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Made from Semiconductors and (Noble) Metals

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Received 30 April 2006

We summarize some of our efforts in synthesizing and characterizing nanoscopic objects fabricated from semiconducting materials and noble metals. The optical properties of colloidal semiconductors (quantum dots) are analyzed, in particular, with respect to their spectral photoluminescence properties (bandgap engineering) and the characteristic emission blinking. The statistical evaluation of the on- and off-states seen in the time-dependent recordings of the photoluminescence emitted from a single nanoparticle confirmed the reported power-law probability distribution, however, with a superimposed decay of the on-state density (which is illumination intensity dependent). This results in a loss of fluorescence intensity upon extended illumination when these particles are used in biosensor assays. Next, a colloid particle-based template protocol for the fabrication of non-trivial Au nanostructures is described. The resulting nano-crescents can be varied in terms of their size and shape. It is demonstrated how their plasmonic resonance characteristics can thus be tuned with respect to the spectral position of their (multipole) absorbance peaks, and their polarization properties.

Keywords: Nano-objects; quantum dots; plasmonic resonant structures; noble metals; single molecule optics; fluorescence spectroscopy; polarization; bio-sensors.

1. Introduction

No matter how many unrealistic expectations we may see associated with nanotechnology and its impact on our daily life there are many aspects of the emerging corresponding nanoscale sciences that are truly exciting for both, experimentalists and theorists. Major challenges for this interdisciplinary research field that is gradually gaining shape at the intersection of the classical disciplines like physics, chemistry, biology, and materials science and engineering will remain in the focus of “nano-scientists”.

Among the many research targets that have been identified recently, the interest in fabricating (synthesizing) nanoscopic objects from different classes of materials has attracted particular attention. This is a prerequisite to gain insight into physical properties that can be fundamentally different from those found in corresponding
macroscopic samples of the same materials and are often highly sensitive to the exact shape. A well-known example is the change in the opto-electronic properties of ultra-small clusters of semiconductors with sizes that are smaller than the radius of an exciton, i.e., the elementary electronic excitation in these materials. Others are the optical resonances that are found in nano-sized samples of noble metals, e.g., in gold colloids, that give rise to the very characteristic spectral properties of these materials used already for centuries in stained glasses, e.g., found in old church windows.

Materials like those have spurred a considerable effort in developing the experimental and theoretical tools needed to address the complex interplay between structure and opto-electronic properties at the nanoscale.

The more we learn how to synthesize such ultra-small objects and to control their three-dimensional arrangement in space the more we are fascinated by the novel fundamental phenomena at this length-scale and their technological implications. A particularly exciting aspect of research with nanoparticles is the possibility to combine such small objects made from very different materials to hybrid aggregates, exhibiting an even wider spectrum of novel physical properties.

Typical examples of nanoscopically small building blocks made from three classes of materials are sketched in Fig. 1. The first category of particles shown are so-called dendrimers, representing organic/polymeric systems. Other than the classical linear macromolecules that are only characterized by an average molecular mass with a more or less broad statistical distribution of their degree of polymerization and with a corresponding "size" that is described by a (average) radius of gyration these novel architectures are true objects in the sense that these polymeric particles all have an identical molecular mass and hence all have the same size. Moreover, due the fact that at least the polyphenylenes shown in Fig. 1 are shape persistent, one is dealing indeed with nanoscopic building blocks.

The next category of materials, shown in Fig. 1(b), represents a very old nanoscopic system known for decades (centuries) as colloidal gold which was recently rediscovered as (or better just renamed) nanoparticles. Classically

![Diagram](image_url)

**Fig. 1.** Nanoscopic objects from different materials: (a) polymeric dendrimers, (b) a gold nanoparticle with a non-trivial shape, and (c) a semiconducting \((\text{Cd}_2\text{Zn}_{1-x}\text{Se})\) cluster, a quantum dot.
synthesized as more or less round or odd-shaped and broadly size-distributed systems one has now developed recipes for the preparation of samples with a very narrow diameter range and one has learned also to fabricate non-trivially shaped objects like the nano-crescents or “nano-croissants” shown in Fig. 2(b). As we will show in the following, these nanoparticles have a fascinating spectrum of optical properties associated with their local plasmon resonances that give them a particular importance in the concert of hybrid nanostructured devices and materials.

And finally, nanoclusters are synthesized by various techniques from semiconducting materials with the option of manipulating their optical properties through smart engineering of their electronic band structure making use of quantum confinement effects. This offers the possibility to tune their spectral photoluminescence characteristics which has given them a particular role as bio-affinity labels or as functional units for opto-electronic devices.

In the following, we will briefly summarize some of our efforts in synthesizing nanoscopic building blocks made from different materials and in elucidating their optical properties. We will focus on some work with quantum dots and the nano-crescents prepared from gold rather than describing in this short report dendrimers and their rich spectrum of functional properties.

2. Quantum Dots from Semiconducting Materials as Bio-Labels

The tunability of the photoluminescence spectra of semiconducting nanoparticles and their remarkable photo-stability which is largely improved compared to organic dyes has given these systems enormous attention for various applications in biosensing, cell and tissue engineering, or opto-electronics. By down-sizing the
diameter to nanoscopically small clusters of typically II/IV-semiconductors or II/VI-semiconductors below the exciton radius of an electron-hole pair in these materials one can tailor their bandgap energy and hence the emission color of the recombination radiation after photo-excitation over a wide spectral range.

Another principle of color tuning is based on the control of the atomic composition of quantum dots, e.g., by alloying core/shell nanoparticles at elevated temperatures. Starting with a pure CdSe core which represents a low bandgap material and adding ZnSe shells of increasing thickness as a high bandgap material results after alloying the three materials at high temperatures in nanoparticles with an increasing atomic ratio of Zn versus Cd and, hence, produces quantum dots with increasing emission energies. An example of a series of nanoparticles with different compositions resulting in different emission colors of their photoluminescence spectra is given in Fig. 2 (right panel, (a)–(e)). From a practical point of view it is particularly interesting that despite the different emission colors of the various particle samples, their absorbance spectra are rather similar, all covering a broad spectral range. That means that quantum dots as color- (fluorescence-) labels in bio-affinity studies represent a series of chromophores that can be all excited with the same laser (wavelength) yet can be tuned in their respective Stokes shift of the emission spectrum to virtually any desired wavelength relative to the excitation wavelength. This is particularly important in a surface plasmon spectroscopic mode of operation in biosensor applications. Here, one makes use of the high optical intensity that can be achieved upon resonant excitation of a surface plasmon mode at the sensor (Au) metal/ aqueous buffer interface. This requires the angle of incidence of the exciting laser beam to be tuned to the respective resonance angle which is wavelength dependent. Thus, the use of quantum dots in these experiments requires only one laser for the excitation of all employed quantum dots resonant for surface plasmon excitation, and this one needs to be incident at one single resonance angle.

The resulting concept of color multiplexing in bio-affinity studies is schematically given in Fig. 3. Hybridization reactions between surface attached oligonucleotide catcher probes and their complementary (or slightly mismatched, e.g., mismatch 1 upon single nucleotide polymorphism (SNPs) detection) DNA single strands are monitored. If each of the different analyte target molecules carries a different quantum dot emitting luminescence of its specific color the analysis of the recorded fluorescence spectra after the binding of a whole mixture of analytes allows for the multiple read-out of parallel binding events in a single measurement.

A test array of various spots of different single catcher probe oligonucleotides and two spots with a binary probe mixture is shown in Fig. 4. The scheme presented in Fig. 4(a) gives the placement of the different probes on the different spots. The green broken ellipse indicates roughly the intensity profile of the laser spot illuminating the array in the following surface plasmon fluorescence microscopic experiment. The right image, Fig. 4(b), taken from the array with a color CCD camera after the binding (hybridization) of 2 different targets from solution to
Fig. 3. Schematic illustration of the interfacial multilayer architecture for color-multiplexed fluorescence detection of surface hybridization reactions between surface attached probe oligonucleotide strands and target analyte strands from solution.

Fig. 4. (a) Array of oligonucleotide catcher probe spots of 3 different single nucleotide sequences (P1, P2, P3) and a mixture of P1 and P2, ink-jet deposited on the chip of the surface plasmon fluorescence microscopy sensor. The green broken ellipse indicates the main area of the laser illumination in the experiment. (b) Fluorescence microscopic image of the array after injection of a mixture of targets. Target 1 is fully matched to probe 1, but nearly fully mismatched to probes 2 and 3, respectively, and carries a red-emitting quantum dot as color label. Target 2 is fully matched to probe 2, but nearly fully mismatched to probes 1 and 3, respectively, and is color coded with a green emitting quantum dot. The yellow color seen on the mixed spot is a CCD camera "artifact" (mixing green and red yields yellow).

their respective probe matrices gives the color distribution according to the codes for the fully matched hybrids (double strand) on the spots, i.e., red for T1 and green for T2, respectively. The spots functionalized with the probe strand, P3, which is completely mismatched to both targets remains dark. The yellow color "emitted" from the spot with the P1 and P2 mixture is an artifact from the camera that transforms the combination of red and green into yellow light. This can be clearly
seen if the emitted luminescence intensity is fed through a spectrometer and is spectrally analyzed (cf. Fig. 5(a)). Only the red and the green emission peaks are seen in the spectrum.

The continuous recording of the emission spectra as a function of time allows for the evaluation of kinetic information for bio-affinity reactions. This is demonstrated in Fig. 5 which displays a series of photoluminescence spectra, taken every 2 min, after injection of the analyte solution into the sensor flow cell. One should point out that, the spectra and, hence, the resulting time dependent increase in photoluminescence in these experiments is integrated over all spots. However, as we could show in surface plasmon fluorescence microscopy studies of hybridization experiments with targets functionalized with organic dyes each spot can be read out separately. Moreover, in this color-multiplexing mode this could be done also for several different target strands binding to one multi-functionalized sensor spot simultaneously.

The quantitative evaluation of the underlying association (hybridization) rate constants that one could derive from such measurements of the time-dependent increase of the luminescence intensity in this case is more complicated than for target strands labeled with a low molecular mass chromophore: the mass-transfer (diffusion) limited transport of the analyte-quantum dot-conjugates across the unstirred layer in front of the sensor surface interferes with the determination of intrinsic rate constants of the association process for these massive semiconductor particles in a much stronger way than for the low molecular mass organic chromophores.\textsuperscript{15} Moreover, the currently available commercial quantum dots used in this affinity study carry between 8–12 target strands (a direct consequence of the multiple functionalization of the particles by the same number of streptavidin units attached to the stabilized clusters). Both effects need to be taken into account if rate constants are to be evaluated.
Another surprising observation is given in Fig. 6: if one continues to take recordings of the photoluminescence intensity beyond the time at which equilibrium between the bulk concentration and the surface binding sites is reached, the luminescence intensity starts to decrease again (cf. the blue curve in Fig. 6). This is not a consequence of analyte molecules starting to desorb again from the sensor surface: the regular SPR signal originating from the adsorbed (optical) mass remains constant (black curve). The next obvious conclusion, i.e., that quantum dots, too, exhibit only a very limited photo-stability would be somewhat surprising and in conflict with the reported stability of this label system.

The solution to this unexpected result came from photo-physical studies with single quantum dots. A series of quantitative evaluations of the photons emitted from individual clusters deposited in high dilution on solid substrates and recorded while scanning the sample in the $x, y$-plane in a single-photon counting mode with a photodiode is given in Fig. 7. In the microscopy mode (Fig. 7(a)) one can identify the individual quantum dots, already with some clear indication of their blinking phenomena (cf. also Fig. 7(d)). A single line-scan (Fig. 7(b)) gives the diffraction limited spatial resolution achievable in these experiments. From the spectral analysis of the emitted photons we can infer the (homogeneous) line-width of a single
cluster, $\Delta \lambda \approx 14 \text{nm}$ (Fig. 7(c)). The most important finding in this context is the statistical analysis of the photon blinking shown in Fig. 7(d).

Figure 8 summarizes the results of a series of experiments taken on individual quantum dots deposited on 2 types of substrates (glass and ITO, respectively, as indicated) and recorded at different illumination power densities (covering 2 orders of magnitude, as indicated). The general behavior is well described by a power law dependence of both, the on- and the off-state histograms. One should note that this is in strict contrast to the behavior of organic dyes where the observed semi-logarithmic decay of the on-state correlates well with the picture of a normal $S_1 \rightarrow S_0$ singulett transition with some occasional detours to the long-lived forbidden excited triplet state which corresponds to the dark state of the chromophore. We should mention that, at the moment there is no physical model that can fully explain the observed behavior. None of the existing theories, e.g., based on a nonlinear photo-induced Auger process or a picture that includes tunneling transitions to external states with both mechanisms resulting in a charged quantum dot which is believed to represent the dark state would be compatible with our finding that neither the conductive nature of the substrate nor the irradiation power have a significant influence on the blinking statistics.
Fig. 8. Statistical evaluation of the blinking as displayed in Fig. 7(d) of single quantum dots deposited on either an isolating (glass) or a conductive substrate (ITO) recorded at different power density of illumination, P, as indicated. Note the general power-law dependence of both, the on- as well as the off-state, with a superimposed power-dependent photo-induced deactivation process seen as an additional loss of long-lived on-states.

What turned out to be important for the sensor application and the observations made there was the finding of an illumination power dependent decay channel that leads to a significant deviation from the power law dependence of the on-/ off- statistics and results in a gradual depopulation of the on-state upon extended exposure to light — just like a photo-bleaching reaction would do!

However, the remarkable difference between these two processes and their impact for practical applications is the fact that the gradual depopulation of the on-state in quantum dots is reversible. This can be clearly seen in the surface hybridization reaction if the experimental procedure is slightly changed as is documented in Fig. 9: if, during the phase at which the luminescence intensity decreases, one turns off the laser for a while (25 min in this case) one observes a partial recovery of the luminescence intensity emitted by the quantum dots — in obvious contrast to a photo-bleaching mechanism.

3. Plasmonic Resonances in Nanostructures from Noble Metals
The last example for the fabrication of nanoscopic structures yet from a totally different class of materials, i.e., (noble) metals, is presented in Fig. 10. A monolayer of
Fig. 9. Association (hybridization) reaction of target oligonucleotide-functionalized quantum dots to the probe matrix on the surface of a sensor like that presented in Fig. 6. However, this time the exciting laser was switched off for 25 min resulting in a partial recovery of the emitted luminescence intensity.

Fig. 10. Schematic description of the fabrication process of nano-crescents: (1) a monolayer of colloidal particles at low coverage are physisorbed to a flat substrate, (2) Au is evaporated at an oblique angle, (3) most of the Au is removed by ion milling, except the Au protected by the colloids used as an etch mask, (4) removal of the colloids.
colloidal particles ranging in diameter from a few tens to a few hundreds of nanometers are physisorbed to a solid flat support Fig. 10(1). After the evaporation of a certain thickness of Au at an oblique angle of incidence (Fig. 10(2)) most of this Au is again removed by ion milling (etching) except the Au that was deposited "underneath" the colloids and hence was protected against the ions etching the surface material away (Fig. 10(3)). After removal of the colloids one obtains an assembly of nano-crescents that are all pointing in the same direction (Fig. 10(4)). By using colloid templates of different sizes and by multiple evaporation cycles with sample rotations in between the individual deposition steps one can easily fabricate crescents of different sizes, and shapes. This procedure is schematically given in Fig. 11 indicating that e.g., the opening angle of the nano-crescents can be easily tuned over a wide range to generate nearly closed C-structures or even complete rings. This is particularly interesting because it allows for the preparation of a variety of different structures with their resulting plasmonic resonances, i.e., their spectral characteristics and/or the achievable field enhancements being strongly dependent on the size, the shape, the base material, the dielectric environment, any coating, etc. of the nanostructure. An example of the tunability of the various multipole resonances in crescents of different sizes are given in Fig. 12. The diameters of the latex colloids used for their fabrication were in the range of 150 to 400 nm, as indicated. One can see that the spectral positions of the absorbance peaks as well as their oscillator strength are strongly dependent on the structures and their size and, hence, can be tuned to any desired wavelength.

Among the many other optical features that are dependent on the details of the size and shape of individual nano-objects, their two-dimensional or even three-dimensional arrangement in space, their optical environment, etc., we only show here the polarization dependence of the plasmonic resonance of a particular type of nanostructure upon illumination with a linearly polarized light. Figure 13 shows the

Fig. 11. Multiple evaporation steps, with sample rotations in between, result in C-structures with an opening angle, \( \theta \), that can be controlled over a wide range (shown is the fabrication of a structure with \( \theta = 90^\circ \) by two evaporation steps).
corresponding absorbance spectra of a sample that was twice rotated by \( \Delta \theta = 45^\circ \). One can see that some of the transitions are mutually orthogonally polarized and, hence, vary in their absorptivity depending on the relative orientation of the linearly polarized excitation light.

4. Conclusions

Our ability to synthesize nanoscopic objects from different types of materials has seen remarkable progress in recent years. Now, we have at our disposal a broad range of building blocks that are all very monodisperse in size and shape, can be tuned in their nanoscopic dimensions and can be characterized with respect to their most interesting properties. The fact that we have nano-objects from organic/polymeric materials as well as from semiconductors and from (noble) metals as elements in our assembly kits\(^{19}\) offers a fascinating chance to eventually build hybrid architectures.
with unprecedented new properties for applications as functional smart materials, in opto-electronics or in the life sciences. Many more steps are needed on the way to the much-referred nanotechnology but the scientific challenges are already today more than fascinating!

Acknowledgments

Partial funding for this project from the German-Israeli Project on Future-Oriented Topics (DIP, D3.1), from the Deutsche Forschungsgemeinschaft (DFG, KN 224/11-2, and SFB 625) and from the Bundesministerium für Bildung und Forschung (BMBF, Project 03C 0299/7 and Project 03N8702, Projektträger NMT) is gratefully acknowledged. We thank Ming-Yong Han, Evelyne L. Schmidt-Osborne, and Thomas Basché for many helpful discussions.

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