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ONE-DIMENSIONAL LUMINESCENCE KINETICS; A SUBMICRON PROBE

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Cylindrical naphthalene wires (10-1200 nanometer diameter) exhibit one-dimensional exciton annihilation kinetics for 10-30 nm wires, three-dimensional behavior for 100-1200 nm wires and a crossover diameter increasing from 4 to 77 K. Nuclear channel pore membranes (polycarbonate) serve as one-dimensional templates. Vycor glass pores are found to be effectively one-dimensional. The triplet exciton migration (multiple hopping) length is 25-50 nm. The recombination involves free and bound excitons.

1. INTRODUCTION

Recently, porous materials and "fractal" networks have been of much interest.[1-4] The difference between a fractal network and a quasi-one-dimensional network is not often all that clear.[1-5] Energy transfer[2,3] and exciton kinetics[4] have been used for the characterization of such networks (e.g. pore networks of porous media). Understanding the characteristics of truly one-dimensional networks and the effects of sample diameter is thus of practical interest.

2. THEORY

Diffusion-limited reaction kinetics in one-dimension differs drastically from the classical behavior.[6,7] The reaction

$$A + A' \rightarrow A' \qquad (1)$$

has a rate-coefficient of the form

$$K = K_0 t^{-1/2} \qquad \text{(1-dim)} \qquad (2)$$

instead of the classical result

$$K = K_0 \qquad \text{(3-dim)} \qquad (3)$$

The reaction (1) applies to exciton annihilation. For materials with defects A' is a trapped exciton and A a free exciton. For perfect materials all excitons are free. In both cases eqs. (2) and (3) are valid. The practical question is: How thin has a wire to be to exhibit the one-dimensional behavior of eq.(2)? Theoretically, the radius of the wire should be smaller than the range of the exciton motion (within its lifetime). This ~~range~~ was recently estimated[4] to be about 100 nm. For triplet excitons the rate coefficient K is derived from delayed fluorescence and phosphorescence time decays.[4] For $A + A' \rightarrow A'$ the pseudo-unary kinetics gives: $K = F/P$. We test eqs.(2) and (3) by writing

$$F/P = K = K_0 t^{-h} \qquad (4)$$

where we expect $h = 1/2$ for 1-dim. and $h = 0$ for 3-dim. kinetics.

3. EXPERIMENTAL METHODS

We have produced thin naphthalene "wires" with diameters ranging from 10 to 1000 nm. The optical set-up and sample preparation have been described before.[4,8] The only significant change involves the use of channel-pore ("nuclepore")[9] polycarbonate membranes. These 6 micron thick membranes come with well isolated, ~~cylindrical~~ pores (Fig. 1). The totality of the h values (negative slopes), for all wires (each at 4 K and 77 K), is given in Fig. 2.

4. RESULTS

We observe that the thinnest wires yield a value $h \cong 0.5$, while the thickest wires give a value $h \cong 0$, for both temperatures. Actually,

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FIGURE 1
Channel-pore membrane: polycarbonate ("Nuclepore"[13]). Enlargement about x 10^4. Pore-length 6 microns.

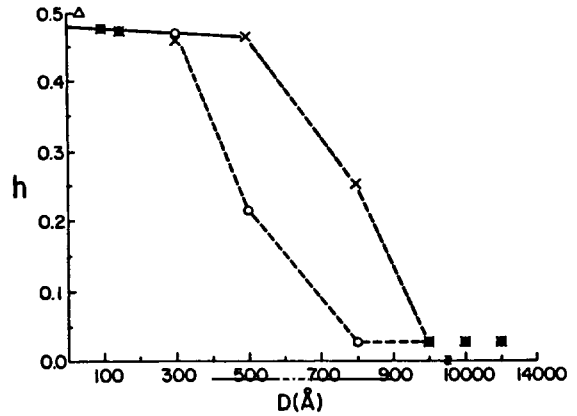

FIGURE 2
Exponent h vs. wire diameter, D (in Angstroms), at 4 K (O) and 77 K (X). Note break in scale.

extrapolating to zero diameter, $h \to 0.49 \pm 0.02$. On the other hand, for the micron sized wires $h \to 0.02 \pm 0.02$. These two limiting values are in excellent agreement with the theoretically expected values of $h = 1/2$ and $h = 0$, respectively. The cross-over (between $h \cong 1/2$ and $h \cong 0$) occurs at diameters of about 500 to 800 A^o at 4 K and 77 K, respectively. The higher value at higher temperatures is consistent with a somewhat faster hopping rate.

5. DISCUSSION

An indirect, rough estimate for the naphthalene cruising range in similarly prepared samples was given[4] as $\lambda = 1000$ A^o. This is in excellent agreement with our present result ($\lambda \cong 500$ A^o). Obviously, for wires with radius $r >> \lambda$ the excitons do not "feel" the pore boundaries while for $r << \lambda$ the excitons are severely confined along two of the three directions.

6. CONCLUSIONS

In summary, we have produced cylindrical molecular crystal wires down to a diameter of 10 nm. The recombination process involves free and bound excitons ("heterofusion"). The triplet exciton kinetics fits a multiple-hopping model. The overall migration range is about 25 nm at 4 K and 40 nm at 77 K. The long-time exciton transport is strictly one-dimensional in the ultra-thin wires. The fractal-like kinetics model works well in a low-dimensional non-fractal system. The exciton annihilation method appears to be a reliable tool for probing spectral dimensions and low-dimensional topologies.

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