Fabrication of Elastomeric Membranes: We fabricated elastomeric membranes by spin-coating a liquid pre-polymer of PDMS (Sylgard 184; Dow Corning, Midland, MI) onto a master. The rate of spinning was set so that the thickness of the layer of PDMS was less than the height of the posts of photosensit (for example, for posts 50 μm high, we spin-coated PDMS at 3000 rpm for 60 s to produce an approximately 45 μm thick film; for posts 5 μm high, we spin-coated a 1.4 mixture of PDMS/toluene at 3000 rpm for 40 s to yield a film less than 3 μm thick. After curing the PDMS, a thicker (~2 mm) layer of the liquid pre-polymer was painted around the outside of the master and cured: this layer made it easier to peel the elastomer from the master.

Fabrication of EL Devices: ITO-coated glass slides were cleaned by sonicing them in a 3:1 mixture of deionized water and detergent (Lysol Deodorizing Cleaner, Reckitt and Colman, Inc., Montvale, NJ) for 15 min, then in water for 30 min, in ethanol for 15 min, and were finally blown dry in a stream of N₂. We placed a PDMS membrane against the ITO-coated slide using a pair of tweezers and the membrane sealed conformally against the substrate. For the TPD/Alq₃ EL device, 40 nm of TPD (courtesy Dr. Martin Cronin, Corning, Midland, MI) onto a master. The rate of spinning was set so that the master.

Fabrication of Photoluminescent Structures: Alq₃ was patterned by thermal evaporation (~0.5 nm/sec; base pressure ~5 × 10⁻⁸ torr) onto the membrane containing 50 μm holes, and the membrane was then peeled away from the substrate using a pair of tweezers. We thermally evaporated 80 nm of Alq₃ (Aldrich, Milwaukee, WI; purified by sublimation) over the entire array of TPD dots using a pair of tweezers. We thermally evaporated 80 nm of Alq₃ (Aldrich, Milwaukee, WI; purified by sublimation) over the entire array of TPD dots using a pair of tweezers.

Fabrication of Multi-color Patterns of EL Materials: We coated a membrane containing an array of open, circular holes (100 μm diameter) with a 4:1 mixture of PDMS/toluene at 3000 rpm for 40 s to yield a film less than 3 μm thick. After curing the PDMS, a thicker (~2 mm) layer of the liquid pre-polymer was painted around the outside of the master and cured: this layer made it easier to peel the elastomer from the master.

Received: October 5, 1998
Final version: January 15, 1999

[17] We have shown previously [Y. Xia, J. Tien, D. Qin, G. M. Whitesides, Langmuir 1996, 12, 4035] that rigid, polymeric meshes can also be formed by micromolding polysulphone.
[20] Polymeric membranes have been used previously to pattern EL materials on ITO substrates: see M. Granstrom, M. Berggren, O. Inganäs, Science 1995, 267, 1479. These authors used commercial microfiltration membranes: the patterns of circles of an EL material were random and there was no way to control the size, shape, or pattern of the circles. Furthermore, the membranes were rigid, did not conform to the surface, and could not be used to pattern curved surfaces.
[22] Creases in these membranes could be avoided by using 2-propanol to minimize van der Waals forces and stop the membrane from folding up: this procedure is acceptable provided the patterning step is the first one so other layers are not affected by the use of a solvent.
[23] TPD has relatively poor adhesion to substrates. When a membrane is brought into contact with a layer of TPD, the TPD will tend to be removed when the membrane is lifted off. We did not observe this effect when (~20 nm) or PVK: we infer that Alq₃ and PVK adhere better than TPD to silicon substrates.
[24] The turn-on voltage of this device was ~14 V, and the quantum efficiency was ~0.013 %. Leakage currents through the Alq₃ layer (in the regions where the TPD was not present) contributed to the low quantum efficiency.

Colloidal Prepared HgTe Nanocrystals with Strong Room-Temperature Infrared Luminescence**

By Andrey Rogach, Stephen Kershaw, Mike Burt, Mike Harrison, Andreas Kornowski, Alexander Eychmüller, and Horst Weller*

Nanometer-sized semiconductor particles (often referred to as nanoclusters, nanocrystals, or quantum dots) belong to a state of matter lying in the transition region between molecules and bulk materials. Because of the quantum confinement effect, nanocrystals show unique physical and chemical properties when they are smaller than the dimension of the exciton.[1–3] Due to the large surface-to-volume ratio, in small particles the surface chemistry of the nanocrystals plays yet another important role. Control of the
nanocrystal size, the size distribution, and the nanocrystal surface leads to an understanding of their special properties e.g. size-dependent bandgap shift, photoluminescence (PL) and electroluminescence behavior, nonlinear optical properties, charge carrier dynamics, and structural and phase transitions. Achievements made by chemists in the synthesis of high-quality nanoparticles and by physicists in their characterization has broadened the focus from pure basic research to real application of nanomaterials in electrical and optoelectronic devices.

Extensive research work has been carried out in the field of synthesis and characterization of high-quality II–VI semiconductor nanoparticles. Wet chemical synthetic routes have been developed for cadmium chalcogenide nanocrystals in non-aqueous solutions using TOP/TOPO (trioctyl phosphate / trioctyl phosphate oxide) capping and in aqueous solutions using various thiols as stabilizing agents. That the emitted color can be tuned by simply varying the size of the nanoparticles, in combination with high-emission quantum yields, makes semiconductor nanocrystals attractive candidates for integration into light-emitting devices (LEDs). Recently such LEDs have been fabricated in a hybrid material consisting of a combination of conducting polymers with CdSe nanocrystals.

Another important technological direction is the use of nanometer-sized semiconductor particles as potential amplifiers operating at 1.3 µm and 1.55 µm wavelengths for telecommunication devices. The alloy Cd₃₋ₓHgₓTe is a well known material for long-wavelength IR detector technologies. For x = 1, bulk HgTe has an inverted band structure and thus an effectively negative band gap of around −0.15 eV at 295 K. Quantum confinement in HgTe quantum dots should increase their effective bandgap giving rise to infrared (IR) luminescence. Although HgTe and Cd₃₋ₓHgₓTe films have been grown by molecular beam epitaxy, to the best of our knowledge there have been no previous reports of HgTe quantum dot growth using either beam or colloidal-particle growth techniques. In this communication we report what we believe to be the first wet chemical synthesis of HgTe quantum dots on a gram scale. The thiol-capped dots are stable towards oxidation, with luminescence covering the 1.3 µm telecommunications fiber window.

Aqueous colloidal solutions of HgTe nanoclusters were synthesized by the passage of hydrogen telluride gas, buffered with nitrogen, through aqueous N₂-saturated mercury(II) perchlorate solutions at pH 11.2 in the presence of thioglycerol as a stabilizing agent. As previously shown, the latter is an effective size-regulating and stabilizing agent for II–VI semiconductor nanoparticles. HgTe nanoparticles from the colloidal solution prepared by this means can be isolated as a powder by precipitation with 2-propanol and, being capped with thioglycerol on the surface, are readily redissolvable in water.

Figure 1 shows the absorption and the room-temperature PL spectra of the sample directly after preparation. The absorption spectrum does not show any striking features other than a long tail extending into the IR (the tail shifts further into the infrared over a period of several days, during which time a slight shoulder just below 500 nm becomes evident). The room-temperature PL emission spectrum of HgTe particles in aqueous solution covers the spectral region from 800 to 1400 nm with a maximum located at 1080 nm. Numerical integration of the peaks in the 800–1400 nm region of the PL spectrum for the HgTe nanoparticles indicates an overall quantum efficiency of approximately 48 % for the sample. The minima seen in the PL spectra of HgTe particles in aqueous solution are due to water re-absorption. They were not observed in the photoluminescence of thin films of HgTe nanocrystals on glass supports. The position of the emission maximum shifts into the infrared with time—which coincides with the red-shift of the absorption tail—and the PL intensity decreases.

For both amplifier and optical source applications it is highly desirable to be able to include luminescent semiconductor nanocrystals in an organic solvent with low optical absorption and scattering losses, rather than using aqueous solutions. Figure 1 also shows the room-temperature PL emission spectrum of HgTe particles precipitated from the aqueous solution and then redispersed in pyridine. Although the quantum efficiency of HgTe nanoparticles becomes lower, a further shift of the PL maximum is achieved so that it is located exactly over the 1.3 µm telecommunications window. The absorption spectrum of HgTe particles in pyridine does not differ markedly from that in aqueous solution.

Figure 2 shows the X-ray diffraction pattern of HgTe nanoparticles. The crystal structure derived from the positions of the wide-angle diffraction peaks clearly indicates a cubic (coloradoite) HgTe phase. The wide-angle diffraction peaks are broadened due to the small particle size. The mean cluster sizes estimated from the full width at half-maximum intensity of the (111) reflection according to the Scherrer equation gives a value of about 3.5 nm.

Fig. 1. Absorption and photoluminescence spectra of HgTe nanocrystals:
Absorption of freshly prepared HgTe particles in water (solid line); luminescence of freshly prepared HgTe particles in water (dashed line); luminescence of HgTe particles re-dispersed in pyridine (dotted line).

Fig. 2. X-ray diffraction pattern of HgTe nanoparticles.
Fig. 2. Powder X-ray diffractogram of HgTe nanocrystals. The line spectrum gives the bulk HgTe coloradoite reflections with their relative intensities.

Fig. 3. High-resolution TEM image of HgTe nanocrystals. Insets show a typical overview image of the sample together with a micrograph of an individual HgTe particle with a corresponding Fast Fourier Transformation (FFT). HRTEM also shows a micrograph of an individual HgTe particle with a corresponding FFT. HRTEM also indicates high sample crystallinity. All the images of single particles exhibited an interplanar distance of 3.73 Å belonging to the (111) lattice plane of the coloradoite HgTe phase, which again is consistent with X-ray diffraction data.

In conclusion, for the first time we have reported the colloidal preparation of thioglycerol-capped HgTe nanocrystals with a size ranging from 3 to 6 nm and coloradoite crystal structure. The most exciting feature of these HgTe nanocrystals is their room-temperature IR luminescence with a reasonably high quantum yield (48%), which partly overlaps with the 1.3 μm telecommunications fiber window. Extended optical characterization of the sample using time-resolved spectroscopy will be the subject of a forthcoming paper.

Experimental

A solution of 0.94 g (2.35 mmol) of Hg(ClO₄)₂ and 0.5 mL (5.77 mmol) of 1-thioglycerol in 125 mL of demineralized water was adjusted to pH 11.2 with 1 M NaOH. The solution was placed in a two-necked flask fitted with a septum and valves and was de-aerated by bubbling with N₂ for 30 min. Under stirring, H₂Te gas (generated by the reaction of 0.08 g of Al₂Te₃ with 10 mL of 0.5 M H₂SO₄ under N₂ atmosphere) was passed through the solution together with a slow nitrogen flow. No heat was applied to the solution because it was found that this quenches the luminescence of the particles. The crude solution was reduced to ~30 mL using a rotary evaporator. 2-propanol was then added dropwise until turbidity occurred and the solution was stirred for 2–3 h. The precipitate containing thioglycerol-capped HgTe particles was separated by centrifugation.

UV-visible absorption spectra were recorded with a Perkin Elmer Lambda 9 spectrometer. A mechanically chopped Argon Ion laser running on all lines (predominantly at 488 nm and 514.5 nm) was used to excite the sample and an InGaAs photodiode was used as a detector. The PL spectrometer arrangement was calibrated with a dilute sample of the organic dye Rhodamine 6 G in ethanol for which the quantum efficiency is known to be ~95%. TEM images of the nanocrystals were acquired on a Philips transmission electron microscope operating at 300 kV. TEM samples were prepared by dropping dilute aqueous solutions of the nanocrystals onto 400 mesh carbon-coated copper grids with the excess solvent immediately evaporated. X-ray powder diffraction was carried out with a Philips X'Pert diffractometer (CuKα radiation, variable entrance slit, Bragg-Brentano geometry, secondary monochromator). Samples for these measurements were prepared by placing finely dispersed powders of CdTe nanocrystals onto standard PVC supports.

Received: October 30, 1998

Ultrathin Microstructured Polypeptide Layers by Surface-initiated Polymerization on Microprinted Surfaces**

By Thomas Kratzmüller, Dietmar Appelhans, and Hans-Georg Braun*

Immobilization of thin biopolymer layers on solid substrates is of particular interest for the development of biosensors,[1] microanalytical devices,[2] or microbioreactors.[3] Furthermore, polypeptides or proteins located on surfaces are regarded as key compounds for the control of biomimetic steps in biomineralization processes.[4–6] Finally, some synthetic polypeptides, such as poly-γ-benzyl-glutamate, reveal interesting material properties, such as piezoelectric[7] or nonlinear optic[8] behavior, when are attached to solid substrates.

The microstructural arrangement in biopolymers is of great interest for the integration of biomolecules into microanalytical or microreaction devices. Patterning of biopolymer layers is commonly achieved using techniques such as photolithography, which was employed for the preparation of structured surfaces. The use of appropriate photolabile protecting groups enables the patterning of a surface with reactive and unreactive functionalities, which can be reacted with biopolymers such as proteins[9,10] or oligo-DNA strands.[11] It has also been demonstrated by different authors[12,13] that capillary extrusion could be another convenient method for the microstructured deposition of proteins on surfaces. Recently microprinting techniques were used to pattern surfaces by direct transfer of protein molecules onto solid substrates.[14]

In this communication we describe a new approach to preparing microstructured polypeptides that are covalently attached to a solid surface. This approach is based on a procedure called microcontact printing (μCP) developed by Whitesides et al.[15] This is a method for chemical surface heterogenization resulting in well-defined microstructured areas. Using this method we have been able to pattern gold surfaces with monolayers of appropriate initiator molecules, which can start the polymerization of N-carboxyanhydrides (NCA).[16] The surface-initiated polymerization results in the growth of thin surface-bound polypeptide layers within well-defined areas. The different steps, which involve surface modification and polymerization, are shown in Figure 1.

Fig. 1. Schematic representation of the preparation of thin patterned polypeptide layers by microprinting and surface-initiated polymerization.

The surface of a PDMS (polydimethylsiloxane) stamp was treated with a chemical compound necessary for local surface modification, in the following called ink. For chemisorption on a gold surface, the ink molecules are terminated with a thiol group. The initiation of the polymerization requires primary amino groups at the opposite end of the molecule. The molecular self-assembly can be achieved by a linear aliphatic chain segment in between the two functional groups. The compound we synthesized (see Experimental) and used as the initiator system was 12-mercaptododecylamine.

In order to obtain a thin layer of initiator for the surface polymerization on a gold surface we used a solution of 12-mercaptododecylamine in ethanol (1 mM) as ink. After the solvent had been evaporated with a gentle stream of nitrogen, the stamp was brought into contact with the gold surface (100 nm on silicon primed with 2.5 nm of Cr). The thiol was transferred from the stamp to the gold and there-