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“Nanostructured hybrid materials for controlled energy release”

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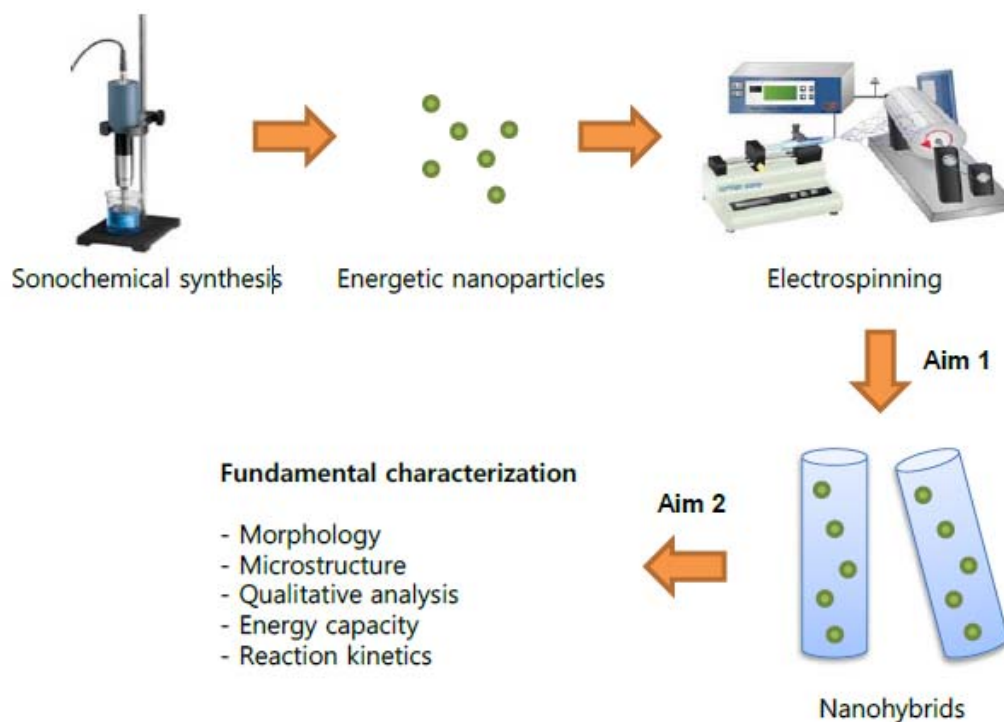
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Abstract: Experiments were performed to confine energetic nanoparticles (aluminum nanoparticles) on to a carbon nanofiber matrix in order to control the reactivity of the aluminum nanoparticles. We achieved nanohybrid materials of aluminum nanoparticles wrapped with Carbon nanofibers (CNFs) by electrospinning method. The morphology of aluminum decorated carbonized CNFs were studied by transmission electron microscopy (TEM). We found that the degree of dispersion of aluminum on CNFs changing depending upon the nature of energetic nanoparticles, surfactant and experimental condition.

1. Introduction

Hydrogen is a promising source for the substitution of fossil fuels since it is a non-limited and non-polluting energy. It has a number of advantages compared to other chemical energy carriers. However hydrogen that itself is not safe source of energy. Therefore, we conducted an experiment with aluminum nanoparticles to control the reaction rate. The aluminum nanoparticles are a key material for hydrogen production. Ultimately, it is important point to know optimal ways to store and exploit hydrogen as a fuel source.

(Scheme describing the overall research outline)



[Research plan]

Aim 1: Explore efficient routes to confining energetic nanoparticles to a matrix via electrospinning.

→ The role of Chonnam National University Research Group

Milestone for Aim 1:

1. Establish reliable ways for encapsulating energetic nanoparticles into a matrix via electrospinning
2. Characterize structurally and qualitatively the obtained nanohybrids.
3. Examine the functionality (hydrogen generation) of the nanohybrids.

Aim 2: Identify major parameters determining energy release (reaction kinetics) from the obtained nanohybrids, and finally understand how the energy release can be controlled from materials point of view.

→ The role of Air Force Research Lab (AFRL)

If the Aim 1 is successfully achieved, we will systematically characterize the nanohybrids with respect to energy content and reaction kinetics. There are several key variables that would affect the energy release, including chemical composition, crystallinity, and microstructure of encapsulated particles. The structural and chemical properties of matrix used may affect the energy release. Moreover, we can control the dimensions of the nanohybrids to change reactants diffusion and effective adsorption surface.

Milestone for Aim 2:

1. Investigate the energy release of the nanohybrids.
2. Examine the relationship between the nanohybrids properties and energy release.
3. Determine parameters that influence significantly the energy release.

2. Experimental Details

Preliminary studies. Recently, Dr. Bunker has shown that the reaction rate of aluminum nanoparticles with water can be retarded by wrapping the aluminum nanoparticles with graphene oxide sheets. On the other hand, our research group at Chonnam National University (CNU) has conducted extensive study on the fabrication, characterization, and energy applications of carbon nanofibers using polymer precursors. In particular, diverse functional nanoparticles such as silicon, metal oxides, V_2O_5 , and graphene have been successfully incorporated into electrospun carbon nanofibers for enhancing charge transfer and/or storage. Therefore, it will be of great utility if we can control the reaction rates of energetic nanoparticles using electrospinning-mediated encapsulation. In addition, we can probably achieve both polymer and carbon wrappings without and with heat treatment. It is important that aluminum nanoparticles maintain their unique properties during the encapsulation.

Aluminum oxide, aluminum nanopowder and dispersion solution of aluminum nanoparticles (sample of aluminum nanoparticles decorated with aluminum oxide and oleic acid are dispersed in dodecane solution) were chosen as energetic nanoparticles. The experiment was allowed to proceed in the order aluminum oxide, aluminum nano powders, dispersion solution of aluminum nanoparticles. These energetic nanoparticles were incorporated into both polymer (polyacrylonitrile) and carbon nanofibers via electrospinning. This carbon nanofibers (CNFs) were carbonized and observed morphology via transmission electron microscopy (TEM).

[Materials]

- Aluminum oxide (Aldrich, Mw: 101.96 g/mol, CAS No. 1344-28-1, Particle size: <50 nm)
- Aluminum nanopowder (particle size: 40 nm, commercialized)
- Dispersion solution of aluminum nanoparticle (aluminum/dodecane: 300 mg/ml) (obtained from Dr. Bunker)
- AOT (dioctyl sulfosuccinate sodium salt, Aldrich, Mw: 444.56g/mol, CAS No. 577-11-7)
- DTAB (n-dodecyltrimethyl-ammoniumbromide, Merk, Mw: 308.35 g/mol, CAS No. 119-91-4)
- PVP (Polyvinylpyrrolidone, Aldrich, average mol wt 10,000, CAS No. 9003-39-8)
- SDS (Sodium dodecyl sulfate, JUNSEI, Mw: 288.39g/mol, CAS No. 288.38)

a) Aluminum oxide

It was pre-experiment for dispersion of the aluminum nanoparticles. Because, the reactivity of aluminum oxide particles are lower than aluminum nanoparticles. Several surfactants

were used to make uniform dispersion of the Aluminum oxide in the matrix such as AOT, DTAB, PVP, SDS.

In order to predict the performance of a surfactant, we conducted experiment in advance. In the pre-experiment, aluminum oxide particles and surfactant was dispersed in distilled water and centrifuged. As a result of this pre-experiment, the solution of dispersed aluminum oxide particles using DTAB and AOT as surfactant were observed with excellent dispersion. So, we decided to use the AOT and DTAB as surfactant. The result of measurement through TEM, surfactant improves the dispersion of aluminum oxide particles in Carbon nanofibers (CNF) and improvement of stability of aluminum oxide particles wrapped with CNF. When comparing the DTAB and AOT, DTAB is more excellent to dispersion of aluminum oxide particles.

- b) Aluminum nanopowder
At first, AOT and DTAB were used as a surfactant. However, as a result of the TEM measurement, DTAB is more excellent to dispersion of aluminum nanopowders. This results were the same as for aluminum oxide particles. So, we experimented by adjusting the amount of DTAB and aluminum nanopowders.
- c) Dispersion solution of aluminum nanoparticles
At first, we have prepared CNF to be used as the surfactant DTAB. The experimental conditions were optimized base on amount of aluminum and DTAB. However, because of the aluminum particles already distributed, it was decided not to use other surfactant. Therefore, we prepared CNF using only dispersion solution of aluminum nanoparticles.

3. Results and Discussion

Aluminum decorated CNF was prepared by electrospinning based on the various experimental conditions such as using various forms of aluminum, different kinds of surfactant and different concentration of surfactants. The morphology of aluminum decorated CNF was observed by TEM in order to find the degree of dispersion of aluminum particles on the CNF. If the degree of dispersion aluminum nanoparticle is more, we can control the reaction rates of aluminum particles. Here, only the results of aim 1 are shown. We sent the materials of polymer (Al/CNF) and carbonized materials (carbon) to Dr. Christopher Bunker in order to get the result of aim 2.

- a) Aluminum oxide
DTAB and AOT have an excellent performance as a surfactant. The surfactants improved the degree of dispersion of aluminum oxide nanoparticles in CNF. Among the two surfactants, DTAB was found to be more excellent for the dispersion of aluminum oxide particles.
- b) Aluminum nanopowder
Here also, the DTAB is more excellent for the dispersion of aluminum nanoparticles than AOT

Based on the results of above experiment, we proceeded the experiment further by adjusting the amount of DTAB and aluminum nanopowders.

Degree of dispersion of aluminum nanopowder was increased by the increased amount of surfactant.

Hence, the experiment was performed by the increase amount of aluminum nanopowder and surfactant DTAB.

Based on the experimental results we found that for the degree of dispersion of the aluminum nanoparticles were promising in the optimized amount of aluminum nanopowder and DTAB.

c) Dispersion solution of aluminum nanoparticles

Experiments were performed using the optimum conditions of the previous experiment (experiment with aluminum nanopowder). When using the DTAB as a surfactant, electrospinning result was impressive, but the result of the TEM was not good. Aluminum particles were not adsorbed onto the CNFs and it is extremely difficult to obtain TEM image because of large aggregation of CNFs. Because it is a state in which the aluminum is dispersed already, it was decided not to use the other surfactant (only dispersion solution of aluminum nanoparticles).

1) The aluminum nanoparticles dispersed after dissolving the PAN

Typically, dissolve the PAN after dispersed aluminum nanoparticles. However, experimental procedure is changed in order to assist the dispersion of the aluminum nanoparticles in this experiment.

Unfortunately, the result of electrospinning was not good. The form of the CNF was not obtained (the shape of the resultant was like film).

2) Increase the amount of PAN with the original manufacturer

Dissolve the PAN after dispersed aluminum nanoparticles and increase the amount of PAN from 10wt% to roughly 14wt%. The reason for increasing the amount of PAN is to enhance the stability of electrospinning.

However, color of the aluminum nanoparticles solution has changed when mixed with PAN. Beside, state of aluminum nanoparticles/PAN solution was changed like cheese (Do not proceed spinning).

3) Time of stirring was changed (the same amount of PAN with experiment 2)

The stirring time for mixed PAN with solution of aluminum nanoparticles was decreased.

Color of the aluminum nanoparticles solution was not changed and result of electrospinning was impressive. These CNFs were carbonized and observed morphology via transmission electron microscopy (TEM). The result of TEM observation was not bad. Aluminum nanoparticles were dispersed to some extent on the CNFs. However, the results were not satisfactory. Further experiments are required using dispersion solution of aluminum nanoparticles.

We conducted an experiment with aluminum oxide, aluminum nanopowder, and dispersion solution of aluminum nanoparticles as energetic nanoparticles. All experiments were made an effort to control the reactivity of energetic nanoparticles. The degree of dispersion of aluminum nanoparticles indicates reactivity control of energetic nanoparticles. So, we tried to improve the dispersibility of the aluminum nanoparticles. In the experiment with aluminum oxide, we were selected surfactant in order to improve the dispersibility of the aluminum nanoparticles. The surfactant improves the dispersibility of the aluminum nanoparticles.

In the second experiments using the aluminum nanopowder, we adjusted the amount of surfactant and aluminum nanoparticles in order to find the optimum conditions for the preparation of excellent nanohybrids. The experiments with dispersion solution of aluminum nanoparticles, lacking something remains a lot. However, after several experiments, it will be possible to obtain better results. The experiment with aluminum nanoparticles will continue to control the reactivity of energetic nanoparticles.

4. Conclusions

Attempts were made to control the reactivity of energetic nanoparticle by confining it on to a carbon nanofiber matrix by electrospinning method. For this purpose, we selected aluminum oxide, aluminum nanopowder as a source for aluminum nanoparticle and AOT, DTAB as a surfactant. Among all aluminum nanopowder and DTAB was found to be a better candidate to confine energetic nanoparticle on to CNF. We are extending our study by using dispersion solution of aluminum nanoparticles as a

source for aluminum nanoparticle.

5. Collaborations

Chonnam National University Research Group works with Dr. Christopher Bunker from AFRL.

- 1) Chonnam National University Research Group is looking for the efficient routes to confining energetic nanoparticles such as aluminum to a matrix by electrospinning method. For this, Dr. Christopher Bunker provided aluminum nanoparticles with excellent colloidal stability in aprotic solvents. We are trying now to encapsulate that samples into polymer and carbon nanofiber matrix.
- 2) We provided two different kinds of samples to Dr. Bunker for measuring the hydrogen generation kinetics of the samples. When we make samples using Dr. Bunker's aluminum nanoparticles, we will also give them to him for measuring the kinetics.
- 3) We will further proceed experiments together to identify major parameters determining the reaction kinetics.