PAPER

Reversible nanoparticle gels with colour switching†

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Assembly of semiconductor nanoparticles into gel structures and their subsequent behaviour is one of the less-developed areas in nanochemistry. We demonstrate here a simple luminescent gel from CdTe nanoparticles in aqueous solution. Its structure can be described as an infinite network from chainlike branched structures. The recrystallization into the solid monocrystalline nanowires is prevented by increasing content of sulphur in the nanoparticles, which drastically increases the recrystallization energy. Brief sonication returns the system into the sol state. This switching behaviour is reversible and is accompanied by equally reversible emission colour switching. Such properties are much needed in a variety of media-responsive (*i.e.* "smart") optoelectronic materials. This system will also be useful as a convenient research tool for the observation of dynamics of aqueous nanoscale colloids.

1. Introduction

Self-organization of inorganic nanoparticles (NPs) has drawn much attention over the last few years due to the large variety of available components and assembly motifs including one-dimensional (1D),[1] two-dimensional (2D)[2] and three-dimensional (3D)[3] NP assemblies. Another aspect that has drawn less attention so far is the fact that self-assembled systems of NPs bridge nanometre and micrometre scales of organization, which opens interesting possibilities for the assembly of photonic/electronic[4] devices, transformative optics[5] and new modalities in biosensing.[6] Even more recent findings highlight the apparent similarity between some self-organized multiparticle superstructures and those spontaneously forming from typical biological macromolecules.[7]

Among many different NP assemblies substantial attention is attracted now by NP gels, which have been known for some time but still investigated to a limited degree. Most examples of NP gels tend to be dry aerogels.[3e,8] The difficulties of forming gels in liquids are related to the strong electrostatic repulsion between NPs in solution and the frequent presence of a thick organic shell around NPs synthesized in organic solvents. In both wet and dry gels, the driving force for gelation is strong anisotropic attraction. Often having bipolar force field around them,[1b] the NPs tend to form chains, and therefore gels. The formation of the NP networks is most of the time an irreversible process due to the deep thermodynamic minimum related to the attraction of polarizable cores from heavy elements. Once gels are formed only very strong chemical modification such as a redox reaction and replacement of a stabilizer was shown to result in a reversible gelation–dispersion process.[9] None of the known NP superstructures in solution assemble or disassemble in response to a simple external stimulus. It would be quite interesting to find a self-assembled NP system with reversible gelation behavior due to the considerable practical importance of such systems for smart materials and better understanding of NP forces in solution. Also, rheological properties of reversible aqueous reversible gels have multiple practical uses, while luminescence makes possible new optoelectronic applications and a unique tool for observation of phase transitions in small dimensions. Among these, reversible 3D networked gels of semiconductor NPs gain even greater importance.

The challenge of finding NP gels which are reversibly responsive to simple external stimuli relies on fine tuning repulsive–attractive interactions between nanocrystals. The energy difference between organized assembly and chaotic precipitation can be just a few kT.[7] In the case of thioglycolic acid (TGA) stabilized CdTe NP, several groups demonstrated efficient control over the interaction energies and anisotropy of interactions[10] by partial removal of TGA. Consequently the self-assembled branched NP chains were formed and aerogels were demonstrated. However, CdTe exhibited a different tendency which made the formation of reversible gels in solution difficult. CdTe exhibits a strong tendency to recrystallize in solution at room temperature producing straight monocrystalline CdTe

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nanowires,[11] which greatly deepens the energetic minimum of the assembled state.[12,10b] If further recrystallization is avoided, the branched chain state can be stabilized. With this perspective, we report here a 3D gel made from CdTe NPs *via* cross-linking of branched NP chains and ultrasound-induced switching from a state NP gel to a state of NP sol followed by the spontaneous reversal. This process occurs under ambient conditions and the resulting gels retain the strong fluorescence after gelation. As one of the interesting features of this system, the luminescence color also changes reversibly from one distinct hue to another which is reproducible and repeatedly accompanies the phase change.

2.   Experimental

2.1   Preparation of thioglycolic acid (TGA) stabilized CdTe NPs

The synthesis of TGA-stabilized CdTe NPs in aqueous solution followed the method reported.[14] Briefly H_2Te gas, which was generated by the reaction of 0.2 g Al_2Te_3 powder with 18 mL H_2SO_4 solution (0.5 M) under N_2 purge conditions, was passed through N_2 saturated $Cd(ClO_4)_2 \cdot 6H_2O$ aqueous solution (0.013 M, 125 mL) at pH 9.5 in the presence of TGA (0.396 mL of 5.7 mM) as a stabilizing agent. The CdTe NPs with the desirable sizes were prepared by adjusting the refluxing time. By using the well-known empirical equation in the literature,[13] the mean diameters of the obtained CdTe NPs used in this study were determined by the position of the exciton peak maximum in UV-vis absorption spectra (see ESI†). Estimated diameters of NPs for smaller (green line) and bigger (red line) particles were 3.1 and 3.4 nm, respectively.

$Cd(ClO_4)_2 \cdot 6H_2O$, TGA, NaOH, and H_2SO_4 were purchased from Aldrich. Al_2Te_3 powder was purchased from Alfa Aesar. The purity of $Cd(ClO_4)_2 \cdot 6H_2O$, TGA, NaOH, H_2SO_4 was above 99%. All chemicals in this study were used as received. Because Al_2Te_3 is readily oxidized in air, it was stored in a glove box when not in use. Caution: Since the intermediate product of H_2Te is highly flammable and toxic by inhalation, a respirator should be worn during the entire synthesis process to avoid possible inhalation of toxic gas.

2.2   Self-assembly process of CdTe NPs and sol–gel switching

According to a modified procedure reported by Tang *et al.*,[12a] CdTe gels were prepared. Briefly, 4 mL of CdTe NP solutions were mixed with 8 mL of methanol to partially remove the TGA stabilizer on the surface of CdTe NPs. This resulted in the precipitation of NPs. The resulting solution was centrifuged at 5900 rpm for 20 min and then the supernatant of the upper clear solution was removed. In order to eliminate excess liquid, the moist NPs were freeze-dried overnight. The dried CdTe NPs were redispersed in 4 mL of water (pH 9.0, adjusted with 0.1 M NaOH solution). The obtained dispersion was allowed to age at ∼15 °C under ambient light for 3 months in glass vials. In order to induce the gel structures into the sol state, sonication was carried out using a 40 kHz bath-type ultrasonics cleaner system (B3500A-MTH, VWR).

2.3   Characterization techniques

Photoluminescence (PL) and UV-vis spectroscopy. Photoluminescence measurements for CdTe NPs and gels were carried

out using a JobinYvon Horiba FluoroMax-3.The emission spectra were obtained by scanning the wavelength at intervals of 1 nm in the range 470–800 nm at an excitation wavelength of 450 nm. UV-visible absorption spectra were recorded using an Agilent UV-vis spectrophotometer. All measurements were performed at room temperature.

Transmission electron microscopy (TEM). TEM was conducted with a JEOL 3011 high-resolution electron microscope equipped with an energy dispersive X-ray (EDX) analyzer. For elemental analysis of gel structures, Cd Lα, Te Lα, and S Kα lines were used. Samples for TEM observation were prepared by dropping a solution of the obtained CdTe gels onto carbon-coated TEM copper grids (400 mesh grids supplied by Ted Pella, Inc.).

X-ray photoelectron spectroscopy (XPS). XPS measurements were taken on a Kratos axis ultra imaging X-ray photoelectron spectrometer.

3D confocal microscopy. The self-assembled 3D CdTe NP hydrogel after 3 months was imaged under a Leica TCS SP2 confocal microscope (Leica Microsystems, Germany) with a 580–650 nm emission filter and a 488 nm excitation laser under 10× and 20× objectives. For 3D confocal imaging, a slab of the luminescent hydrogel was imaged for 100 μm depth with a 1 μm interval. Achieved images were combined and stacked using Leica image software to generate a 3D projection.

3.   Results and discussion

CdTe NPs coated with TGA were synthesized in aqueous solution using an arrested precipitation strategy.[12,15] Two different sizes of NPs were prepared: the green- and orange-emitting TGA-stabilized CdTe NP solutions. The estimated diameters for smaller and bigger NPs were 3.1 and 3.4 nm, respectively (ESI†). TGA was partially removed by washing in methanol and redispersed in pH 9.0 water. It needs to be pointed out that unlike the previous works that showed recrystallization of NP chains into single-crystalline nanowires (NWs),[1b] the self-assembly process in this study was carried out under ambient light (*i.e.*, standard fluorescent light fixtures), which is likely to lead to partial photooxidation,[15] and self-assembled CdTe chains without NW formation by photo-treatment were reported elsewhere.

After prolonged storage, the solution became slightly turbid, and then the dispersion started to coagulate in a voluminous gel. It was self-supporting and had physical integrity; it was also emissive under UV illumination (Fig. 1b,c). Typical photoluminescence (PL) spectra obtained from CdTe NP solutions (dashed line) and corresponding gels (solid line) demonstrate a strong red shift of 30–40 nm after gelation, namely from λ_{fl} = 561 to λ_{fl} = 590 nm and λ_{fl} = 593 to λ_{fl} = 631 nm for smaller and larger NPs, respectively. Very little change in position of the PL peak was observed in previous NP gel studies.[11] The red shift is also associated with a reduction of quantum yield[16] (QY)from 14.0% in free NPs to ∼0.6% in the gel. One can speculate that the QY in the gel state is lower because the points of contact of NPs create exciton traps.
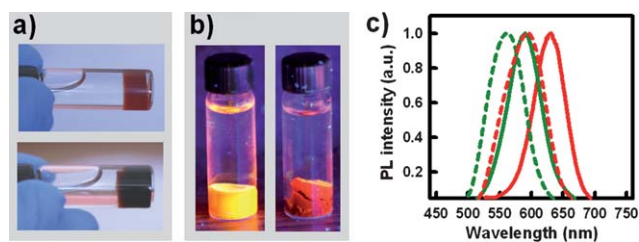
Fig. 1 (a) Photographs of formed CdTe gels, (b) CdTe gels under UV light, (c) Luminescence spectra of as-synthesized CdTe nanoparticles (dashed lines) and resulting gel (solid lines) marked by the corresponding colours.

Despite QY reduction, the optical activity is high enough to obtain confocal microscopy images under ambient conditions. As expected, the gel reveals continuity and integrity in the gel phase in different projections (Fig. 2a).Typical TEM images in Fig. 2b and c illustrate that, indeed, the gel has a structure of networked chains which is analogous to that of gels from organic and inorganic polymers. Numerous cross-links can be easily seen in the CdTe gel (Fig. 2c and d). Instead of the NWs, network consists of individual intact CdTe NPs (inserts of Fig. 2c and d). The crystal lattices of the particles are often in very close contact with each other. Some of them form nanorod sections due to spontaneous recrystallization taking place with a minority of NPs.

Considering the formation of these gels, one needs to inquire whether, as these NPs do not merge and recrystallize into NWs completely as in the previous studies,[1] what is the origin of the luminescence shift red shift upon gelation. The latter could be potentially attributed to three possible contributions: (a) chemical transformation of the NPs, (b) growth in size combined with partial reduction of size quantization effects due to NP closeness and to (c) Förster resonance energy transfer (FRET) from smaller NPs to larger ones.[16] The closeness of the NPs in the gels could potentially act in all three of these effects.

Recalling the fact that the gelation process occurs in light and the fact that light can cause some profound changes in NP assemblies,[17] one can speculate that partial photooxidation can take place on the surface of NPs and provide the clue to these questions. EDAX and XPS spectra of the original NPs and those forming gel indeed strongly indicate photooxidation (Fig. 3). XPS peaks in the Te 3d region demonstrate substantially increased Te–O peaks at the binding energies of 575 and 586 eV after gelation (Fig. 3b). Importantly, EDAX spectra demonstrate stronger a signal from S atoms than in the original NPs.[17] Based on these results and literature data,[3,4] it is quite clear that along with gelation the NPs undergo chemical transformation and a part of Te is oxidized and is replaced by S. Additionally this point can be supported by the X-ray diffraction patterns clearly showing the broadened peaks corresponding to both CdS and CdTe.

Therefore, regardless of whether the resulting NPs have a core–shell or alloy morphology, the energy of cubic-to-hexagonal lattice restructuring accompanying the NP-to-NW transition is increased.[18] This explains the fact that the transition is stopped at the point of NP chains and leads to the formation of the gel. Considering that replacement of Te with S should lead to a blue shift, not a red shift, of luminescence, and no significant growth of NPs in TEM images compared to the original ones can be seen, the luminescence red-shift should be attributed to the FRET rather than to other potential reasons.

Further confirmation for that can come from the realization of the reversible dispersion–gelation process, which also has its own significance. Considering that the resulting CdS-CdTe NPs are relatively robust, one can apply quite strong external stimulus. Instead of a chemical trigger used previously,[9] we decided to use ultrasonication as we were interested whether the destruction of the gels could be followed by its recovery. Indeed, the sonication stage was able to destroy the gel resulting in a dispersion equally as good as the one we had originally (Fig. 4). Brief sonication for
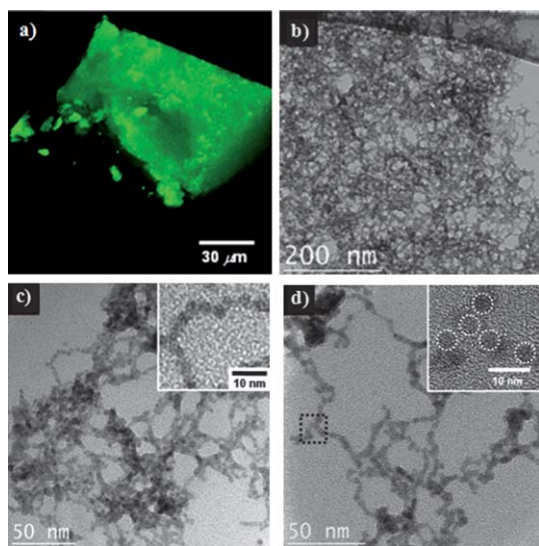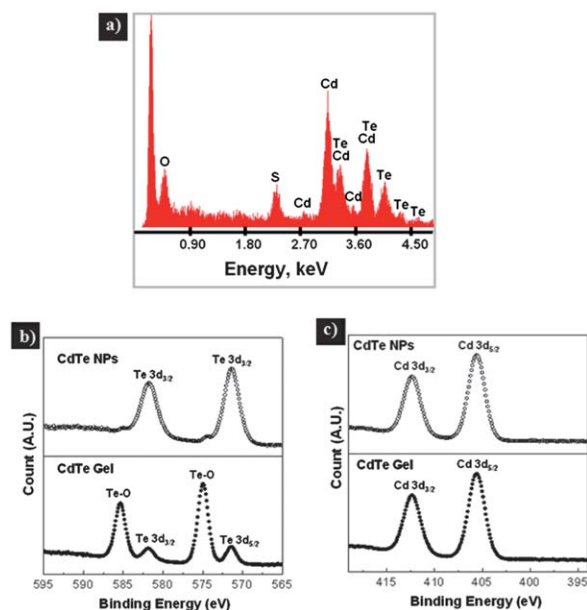

Fig. 2 (a) Representative 3D confocal image of CdTe gel, (b) TEM image of gel on the TEM grid, (c) and (d) TEM images of different parts of a hydrogel fragment, inserts are the high magnification images.

Fig. 3 (a) EDAX spectrum of CdTe gel, (b) XPS spectra of Te 3d and (c) Cd 3d peaks from CdTe NPs and CdTe gel.

20 s resulted in a homogeneous and transparent sol (Fig. 4c) with luminescent maxima blue-shifted from those for starting NPs (not gels!) by 5–8 nm which increases the colour contrast between the dispersed and gelled state even more. When ultrasound irradiation was stopped, flakes immediately formed within 2–4 s and began to precipitate at the bottom of the solution. The reformation of the original hydrogel structure took about 5 h (Fig. 4a). Note that the second gelation is much faster than the first gelation, which is associated with the completion of the oxidation process and/or incomplete destruction of the NP chains by sonication as evidenced by the observation of some of the stable NP chains soon after sonication of the solid gel Fig. 5b).

The completion of the switching from sol to gel state for each cycle was also confirmed by PL spectra for supernatant. No significant shift of the spectral position adsorption peaks was observed in the initial time other than the cessation of sonication (Fig. S3 in ESI†) or much later. After complete gelation, negligible UV-vis absorption and PL intensities (∼1000 times lower PL intensities compared to those of gels) were observed for supernatants. The structure of re-formed CdTe gels was very similar to that of the initial one (Fig. 5b).

Importantly, there was an accompanying orange-to-red switching of the luminescence of larger NPs of the sol and gel, respectively which was completely reversible (Fig. 4c). The transition of NPs between the sol and gel states could be repeated many times, with completely repeatable shifting of the position of the PL peaks back and forth, which is consistent with FRET. Intentional addition of 5% of nanoparticles emitting at 532 nm (green) did not change the final peak position, which is also consistent with FRET. Partial recovery of the quantum yield of NPs upon formation of the sol with QY = 13% was also observed. The same effects were also observed for smaller NPs with the difference that the switching occurred between green and orange luminescence. Altogether, these data give a clear indication that electron/energy exchange conditions can be changed back and forth, which can provide us with clues about the potential optical properties of the smart materials based on these gels and/or their structural blueprint.
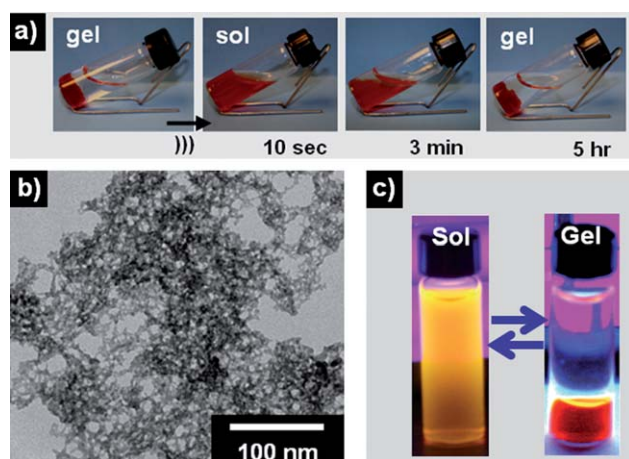

Fig. 4 Sol–gel switching of CdTe NP gels. (a) Photographs of ultrasound induced sol–gel transition. (b) Representative TEM image of reformed CdTe gels. (c) Colour changes depending on sol–gel switching under UV light.
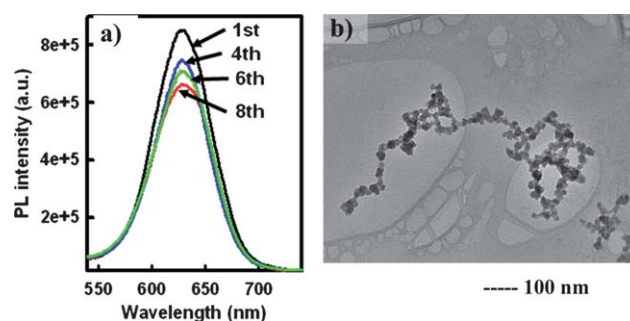

Fig. 5 (a) PL spectra of CdTe gel depending on cycles of sol–gel transition. (b) TEM image of the NP dispersion 20 min after the first sonication.

4. Conclusions

In conclusion, we demonstrated a simple approach to luminescent NP gel formation in aqueous solution. Self-assembly of CdTe NPs resulted in an elaborate branched chain network. Brief sonication of the gel enabled transition into the sol state. The phase switching behaviour was nearly reversible and repeatable and accompanied by the equally reversible shift of the luminescence colours which is the main difference with the gels studied by Eychmüller, Gaponik and Brock. Additionally the switching behaviour in our system does not require drastic chemical modification of the stabilizers but rather brief sonication, and therefore is simple and convenient. This property can easily be adapted to sensors with luminescence color transition as a read-out parameter and other media-responsive/adaptable devices and materials, such as actuators. From a fundamental perspective, these gels represent a nice model system for the studies of dynamics of nanocolloids with a convenient optical tool to register structural transitions.

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