZIF-8 and ZIF-90). We describe the formation of composite films with minimal absorption and scattering, which are formed by cycled growth and which yield highly transparent coatings, while retaining the bright and narrow photoluminescence of the NPLs in a solid-state composite. The porous ZIF framework layer acts as functional encapsulation of the NPL emitters. This is shown by the influence of the adsorbed guest molecules water and ethanol by the ZIF and sensed by a change in the photoluminescence of the incorporated NPLs. The transmittance of the composite films is higher than in the uncoated glass substrate rendering it a photoluminescent antireflective coating. Molecules that interact with the nanoplatelets directly, such as water, pass through the ZIF and lead to an increased photoluminescence of the composites. On the other hand, the adsorption of ethanol changes the relative permittivity of the ZIF and decreases the photoluminescence of the composite, an effect not observed for pristine NPL emitters. The incorporation of CdSe/CdS NPLs emitters into ZIFs provides a powerful tool for the fast formation of smooth and transparent, yet emissive composite thin films with efficient encapsulation of the nanostructures by the ZIFs and enables an application towards photoluminescence-based optical gas sensing [8].

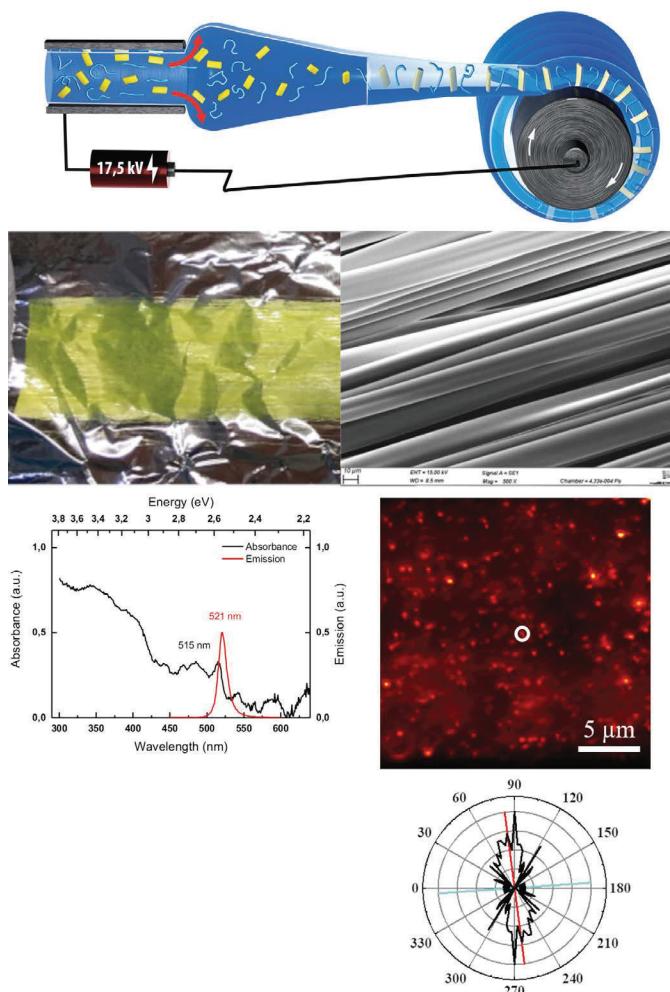


Fig. 2: Scheme of SJES of highly photoluminescent CdSe/CdS NPLs which align perpendicularly to the fiber direction due to the Barus effect. Middle panel: Photograph of the PMMA fibers with 0.01 wt % of NPLs and SEM image of the PMMA fibers, lower panel: absorbance and emission spectra of the NPLs inside the PMMA fibers and 3D single NPL polarization spectroscopy of the NPL circled in the image above. Measurements of hundreds of single NPLs show that they align in average perpendicularly to the fiber direction which is shown by the blue bar corresponding to the fiber direction in the image above [7].

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Jannika Lauth hat Chemie (mit Schwerpunkt Physikalische Chemie in der Doktorarbeit) an der Universität Hamburg studiert und wagte sich anschließend als Postdoktorandin in die Angewandte Physik und das *Chemical Engineering* an die TU Delft. Ihr Interesse und den Spaß an der nasschemischen Synthese kolloidaler Nanomaterialien und der zeitaufgelösten Spektroskopie (transiente Absorption bei Raumtemperatur und kryogenen Temperaturen sowie zeitaufgelöste Terahertz-Spektroskopie) zur Charakterisierung der Photophysik unterschiedlichster Materialien verwendet sie, um die Chemie und die Physik zu verbinden. Seit 2022 ist ihre Arbeitsgruppe delokalisiert, ein Teil arbeitet an der Universität Tübingen, wo Jannika Lauth als Juniorprofessorin die Arbeitsgruppe für „Ultraschnelle Spektroskopie und Optoelektronik von kolloidalen 2D Halbleitermaterialien“ leitet, der andere Teil ist an der Leibniz Universität Hannover tätig, an der sie im Rahmen des Exzellenzcluster PhoenixD eine eigenständige Arbeitsgruppe für 2D Halbleiter und transiente Absorptions-Spektroskopie betreut. Das Beste aus zwei Welten! Oder auch der „ganz normale Wahnsinn“ der akademischen Karriere auf dem Weg zur Professur...

Sie freut sich sehr über die Entwicklung und das stets offene Ohr der DBG und des St.A für die yPC, die als Institution und mit hochmotiviertem jungem Team nicht mehr wegzudenken und der Antrieb sowie die wichtige Zukunft der BDG sind. In ihrer Freizeit ist Jannika Lauth immer noch begeisterte Reiterin und mindestens 1x am Tag auch bei schlechtem Wetter draußen, um potentielle in kinetische Energie umzusetzen.

