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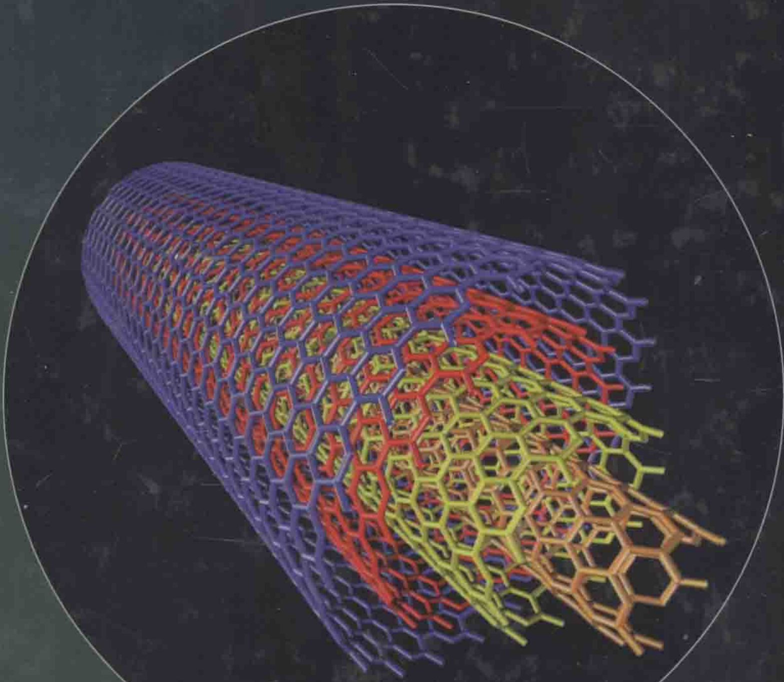

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PREFACE

Understanding and utilizing the interactions between environment and nanoscale materials is a new way to resolve the increasingly challenging environmental issues we are facing and will continue to face. Therefore, the applications of nanotechnology in environmental engineering have been of great interest to many fields, and consequently, a fair amount of research on the use of nanoscale materials for dealing with environmental issues has been conducted.

The aim of this book is to report on the results recently achieved in different countries. We hope that the book can provide some useful technological information for environmental scientists and assist them in creating cost-effective nanotechnologies to solve critical environmental problems, including those associated with energy production.

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CONTENTS

CHAPTER 1

Responses of *Ceriodaphnia dubia* to Photocatalytic Nano-Titanium dioxide Particles

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1. INTRODUCTION

Nanotechnology is fast growing in the past decade. Due to unique physical and chemical properties, nano-sized materials have found many applications in many fields, including electronics, manufacturing, medicine, and daily goods. Among various common nanomaterials, titanium dioxide (TiO_2) is becoming one of the most commonly deployed due to its photoactive property. Many applications, such as manufactured semiconductor, solar cell, and environmental remediation are made of titanium dioxide [1–3]. Household products, such as self-cleaning surfaces and antifogging mirrors have also been made by coating nano-TiO_2 to improve the superhydrophilic property that provides the characteristics of water-repellent and low-particle adhesion on material [4]. However, benefits brought by nanotechnology might come with dangers. Extensive applications of nanomaterials would lead to their release into environment eventually. The release of nanomaterials to the environment can have severe ecological and health consequences. This is of particular concern as the nanomaterials benign in their bulk phase can be toxic to the aquatic organisms due to their unique physical, chemical and biological properties. There are a number of studies on the effect of toxicity of nanoparticles on animals, but only few studies are available on ecotoxicology, with the effect of fullerenes (C_{60}) and titanium dioxide being the most extensively investigated. Several authors have reported the impacts of C_{60} on aquatic organisms [5–7]. Kerstin and Markus [8] and Lovern and Klaper [9] studied the toxicity of TiO_2 to daphnia and algae. While results clearly showed significant impacts of nanomaterials on aquatic organisms, little is dealt with the effect of particle size on aquatic organisms.

In this study, experiments were conducted to assess the effect of particle size on the toxicity of nano-TiO_2 to *Ceriodaphnia dubia*. *C. dubia* is very sensitive to environmental changes (listed as one of the United States Environmental Protection Agency [USEPA]-recommended test organisms for toxicity) and has been used in many toxicity studies, i.e. pesticides, herbicides, heavy metals, and many other toxic substances [10–13]. Furthermore, *C. dubia* is present commonly in freshwater pools and lakes around the world and plays an important role in ecosystems. The diets of *C. dubia* contain algae and many consumers of higher trophic levels, such as fish, amphibians, and aquatic insects. It is a primary consumer in a very important ecological position, which links the primary producers and higher animals. Impacts on the survival and reproduction of *C. dubia*, directly or indirectly will affect the stability of ecosystem.

2. MATERIALS AND METHODS

2.1. Test Organism and Culture Maintenance

Test organism, *C. dubia*, was purchased from Aquatic BioSystem Inc. (Fort Collins, Colorado). Cultures maintenance and preparation of dilution water or "synthetic, moderately hard, reconstituted water" followed the USEPA guidelines [14]. In brief, mass and individual cultures were incubated in the growth chamber, inside a climate control room with a light intensity of 70–120 ft-c, followed by a 16-h light/8-h dark photoperiod and a room temperature of 24 °C. Both mass and individual cultures were daily fed with the green algae *Selenastrum capricornutum* (renamed as *Pseduokirchneriella subcapatitata*) and with a combination of yeast, cerophyll and trout chow (YCT), also purchased form Aquatic BioSystem Inc. Individually cultured organisms were raised in 30-mL plastic cups with 15 mL dilution water and were daily fed with 100 μL of green algae and 100 μL ofYCT. A mass culture was raised in 1-L beaker with 1 L of dilution water and was daily fed with 4–6 mL of green algae and 4–6 mL of YCT. The water was changed every 2 and 7 days in individual and mass cultures, respectively.

2.2. Effect of Particle Size

To understand the effect of particle size on the survival rate of *C. dubia*, 11 particle sizes, ranging from 4.7 to 1467 nm, in the form of TiO_2 were applied in the 24-h acute toxicity test. Reade5 (5.2 nm) was purchased from Nanostructured & Amorphous Materials Inc (Houston, Texas), UV-100 (4.7 nm) was purchased from Hombikat Inc. (Japan), ST-01 (5.3 nm) and ST-21 (23 nm) were purchased from Ishihara Sangyo Kaisha LTD. (Japan) and P25 (34 nm) was purchased from Degussa Corporation (Frankfurt, Germany). Five different particle sizes of TiO_2, namely, 46, 116, 204, 636 and 1467 nm were made in our laboratory using thermal-treatment of P25 (Y660, Y780, Y840, Y970, and Y1100) [15]. Thermal-treatment was also used to generate 13 nm particles (Y350) by heating UV-100 at 350 °C. Particle size was determined by Brunauer-Emmiet-Teller (BET) measurements. Table 1.1 lists the nanoparticles used in toxicity tests, their crystal composition and their primary and secondary particle sizes.

Nine concentrations (0, 10, 30, 60, 100, 200, 400, 800, and 1000 mg/L) were used to determine the dose–response curves for all particles. TiO_2 can be easily suspended in water solution; therefore special preparation for test suspensions is not required. Test suspensions were freshly prepared by mixing the given amount of TiO_2 particles and the dilution water, right before use. The concentrations from 10 to 800 mg/L were diluted to 15 mL

Table 1.1 Summary of particle information, including particle name, primary particle size, secondary particle size, rutile component (%), and sources of particle

Particle	Primary particle size (nm)	Secondary particle size (nm)	Rutile component (%)	Source[a]
Rease 5	5.2	749	0.5	NAM
ST-01	5.3	700	0	ISK
UV-100	4.7	715	0	HB
Y350	13	1752	0	UD
ST-21	23	905	0	ISK
P25	34	1859	27	DC
Y660	46	672	27	UD
Y780	116	682	28	UD
Y840	204	644	47	UD
Y970	636	900	51	UD
Y1100	1467	773	100	UD

[a] NAM, Nanostuctured & Amorphous Materials Inc; ISK, Ishihara Sangyo Kaisha LTD; HB, Hombikat Inc; DC, Degussa Corporation; UD, University of Delaware.

of total volume in 30-mL plastic cups (test chamber) from 100 mL of stock solution, which was 1000 mg/L in concentration. To design an environmentally relevant protocol, no surfactant was applied to stock solutions for particle dispersion. All stock solutions were treated with ultrasound at a power of 24 W for 1 minute.

Each experimental set included nine test chambers for nine concentrations in each particle. Each test chamber included 15 mL of test suspension and five *C. dubia* neonates that were less than 24 h old. Each experimental set was repeated four times and treated as one replicate. At least, two and up to four replicates were applied to each particle size. As per USEPA guidelines, each concentration required only 20 neonates to give reliable statistic analysis. During experiment, different individual culture boards incubated in different time periods might have different LC50 results for same particle size. To eliminate the errors rising from the four experimental sets per particle size in one individual culture board, only two experimental