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Ecotoxicity Evaluation and Suggestion of Remediation Method of ZnO Nanoparticles in Aqueous Phase

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Abstract**—**We investigated ecotoxicity and performed experiment for removing ZnO nanoparticles in water. Short term exposure of hatching test using fertilized eggs (*O. latipes*) showed deformity in 5ppm of ZnO nanoparticles solution. And in 10ppm ZnO nanoparticles solution delayed hatching was observed. Hereine, chemical precipitation method was suggested for removing ZnO nanoparticles in water. The precipitated ZnO nanoparticles showed the form of ZnS after addition of Na_2S, and the form of $Zn_3(PO_4)_2$ for Na_2HPO_4. The removal efficiency of ZnO nanoparticles in water was closed to 100% for two cases. In ecotoxicity evaluation of as-precipitated ZnS and $Zn_3(PO_4)_2$, they did not cause any acute toxicity for D. magna. It is noted that this precipitation treatment of ZnO is effective to reduce the potential cytotoxicity.

Keywords**—**ZnO nanoparticles, ZnS, $Zn_3(PO_4)_2$, ecotoxicity evaluation, chemical precipitation.

I. Introduction

RECENTLY, the consumption of nanomaterials is highly increasing due to their unique physicochemical properties. From 2005 to 2010, annual increasing rate of nanomaterials consumption is about 468% [1]. But research on ecology risk for these nanomaterials have is just beginning step. ZnO nanoparticles are one of the most usually used nanomaterials. They are used a lot in making cosmetics like sunscreen due to their UV-screening effect. In addition, ZnO is also used in making tires as resisting wear agents. ZnO nanoparticles contained in cosmetics are readily exposed into aqueous phase when consumers wash them off after using cosmetics like sunscreen. In the case of tires, when they are weared, ZnO nanoparticles are emitted in air and then settled down on the ground, followed by wash out into the river [2], [3].

Therefore, we need to develop technique for removing ZnO nanoparticles as well as evaluate ecotoxicity about ZnO nanoparticles in water. In this research, we evaluated ecotoxicity of ZnO nanoparticles in water using a fish and water flea. And then we suggested the remediation method for ZnO nanoparticles in water by chemical precipitation method.

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II. Experiment

A. Ecotoxicity Evaluation of ZnO Nanoparticles in Water Short Term Exposure Hatching Test

Orvzias Latipes were used as a fish sample for ecotoxicity evaluation of ZnO nanoparticles in water. Concentration of ZnO nanoparticles was adjusted by diluting with 5000 ppm ZnO colloid solution (Sigma Aldrich). Four fertilized eggs harvested from paired adult fish in each concentration were exposed in concentration of 2.5, 5, 10mg/L ZnO for ten days and its hatching rate and developmental deformity was observed at 20°C in chamber (Fig. 1).

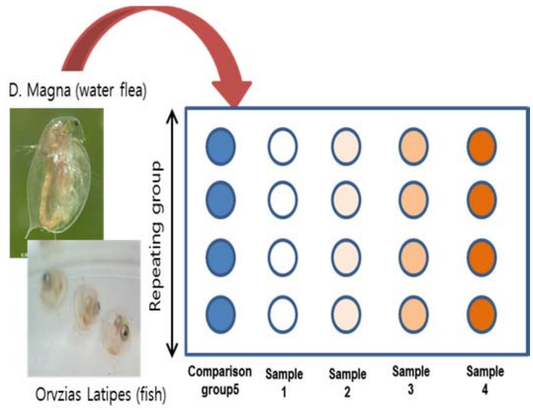


Fig. 1 Experimental procedure for evaluating ecotoxicity

B. Remediation of ZnO Nanoparticles in Water

0.05-0.25M of Na_2S or Na_2HPO_4 was added in 100ppm ZnO nanoparticles solution and the resulting solutions was mixed with voltax mixer (G560E, Scientific Ind.). And then immediately UV analysis (UV-18000, Shimadzu) of the solutions was performed to check the removal efficiency of ZnO nanoparticles. The morphology and species of precipitates were analyzed by TEM (JEM-1010, JEOL) and EDX (7200-H, Horiba), respectively.

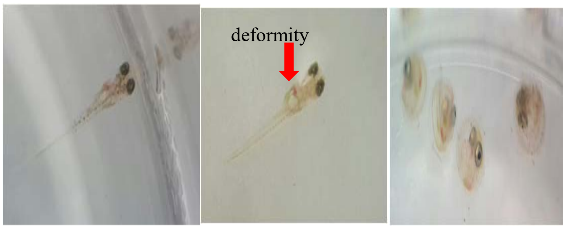
C. Acute Toxicity Evaluation of as Precipitated ZnS and $Zn_3(PO_4)_2$

ZnO nanoparticles are readily precipitated in the form of ZnS or $Zn_3(PO_4)_2$ for reducing the potential risk. But if the precipitate has another risk, this precipitation technique is useless. Therefore, We conducted 48 hr acute toxicity test to evaluate toxicity reduction of ZnS or $Zn_3(PO_4)_2$ using *D. magna*. Twenty neonates less than 24 hr old were exposed in four replicates of each concentration. Endpoint was immobility and EC_{50}s was used for toxicity values.

III. Result and Discussion

A. Ecotoxicity Evaluation of ZnO Nanoparticles in Water

After exposure of *Oryzias latipes* eggs into prepared test solutions, its hatching rate, and deformity was observed. After 9 days exposure, all eggs including comparison group were hatched, except 10 mg/L ZnO nanoparticles. Also we found that the occurrence of deformity in 5 mg/L ZnO nanoparticles. And all eggs in 10 mg/L ZnO nanoparticles were hatched at 10 days. Namely, we could see 10 mg/L ZnO nanoparticles affect growth-retardation (Fig. 2).



(a) (b) (c)

Fig. 2 Result of ecotoxicity evaluation using *Oryzias latipes* with different concentration of ZnO nanoparticles on ninth day after exposure ((a) comparison group, (b) occurrence of deformity in 5mg/L ZnO nanoparticles, (c) growth retardation in 10mg/L ZnO nanoparticles)

B. Remediation of ZnO Nanoparticles in Water

We put 0.05~0.25M Na_2S as a source of sulfur supply and Na_2HPO_4 as a source of phosphorus supply into 100 ppm ZnO nanoparticles respectively. When Na_2S were mixed with 100ppm ZnO nanoparticles, the solution became opaque. As the concentration of salt was increasing, the color of precipitate was changing from white to yellow. On the other hand when we put Na_2HPO_4 into the same condition, the solution was murky at low concentration and transparent at high concentration because $Zn_3(PO_4)_2$ was precipitated immediately when we put Na_2HPO_4 a lot (Fig. 3)

After putting precipitant and mixing, we performed UV analysis of the solution immediately. Because ZnS floated in water, the turbidity was increased so that UV detected it. And we saw irregular peak on 370 nm about ZnO. In the case of $Zn_3(PO_4)_2$, any peak was not detected because most $Zn_3(PO_4)_2$ were already precipitated. We calculated removal efficiency from the result of UV analysis and removal efficiency was almost 100% on all of both methods (Fig. 4 and Table I).

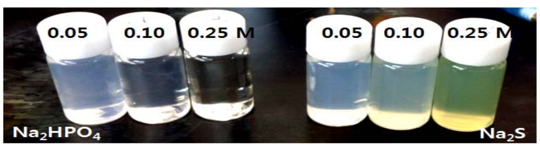


Fig. 3 Photo of precipitating ZnO nanoparticles using Na_2S and Na_2HPO_4 with different concentration

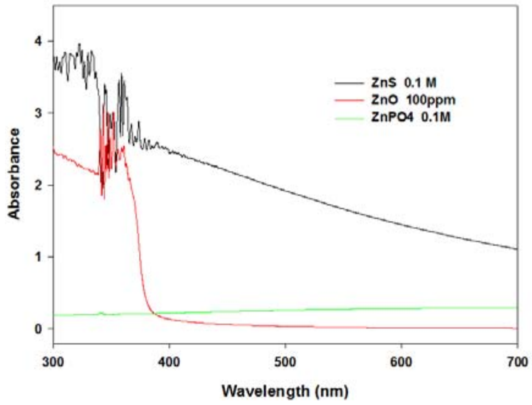


Fig. 4 UV analysis of 100ppm ZnO nanoparticles and of ZnS and $Zn_3(PO_4)_2$ after mixing 0.1M Na_2S and Na_2HPO_4 with 100ppm ZnO nanoparticles respectively

TABLE I
Change of Concentration, HDD and Removal Efficiency before and after Precipitating ZnO Nanoparticles

Sample	ZnO 100 ppm	ZnO + Na_2S salt	ZnO + Na_2HPO_4
Concentration (ppm)	> 100	0.033	0.147
HDD (nm)	65-70	sediments	sediments
Removal efficiency (%)	-	100	99.99

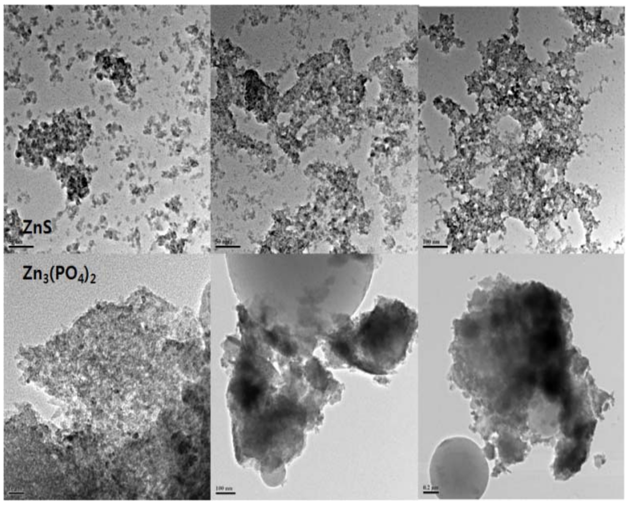


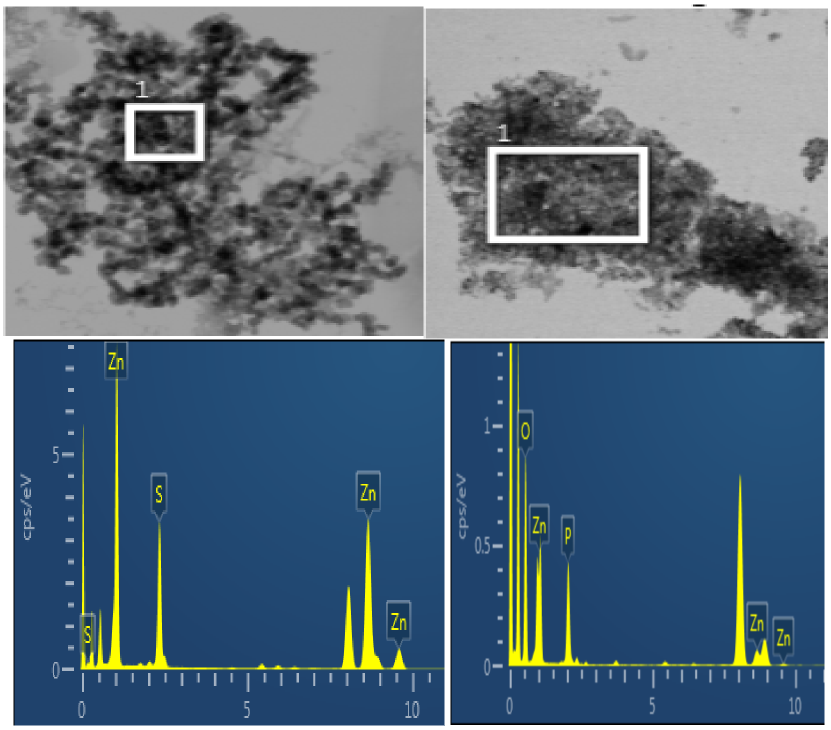
Fig. 5 TEM analysis of precipitated ZnS and $Zn_3(PO_4)_2$

We performed TEM analysis to investigate the shape of the precipitates. ZnS showed polymeric gel network which consisted of cohesion with small particles. On the other hand, $Zn_3(PO_4)_2$ showed the shape of aggregated sol which huge particles grew (Fig. 5).

We also performed EDX analysis to investigate molecular composition. Combining ratio of ZnS was Zn : S = 1: 1.3 so that we could confirm Zn and S was almost combined by 1 : 1. And this is the same as [4].

In the case of $Zn_3(PO_4)_2$, combining ratio of Zn and PO_4 was Zn : PO_4 = 1 : more. So we thought more PO_4 coated surface of ZnO in the form of amorphous shape or formed HOPEITE like

$Zn_3(PO_4)$•$4H_2O$ [5] (Figs. 6 and 7).



(a) (b)

Fig. 6 EDX analysis of precipitated ZnS and $Zn_3(PO_4)_2$ (a) ZnS, (b) $Zn_3(PO_4)_2$

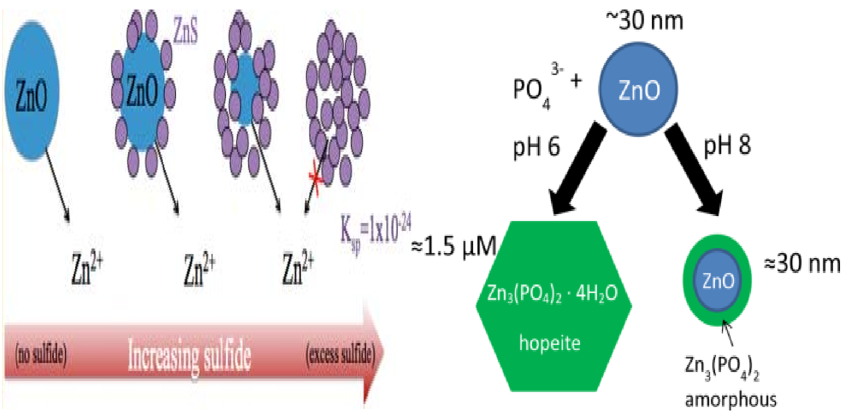


Fig. 7 Expectation picture of reacting ZnO with Na_2S and Na_2HPO_4 from EDX analysis

C. Acute Toxicity Evaluation of as Precipitated ZnS and $Zn_3(PO_4)_2$

We performed acute toxicity evaluation using water flea(D. Magna) of as-precipitated ZnS and $Zn_3(PO_4)_2$ which was produced by precipitating ZnO to remove ZnO nanoparticles in water. 24hr and 48hr EC_{50}s of ZnO was 11.23 mg/L and 5mg/L, respectively showing increase of toxicity according to exposure period. On the other hand, we could not obtain EC_{50}s of ZnS and $Zn_3(PO_4)_2$ in maximum 10mg/L of each chemical which implies toxicity reduction (Table II).

TABLE II
ACUTE TOXICITY EVALUATION OF ZNO, $ZN_3(PO_4)_2$ AND ZNS

Classification	ZnO	$Zn_3(PO_4)_2$	ZnS
24hr EC_{50}, mg/L	11.23(8.68-13.79)*	> 10	> 10
48hr EC_{50}, mg/L	5.02(4.09-5.94)	> 10	> 10

IV. CONCLUSION

We performed ecotoxicity evaluation using Orvzias Latipes for investigating whether ZnO nanoparticles have risk in water. The result showed the occurrence of deformity in 5 mg/L ZnO nanoparticles and growth retardation in 10 mg/L ZnO nanoparticles. We precipitated ZnO nanoparticles using Na_2S or Na_2HPO_4 in the form of ZnS or $Zn_3(PO_4)_2$ respectively to remove them from water. The removal efficiency of ZnO nanoparticles in water was almost 100% on all of both methods. ZnS was precipitated by reacting Zn: S = 1 : 1. In the case of Na_2HPO_4, Zn was reacted with more PO_4 so that we thought more PO_4 coated surface of ZnO or formed HOPEITE like $Zn_3(PO_4)\bullet 4H_2O$. Any acute toxicity was not found with Synthesized ZnS and $Zn_3(PO_4)_2$ in toxicity evaluation using water flea (*D. magna*) so that we could confirm risk was reduced than ZnO.

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REFERENCES

[1] Woodrow Wilson Center PEN CPI (September, 2011)
[2] Mei Li, Lizhong Zhu and Daohui Lin, “Toxicity of ZnO nanoparticles to E. coli: mechanism and the influence of medium components”, Environ. Sic. Technol., 45(5), 1977-1983, 2011.
[3] Rui Ma, Clement Levard, Jonathan D. Judy, Jason M. Unrine, Mark Durenkamp, Ben Martin, Bruce Jefferson and Goregory V. Lowry, “Fate of zinc oxide and silver nanoparticles in a pilot wastewater treatment plant and in processed biosolids:, Environ. Sci. Technol., 48(2), 104-112, 2014.
[4] Rui Ma, Clement Levard, F. Marc Michel, Gordon E. Brown, Jr., and Gregory V. Lowry, “Sulfidation Mechanism for Zinc Oxide Nanoparticles and the Effect of Sulfidation on Their Solubility”, *Environ. Sci. Tech*., 47(6), 2527~2534, 2013.
[5] L. Robertson, M. Gaudon, S. Pechev and A. Demourgues, “Structural transformation and thermochromic behavior of Co2+-doped Zn3(PO4)2·4H2O hopeites”, J. Mater. Chem., 22, 3585-3590, 2012.