Propagation of Terbium ions through the SWNT gel

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Direct diffusion measurements, time-resolved photoluminescence (PL), and steady-state PL spectroscopy are found to be useful tools to investigate mechanisms of ion propagation through the single-wall nanotube (SWNT)/hydrogel matrix. SWNTs immobilized in different soft matter matrices have been widely used for optical characterization [1,2,3]. The matrix not only provides a mechanical support for the SWNTs, it also partially screens the SWNTs from their environment. It is a vibrant question of how the SWNTs can still interact with the environment in the conditions of partial confinement [4]. We select terbium (Tb) ions, because of their unique PL properties. Silica gels with SWNTs dispersed with sodium deoxycholate (DOC), "empty" silica gels (not containing SWNTs), and DOC/water solutions were studied, providing environments with a controlled degree of ion interaction and confinement. A homemade confocal microscope setup was used to monitor the intensity of PL signal over a period of time, which allowed us to calculate the diffusion rate of Tb ions.

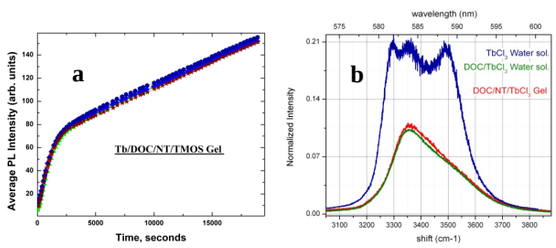

Fig.1 a. Integrated PL intensity (540-550nm, at 488 nm excitation) of Tb in SWNT/DOC hydrogel.
b. Superimposed PL spectra of Tb ion in water solution, DOC solution, and SWNT/DOC hydrogel at 488 nm wavelength of excitation.

The PL emission intensity of Tb ions diffusing into TMOS/SWNT/DOC gels from $TbCl_3$/water solution (Fig.1a) shows at least two regions with different kinetics of ion propagation. One can explain this by considering ion diffusion through regions with very dissimilar properties/morphologies. Even though our hydrogel is composed of 90% water, the process does not resemble normal diffusion. To describe the physics of ion propagation in such system one needs to understand micelle formation mechanisms, as well as the Tb/SWNT interaction.

PL spectra of these three systems demonstrate substantial difference between gels and water solutions. For example, the 585 nm peak, corresponding to $^5D_4 \rightarrow {}^7F_4$ transition in the Tb/water solution has much more complicated fine structure, as compared to both Tb encapsulated in DOC micelles, and TMOS/NT/DOC gels (Pl is taken at 488 nm line of excitation) (Fig.1b). Similarity of the peak shape and absence of the peak fine structure in DOC/Tb solution and NT/DOC/Tb gel gives us a hint that the formation of the DOC micelles around Tb ions may play an important role. We speculate that DOC encapsulation results in better screening of Tb ions from the water molecules.

Another interesting signature of Tb encapsulated systems was revealed by the time-resolved PL spectroscopy. The PL decay trace for a NT/DOC/Tb gel is shown in Fig. 2a with a PL decay time of 2.33 ms. This value is 5 times longer than in the Tb/water solution. For all studied samples the decay time reflects the degree of ion screening from the water environment (Fig. 2b) due to encapsulation and the gel morphology.

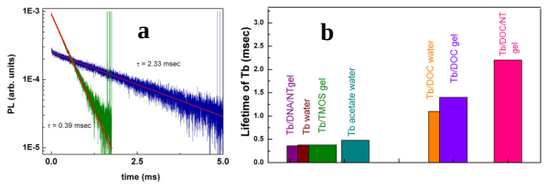

Fig 2 a. Decay curves of the $^5D_4 \rightarrow {}^7F_4$ luminescence of Tb in water solution, and SWNT/DOC hydrogel at 488 nm wavelength of excitation. b. PL lifetime diagram for Tb in different surounding .

In conclusion, we measured the diffusion rate of Tb ion propagating through the SWNT/DOC gel. The PL lifetime of 2.3 ms for Tb incorporated in SWNT/DOC gel have been measured. Our observations are consistent with the formation DOC micelles around the ions.

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