Proton exchange mechanism of synthesizing CdS quantum dots in nafion

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Nanocrystals of CdS are synthesized in the proton exchange membrane nafion in different sizes in the range 1.6 to 6 nm. To understand the process leading to the formation of these quantum dots, we have probed the proton exchange by ac conductance measurements in the frequency range 100 Hz to 13 MHz. Nafion shows good electrical conductivity due to proton transport probably via the Grothuss mechanism. Incorporation of cadmium ions by replacement of the hydrogen ions in the sulphonic acid group resulted in a large decrease in conductance indicating the reduction of the mobile carrier density. The conductivity plots all show strong frequency dependence with higher conductance towards the higher frequencies where a near-flat frequency response is seen. After the formation of CdS clusters, there is a partial recovery of conductance corresponding to the reinstatement of the protonic carriers on the side groups. The conductivity of the nafion films embedded with the semiconductor quantum dots exhibits a size-dependence with the highest conductivity obtained for the largest clusters. These findings lend clear experimental evidence for the model of synthesis of quantum dots in nafion by the exchange mechanism.

1 Introduction

The Mott-Wannier type of excitons in semiconductor nanocrystals have attracted attention in recent years in view of their novel optical properties. When the crystal size is typically smaller than the exciton Bohr radius, the electronic level structure is considerably modified with the level spacings dependent on the size of the crystallite, exhibiting the well-known quantum size effect or “blue shift” in the optical spectra. The optical absorption transition energies move towards higher photon energies as the size of the crystallite is lowered. CdS is a large band gap (2.4 eV) semiconductor crystallizing in the wurtzite structure in the bulk form. When grown as a microcrystallite, it takes the cubic zinc blende structure in the polymeric matrix nafion. The linear and nonlinear optical properties of CdS quantum dots in nafion prepared by the chemical route have been studied already. Nafion is a proton exchange membrane with a structure well-suited to the growth of the clusters in controlled ranges of sizes. The polymeric ions and absorbed electrolyte phase separate from the fluorocarbon backbone into approximately spherical clusters of about 4 nm diameter connected by short narrow (1 nm wide) channels. The configuration results from an energy minimization between the hydrophobic interaction of water with the backbone and the electrostatic repulsion of the proximate sulphonate groups.

Fig. 1 — (a) Chemical structure of nafion. (b) Model of the porous structure of nafion.
The route of synthesis followed in the preparation of the clusters is as follows:

(1) The virgin nafion is embedded in a solution of cadmium acetate (with the concentration and time chosen suitably).

(2) After cleaning and drying, the membranes are exposed to hydrogen sulphide gas.

(3) The films are then subjected to ammonia passivation.

The sizes of the CdS quantum dots so prepared have been determined by techniques including Transmission Electron Microscopy and X-ray diffraction. It is believed that in the above route of preparation, the cadmium ions first replace the hydrogen ions by an exchange reaction and then react with the hydrogen sulphide gas to form nuclei of CdS molecules which cluster to form the nanophase. There however is no independent experimental evidence for such a conjecture. The present study was aimed at providing the needed experimental evidence for the exchange mechanism.

2 Experimental Results

The ac conductance is measured at room temperature, using the HP 4192A LF impedance analyzer in a conductivity cell that provides for maintaining the temperature of the sample in a controlled manner. Fig. 2 shows the measured resistivity of undoped nafion and the conductance of the membrane after cadmium exchange, after ammonia passivation and after CdS quantum dots of 2 nm size are introduced. It is clearly seen that pure nafion exhibits a large conductivity throughout the frequency region and the first stage of ion exchange with cadmium ions resulted in a reduction of the conductivity. Ammonia passivation does not substantially alter the values but once the CdS dots are formed, there is a significant increase in the conductivity. Fig. 3 shows the detailed dependence of the resistivity behaviour on the sizes of the dots.

In order to obtain information on the nature of the carriers, the time dependence of the dc current is followed for the undoped nafion (Fig.4). There is a clear polarization behaviour reminiscent of the ionic carriers with only small, if any, of electronic component in the current.

3 Interpretation

Nafion in the undoped form is a protonic conductor. The protonic mechanism is likely to be of the Grothus type with the proton hopping assisted by water molecules. The effective number of protonic carriers is very high in the nafion membrane. When the cadmium ion exchange takes place, this effective number of carriers is drastically reduced and there is correspondingly a large fall in conductivity. The conduction is still protonic with a much diminished concentration of the carriers. The cadmium ions are comparatively immobile.

![Fig. 2 — Electrical resistivity versus frequency, at different stages: 1: undoped films 2: After Cd-ion exchange 3: After ammonia passivation 4.](image)

![Fig. 3 — Electrical resistivity versus frequency for undoped nafion films and films doped with CdS quantum dots of different sizes: 1: undoped nafion 2: 1.8 nm 3: 2.0 nm 4.](image)
and are not expected to contribute to the conduction process directly. With the formation of the CdS dots, following the exposure to the hydrogen sulphide gas, part of the cadmium ions are released from the sulphonic groups and are probably replaced by hydrogen ions. This effect is the largest for the clusters of the largest size because of the obviously greater numbers of cadmium ions which had originally replaced the mobile carriers the reverse of which process is responsible for the partial recovery of the conductivity. The mechanism of the protonic conduction must be a modified version of the Grothus model as it is the embedded CdS clusters which should aid in the proton transport, instead of the water molecules.

4 Conclusion

The results on the measurement of the changes in the electrical conductivity of the nafion membranes have provided a clear evidence of the exchange mechanism of synthesizing the CdS quantum dots. This is the first experimental proof for the operation of the proton-cadmium ion exchange in the ion-exchange membrane nafion. More quantitative studies on the mobility and concentration of the carriers in the polymer could be rewarding.

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