Solution-Growth of Zinc Oxide Nanowires for Dye-Sensitized Solar Cells

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Abstract:

Zinc oxide nanowires grown from aqueous solutions of methenamine and zinc nitrate are used in dye-sensitized solar cells. The growth mechanism of the ZnO nanowires and the solution chemistry is not yet well understood. During the reaction, heterogeneous growth of nanowires is limited by homogenous nucleation of ZnO particles. The reaction kinetics were studied by complexometric titration. It was determined that homogeneous nucleation of ZnO particles is first order in methenamine and zinc nitrate concentration. The kinetics of the heterogeneous growth of ZnO nanowires was also studied to determine if the nanowire growth follows the same kinetics as the homogenous ZnO particle growth.

Introduction:

Dye-sensitized solar cells (DSSCs) have the potential to convert solar power to electricity efficiently and at a low cost, making it promising solar cell architecture for large scale solar energy implementation. There are three main components to a DSSC; (1) a ~10 μm thick film of wide band gap semiconductor nanoparticles such as TiO_2 or ZnO nanoparticles, (2) a monolayer of organic dye molecules absorbed onto the semiconductor, and (3) a liquid electrolyte containing the redox couple I^-/I_3^- which interpenetrates the dye-coated nanoparticles. When a photon excites the electron in the dye, it is injected into the semiconductor and is carried to the anode and through the load to the cathode where it reduces the I^- in the electrolyte. The I_3^- then regenerates the dye thus completing the circuit.

In conventional nanoparticle DSSCs, the electrons diffuse to the anode by hopping 103-106 times between particles [1]. With each hop, the electron can recombine with the electrolyte. The diffusion rate and recombination rate are both on the order of milliseconds, allowing recombination to limit the efficiency of the DSSC. However, ZnO nanowire DSSCs provide a direct path to the anode, which increases the diffusion rate without increasing the recombination rate and could therefore increase the efficiency of DSSCs.

In the solution growth of ZnO nanowires, two types of crystal nucleation compete. Homogenous nucleation produces undesired ZnO particles and heterogeneous nucleation produces nanowires. In the existing procedure, the homogenous nucleation of ZnO particles dominates and depletes the precursor limiting the wire growth. To understand the kinetics and to hypothesize a mechanism that replicates the data, the rate of Zn^{2+} depletion was observed with time and various initial concentrations of reagents.

Experimental Procedure:

To determine the Zn^{2+} concentration, complexometric titration with ethylenediaminetetraacetic acid (EDTA) was used [2]. First, homogenous nucleation of ZnO was monitored. The reaction took place in 15 ml centrifuge tubes with 10 ml of DI water containing 0.016 M of $Zn(NO_3)_2$ and 0.025 M of methenamine. The tubes

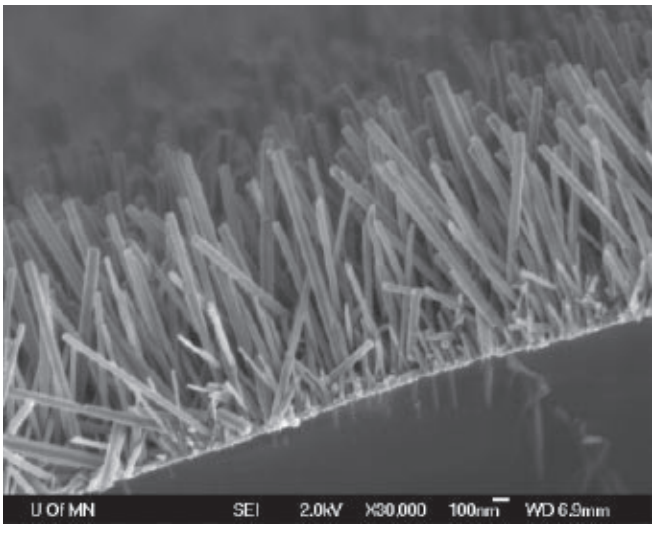

Figure 1: SEM image of ZnO nanowires at 240 minutes.

were placed in an oven set at 95°C and were removed at various time intervals. The tubes were centrifuged at 3000 rpm for 30 minutes to remove suspended ZnO particles from the solution, which interfere with the titration. Then 1 ml of the solution was placed in a beaker with 25 ml of DI water and 5 mL of pH 10 ammonium buffer. While stirring vigorously, a drop of eriochrome black T indicator was added and the solution was titrated with 0.002 M EDTA. The procedure was repeated with 0.050 M and 0.0125 M methenamine to see the effect of methenamine concentrations.

It was hypothesized that the depleted Zn^{2+} became ZnO particles and there was no unaccounted for Zn^{2+}. To justify this statement, particles were collected from the tubes and weighed. The structure of particles was also found using x-ray diffraction.

ZnO nanoparticles were synthesized by mixing of 0.001 M of zinc acetate and 0.0016 M of NaOH at 35°C with isopropanol as solvent [3]. The nanoparticles were rocker coated onto (100) silicon substrates. The substrates were annealed at 450°C for 30 minutes. Then, substrates were washed with DI water. The substrates were coated, annealed, and washed again.

Heterogeneous nucleation was monitored by placing the coated silicon substrates inside the centrifuge tubes. When the tube was removed from the oven, the substrates were taken out and washed. Horizontal views of the substrates were taken with SEM JEOL 6500 model, see Figure 1. The lengths of nanowires were measured and average nanowire lengths were determined as a function of time.

Results and Conclusions:

Figure 2 shows no significant change in Zn^{2+} concentration was observed until 50 minutes. The temperature profile of the solution indicated that the solution comes to its final temperature of 95°C at this time. To remove the temperature effect, rate constants were calculated by finding the slope of the $\ln[Zn^{2+}](T)/[Zn^{2+}](T_0)$ versus $(T\text{-}T_0)$, where T_0 is the time 95°C was reached. The contribution of Zn^{2+} concentration to the depletion rate was determined to be first order. Methenamine concentration was also determined to be first order. As seen in Figure 3, the rate constants change with initial concentration of methenamine.

When the heterogeneous reaction was done simultaneously in the tube, similar rate constants were derived. It is safe to conclude that heterogeneous did not interfere with the homogeneous reaction. As can be seen in Figure 4, the average wire length increases with time, but its kinetic behavior cannot be concluded.

Future Work:

The rest of the substrates that were made must be imaged with SEM to make more graphs similar to Figure 4, which shows the wire growth over time. The data will then be compared with the titration data to discuss the possible relationship between heterogeneous and homogenous nucleation.

Acknowledgments:

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References:

[1] Baxter, J. B.; Walker, A.; Ommering, K.; Aydil, E. Nanotechnology June 2006, 17.

[2] Boercker J. Synthesis of ZnO Nanowires and TiO_2 Nanowires for DSSC, April 2006.

[3] Searson et. al. J. Coll, Inter. Science 2003,

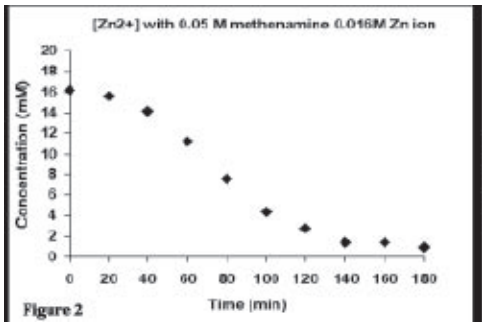

Figure 2

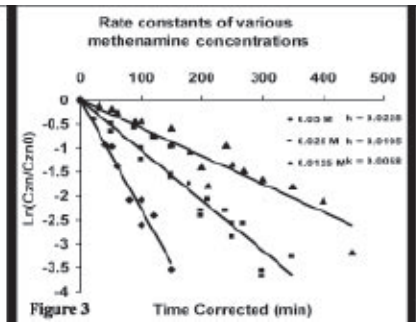

Figure 3

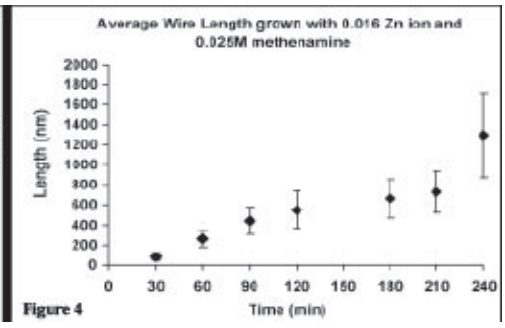

Figure 4