SIZE QUANTIZATION OF FeS$_2$ (PYRITE) PRODUCED IN A POLYMER MATRIX

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Quantum or Q-particles of FeS$_2$ were synthesized in an ion-exchange polymer (Nafion) matrix by treatment of Fe^{2+}-exchanged polymer with H$_2$S and S at 120°C for 16 days. For comparison Q-FeS$_2$ was also prepared in MeOH and MeCN. Size quantization effects were determined from the absorption spectra. Compared to bulk FeS$_2$ ($E_g = 1.0 \pm 0.2$ eV), a blue-shift of about 0.5 eV was observed for the absorption edge of the Q-particles prepared in Nafion, while a shift of about 1.0 eV was observed for the Q-colloidal particles suspended in the organic solvents. The smaller blue-shift for the sample prepared in Nafion may be related to the effect of moisture on particle growth.

We report here the synthesis of quantum or Q-particles of FeS$_2$ in the ion-exchange polymer Nafion (Nafion is a perfluorosulfonated ion exchange polymer) [1] matrix. These particles were formed by exchanging ferrous ion followed by dehydration and reaction with hydrogen sulfide and sulfur. Semiconductor particles (e.g. of CdS) can be generated in a Nafion matrix by exchanging metal ion (Cd^{2+}), followed by treatment with a suitable precipitant (H$_2$S) [2]. Much smaller CdS particles can be formed in Nafion, if the H$_2$S is reacted with dehydrated cadmium-exchanged Nafion in the gas phase [3,4]. The Q-particles [5] had larger bandgaps than the bulk material (up to 2.76 eV) and were identified with particles with diameters as small as 50 Å. The preparation of semiconductor chalcogenides, from molecular DcX (X=Se, S) to bulk material, in Nafion can also be accomplished by an ion-dilution technique [4]. The absorption onset for the cadmium chalcogenides formed in this manner can be tuned over a range of more than 3.5 eV by varying the Cd^{2+}/Ca^{2+} ratio in the solution used to exchange the acidic form of the ionomer membrane. The synthesis of pyrite is less straightforward and often requires high temperatures. For example, Tributsch and coworkers [6] synthesized pyrite crystals by heating H$_2$-reduced iron powder and high purity sulfur lumps at 650°C in evacuated and sealed quartz ampules in the presence of a small amount of iodine. However,

the use of a high temperature is a significant disadvantage for our purpose of synthesis of small particles in Nafion. Berner [7] reported that pyrite can be synthesized at neutral pH in concentrated sulfide solution and in natural sediments by the reaction of precipitated FeS with elemental sulfur at 65°C. Moreover, the kinetics of pyrite formation in the reaction between FeS, sulfur, and H$_2$S in aqueous solution have also been investigated [8]. The same approach was modified for synthesis of pyrite in Nafion.

Nafion 115 (1100 g/eq., 5 ml thickness; E.I. DuPont de Nemours, Inc., Wilmington, DE) was cleaned, by boiling in concentrated HNO$_3$ twice, then rinsing in boiling Millipore water twice; it was then stored in Millipore water. The protonated Nafion samples were soaked in 1 M FeSO$_4$(aq) overnight. After rinsing in Millipore water, their surfaces were blotted with soft tissue paper (Chem Wipes), and the samples were dried in a vacuum oven at 120°C for 4 h. The samples were transferred into a tube under vacuum and then exposed to 1 atm of H$_2$S with elemental sulfur (Millinckrodt, Paris, TX) contained in the tube. The tube was finally sealed and the gas phase reaction was allowed to take place at 120°C for 16 days. The same experimental conditions were used to synthesize FeS$_2$ powder by the reaction between dissolved ferrous ion and aqueous thiosulfate [6], according to the equation

$$Fe^{2+} + 4S_2O_3^{2-} \rightarrow FeS_2 + 3S + 3SO_4^{2-} . \qquad (1)$$
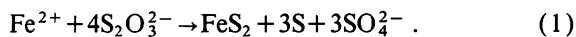
In this reaction elemental sulfur is produced and thiosulfate thermally decomposes to H_2S and SO_4^{2-}.

To demonstrate the formation of FeS_2, the samples were quantitatively analyzed after they were removed from the tube and heated in a vacuum oven at 120°C for several hours to get rid of any excess unreacted sulfur. The samples were first decomposed by wet oxidation with bromine and nitric acid [9]. The reaction may be represented as follows:

$$FeS_2 + \tfrac{15}{2}Br_2 + 3HNO_3 + 8H_2O$$

$$\rightarrow Fe(NO_3)_3 + 2H_2SO_4 + 15HBr .$$
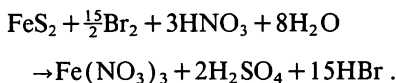
The determination of sulfur was based on the oxidation of sulfide to sulfate and the precipitation of the latter as barium sulfate. The iron was determined spectrophotometrically be adding 1,10-phenanthroline (99+% Aldrich, Milwaukee, WI) to the solution after the iron was reduced from the 3+ to 2+ state with pure powdered aluminium (Fisher, Fairlawn, NJ). The amount of iron was then determined by comparison to a standard calibration curve. The final results for both samples confirmed the formation of FeS_2. Note that a commercial FeS_2 powder (AESAR, 99.9% Seabrook, NH) analyzed by this method demonstrated the reliability of this approach. Moreover a blank with Nafion alone analyzed by this method showed only a negligible amount of Fe and S, demonstrating the lack of interference by polymer sulfonate.

To investigate the size quantization effect, several different pyrite samples, from Q-state to bulk material, were prepared by the same approach and the absorption spectra were taken for comparison. The absorption spectra were taken either on an HP model 8451 A (Hewlett–Packard, Palo Alto, CA) diode array or a Cary 17 (Varian, Palo Alto, CA) spectrophotometer.

Fig. 1 shows the absorption spectra of the two bulk material samples. An FeS_2 film (≈ 1.5 μm thick) was prepared by evaporating FeS_2 powder onto glass substrates in a vacuum chamber ($\approx 1.5 \times 10^{-6}$ Torr). The dry suspension sample was prepared by depositing several drops of FeS_2 (≈ 10 μm particle size) suspension on the quartz cell and pumping to dryness. The absorption edges of both samples were at ≈ 1060 nm corresponding to an energy gap of ≈ 1.17 eV. The reported value for the energy gap of bulk FeS_2 was about 1 ± 0.2 eV [10–19]. Compared to bulk

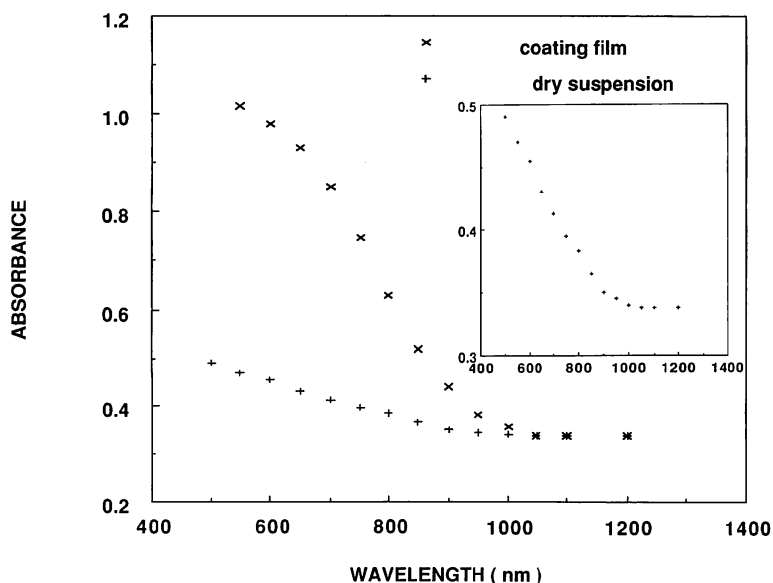Fig. 1. The absorption spectra of two bulk FeS_2 samples, ×, FeS_2 film (≈ 1.5 μm thick); +, dry suspension (≈ 10 μm).
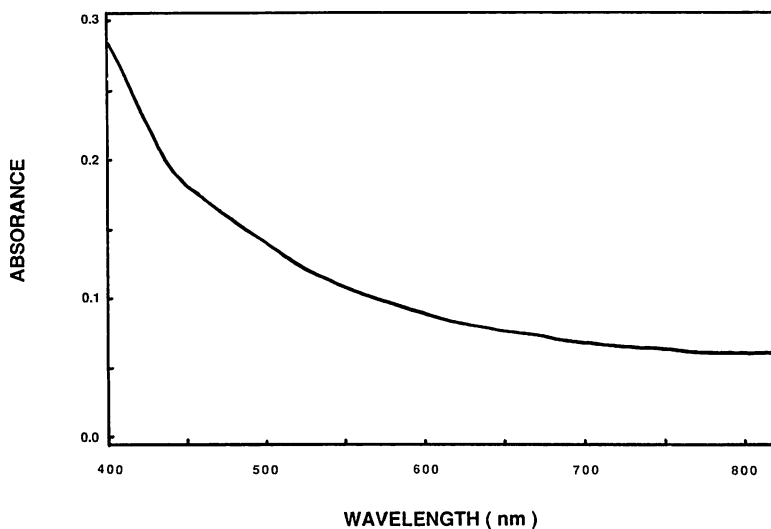
Fig. 2. The absorption spectrum of FeS_2 particles prepared in Nafion with blank Nafion as reference.

FeS_2, a blue-shift of about 0.5 eV was observed for the absorption edge of the Q-particles prepared in Nafion, as shown in fig. 2.

As reported earlier [20], Q-colloidal particles of FeS_2 can also be prepared from bulk material by intensive stirring. There have also been several reports [21-24] of CdS colloids prepared directly in an organic solvent such as MeCN, with rapid precipitation under conditions where particle growth is hindered. Colloidal dispersions of FeS_2 were prepared both in MeOH and MeCN as follows. After 200 mg of FeS_2 powder was introduced in to a beaker containing 40 ml of solvent, the mixture was intensively stirred for 1 day. The mixture was allowed to settle for another day. The supernatant solution, which was colorless and transparent, contained FeS_2 colloid.

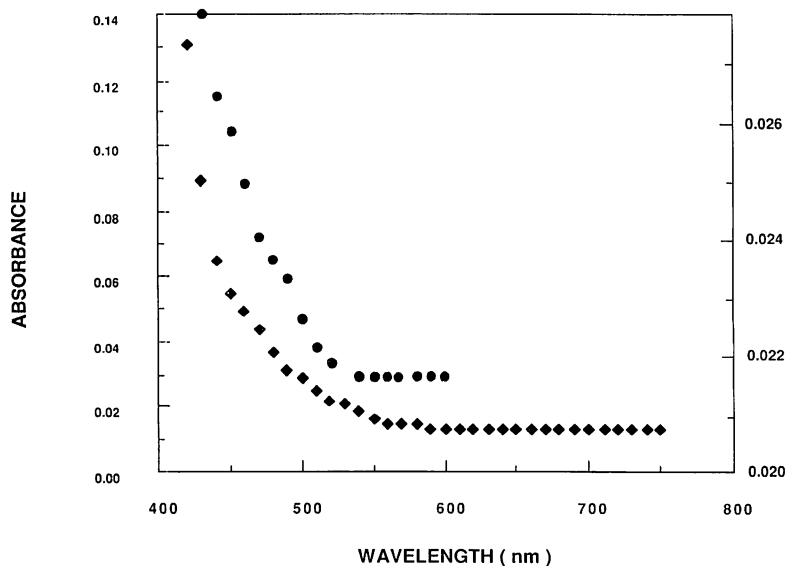Fig. 3. The absorption spectra of FeS_2 colloidal dispersion prepared in CH_3OH (♦, left scale) and CH_3CN (●, right scale) from bulk material.

This solution was then centrifuged and used in the absorption spectrum measurements.

Compared to bulk FeS_2, a blue-shift of about 1 eV was observed for the absorption edge of the small semiconductor particles suspended in both MeOH and MeCN, as shown in fig. 3.

The sample prepared in Nafion has a smaller blue-shift than the colloidal dispersion samples prepared in organic solvents. This may have something to do with the effect of moisture on particle growth, as reported for CdS samples prepared in Nafion [4]. After removing the excess H_2S, when open to the humid air, the film changed from a clear colorless film to a clear yellow film in minutes. Future work will concentrate on the systematic study of the moisture effect on FeS_2 particles prepared in Nafion.

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