

# CELLULOSE-BASED SYNTHESIS OF PHOTOCATALYTIC CADMIUM SULFIDE SEMICONDUCTOR NANOCRYSTALS WITHIN MICROPOROUS FIBERS FOR GENERATION OF HYDROGEN FROM WATER AND SUNLIGHT

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*Received June 25, 2012*

A simple general procedure for the cellulose-based creation of non-agglomerating nanocrystals ranging in size up to 30 nanometers is described. The nanocrystals are located within the micropores of a low-cost, commercially available, hydrophilic cellulosic matrix and are separated by the water-permeable walls of the pores. The successful application of the procedure to the formation of the water-splitting semiconductor cadmium sulfide within the fibers of a commercial pulp derived from Western Red alder (*Alnus rubra* Bong) wood is evidenced by the bright yellow color of the fibers and is confirmed by gravimetric analysis, X-ray mapping, as well as by atomic force and scanning electron microscopy.

**Keywords:** cellulosic nonwovens, microporous fibers, paper, semiconductors, nanocrystals, photocatalysis

## INTRODUCTION

Elemental Hydrogen, as an alternative, non-polluting, sustainable energy source for vehicles, is being extensively studied worldwide and is in actual commercial use in Iceland,<sup>1</sup> where the gas is generated from geologic volcanic sources. Elsewhere in the world, much research<sup>2-8</sup> on hydrogen generation is currently ongoing, but the key question still to be answered is how this attractive hydrogen fuel will be obtained economically. One promising approach is simply to split water with sunlight aided by a semiconductor photocatalyst. Unfortunately, most of the semiconductors that can function as photocatalysts to split water do not have the correct band gap to utilize visible light fully. Cadmium sulfide (CdS), which has a band gap of about 2 eV, apparently does not have this deficiency. Recently, an effective, laboratory scale system based on nanocrystalline CdS and devised in China has received much publicity.<sup>9</sup>

However, the use of nanocrystals in an industrial scale process poses some challenging chemical engineering problems. These include the difficulty of manufacturing and managing an

aqueous suspension of fine particles together with the propensity of the nanocrystalline materials to undergo agglomeration with a diminution of the catalytic activity due to the loss of surface area. The mechanism of this unconstrained nanoparticle fusion has been recently elucidated by two groups by the employment of special electron microscopy techniques.<sup>10</sup> Apparently, nanocrystal growth is a subtle process of rotation and orientation, followed by fusion and the healing of defects.

The practical chemical engineering challenges of practical nanocrystal use might be met by the synthesis of a non-agglomerating photocatalyst, which is simultaneously both nano- and micro-sized. This apparently impossible combination could be achieved by locating the nanocrystals within a larger micro-sized matrix so that agglomeration is prohibited therein and the composite is sufficiently large so as to avoid the handling of tiny particles.

This article describes the synthesis of such composites in which the nanocrystals are cadmium sulfide, distributed throughout and *Cellulose Chem. Technol.*, **47** (1-2), 1-4 (2013)

constrained within a matrix, which is a microporous cellulose fiber, exemplified by a commercial wood pulp, cotton or regenerated cellulose. The fibers can be subsequently employed separately or in the form of paper and nonwovens, as well as in conventional woven or knitted fabrics.

The lowest cost cellulosic fibers (pulp) are those first derived by the industrial chemical conversion of wood to paper. In this research, these were the type of fibers mostly employed as the matrix. The pore dimensions created therein by the chemical removal of the lignin macromolecules and hemicelluloses range in size from 6 to 300 Å (0.6 to 30 nm).<sup>11,12</sup> The volume of these pores is about 2 mL per gram in fibers that have not been dried and are as created from wood as the so-called “never-dried pulp”. This pore volume corresponds to the so-called fiber saturation condition where all the pores are filled with water.

When fibers or assemblages in this “never-dried” condition are contacted with an aqueous solution of a soluble cadmium salt, the small cadmium ions (ionic radius 0.97 Å)<sup>13</sup> diffuse into the water contained in the much larger fiber cell wall pores and the concentration of cadmium salt solution outside of the fibers is diminished by the amount of water in the pores. After equilibrium is attained, filtration removes the diluted cadmium salt solution outside the fibers but leaves the pores within the fiber filled with a cadmium salt solution in a state of fiber saturation. Because of the small size of the pores, removal of the cadmium salt solution from the fibers by pressure filtration is practically impossible.

Upon exposure of these wet fibers or assemblages to hydrogen sulfide gas, the gas dissolves in the water of the contained cadmium salt solution and thereafter reacts with the cadmium ions therein to form insoluble cadmium sulfide inside the pores of the fiber cell walls. Since the volume of each of the pores is nanosized, the size of the cadmium sulfide precipitated therein must be even smaller. Because the length of the fibers is about 2 mm and the width about 30 microns, this procedure yields bright yellow nanocrystalline cadmium sulfide within an easily handled, micro-sized matrix of individual cellulose fibers. When the counterion of the cadmium salt is chloride or sulfate, the corresponding mineral acids are formed and are removed by washing with water.

A variety of other inorganic structures can

likewise be created within the pores of cellulosic fibers<sup>14,15</sup> and a broad range of new cadmium-based candidate compositions have been described in the patent literature.<sup>16,17</sup>

## EXPERIMENTAL

### Materials

The cellulose fibers were from a never-dried commercial kraft pulp (NDP) of Western red alder (*Alnus rubra* Bong). The cadmium sulfate was of analytical grade, while the sodium sulfide and 98% sulfuric acid were of technical quality.

### Methods

#### *Preparation of CdS-cellulose fiber composites*

A uniform aqueous suspension of the snow-white pulp (NDP) fibers (7 g) was filtered through a screen under reduced pressure to form into a wet paper-like nonwoven sheet that was then immersed in an aqueous solution (7 g) containing cadmium sulfate (100 mg). After 1 h, the impregnated sheet was collected, subjected to reduced pressure to remove extrafibrillar cadmium sulfate solution, and then exposed for 12 h to an atmosphere of hydrogen sulfide, separately generated by treatment of sodium sulfide with sulfuric acid. The bright yellow sheet created was thrice resuspended in water and reformed by filtration before being air-dried for 24 h. The ash content, in triplicate, was then measured gravimetrically after combustion at 500 °C for 3 h.

#### *Scanning electron microscopy of CdS-containing cellulose sheets*

Dried sheets were cut into square samples with a surface area of approximately 1 cm<sup>2</sup>. The samples were smoothed using an electropolishing layer and scanned at 10,000x magnification with a Sirion XL30 FEG scanning electron microscope (FEI Co. Hillsboro, OR 97124). The electrons were accelerated at between 5 and 10 keV. The surface morphology of the samples was determined with the energy-dispersion X-ray analyzer of the SEM equipment.

#### *Atomic force microscopy of CdS-containing cellulose sheets*

The formed sheets were dried and cut into small squares with a surface area of approximately 1 cm<sup>2</sup>. These samples were stored in a vacuum chamber to avoid any contamination. A Nanosurf Easy Scan 2 AFM system (Nanosurf Inc., Boston, MA, 01906) with long contact Mode SFM tip with a 0.2N/m spring constant was used to obtain local topographic plots of the sample.

## DISCUSSION

The readily commercially available forms of cellulose fibers are delignified wood fibers, cotton and regenerated cellulose (rayon), which can be

assembled into the form of paper, nonwovens or woven and knitted fabrics by established technologies. Each of the fibers in these structures possesses an intrinsic pore structure that has been extensively characterized.<sup>11,12</sup> The onset of the precipitation of the cadmium sulfide within the fibers is immediately apparent from the color transition of snow-white fibers to bright yellow as the impregnated fibers or structures are exposed

to the hydrogen sulfide gas. The visual intensity of the yellow color is increased as the concentration of the cadmium ion in the impregnating solution is augmented (Fig. 1). The yellow color cannot be mechanically removed from the fibers by repeated washing with water and the amount of the cadmium sulfide trapped within the fibers can be conveniently measured by gravimetric analysis.

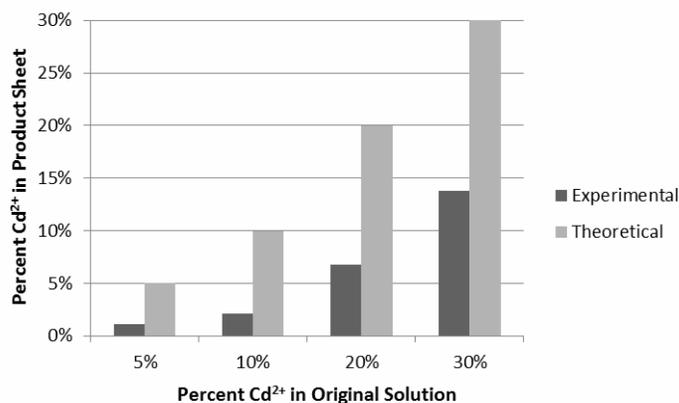


Figure 1: Comparison of theoretical and experimental amounts of precipitate found in sheets designed to contain 5, 10, 20 or 30% of cadmium sulfide

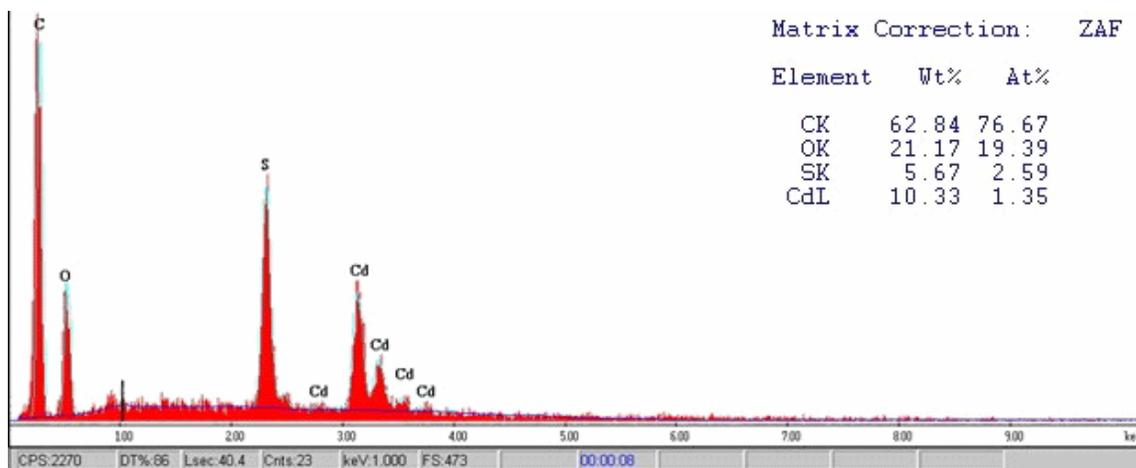


Figure 2: X-Ray analysis of fibers containing 10.33% of cadmium sulfide

The fibers containing cadmium sulfide were further characterized by X-ray examination of a sheet containing about 10% of the sulfide (Fig. 2).

The location of the cadmium sulfide within the fiber structure is additionally evidenced by the failure of atomic force microscopy to detect the

presence of any nanocrystals on the exterior fiber surface (Fig. 3).

Furthermore, scanning electron microscopy demonstrated the presence of the cadmium sulfide nanocrystals within the fibers. Due to the performance characteristics of the X-ray analyzer,

the fiber is invisible, and only the cadmium

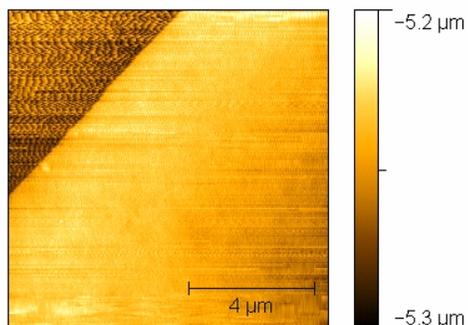


Figure 3: An atomic force microscopy image of the outside wall of a single cadmium-containing fiber taken at a resolution of 10 by 10 nm. No cadmium sulfide crystals can be observed on the outside fiber surface

sulfide crystals can be observed (Fig. 4).

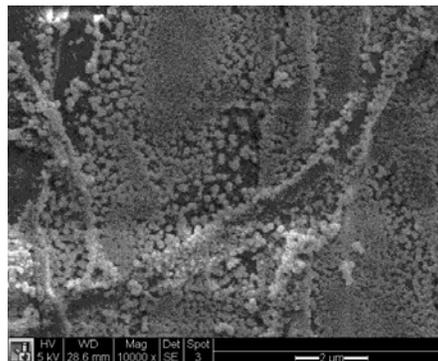


Figure 4: A scanning electron microscopy image of a cadmium-containing fiber. Due to the performance characteristics of the X-ray analyzer, the fiber is invisible, and only the cadmium sulfide crystals can be observed

## CONCLUSION

This research has shown that low-cost, commercially available, hydrophilic and microporous cellulose, in fiber, sheet or fabric form, can function as an easily handled matrix for the preparation of nanocrystals constrained from agglomeration by location within the containing nanosized pores. When these assemblages contain photocatalytic semiconductors, new and potentially substantial market opportunities for cellulose can be envisaged.

**ACKNOWLEDGEMENTS:** Thanks are due to Assoc. Dean E. A. Riskin of the College of Engineering for the award of funds to support the SEM studies and to Professor R. M. Overney for access to his AFM facilities.

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