

Synthesis of Cu₂O nanocrystals and their agricultural application

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Submitted May 1, 2014

A series of cuprous oxide (Cu₂O) nanocrystals with different structures were synthesized by reductive reaction. The nanocrystals were obtained in an aqueous mixture of CuSO₄, fructose, NaOH and templates at 45-75°C. We developed a facile one-pot route for the synthesis of Cu₂O by simple adjustment of the template quantity. The novel particles were analyzed by SEM and XRD. These verified that the average sizes for the cubic, octahedral, petaloid and spherical structures were approximately 450, 180 and 360 nm, respectively. The octahedral Cu₂O was selected for the further experiments due to the smallest size of its particles. The agricultural application performance like anti-alga experiments and inhibition zone method showed that about 4.9×10³ N.cm⁻² diatom was noticed on the surface and the inhibition rate of the novel mixture towards *Colletotrichum capsici* was 90%, as soon as 70 mg nano-Cu₂O was added into 100 mL culture media. Similar results were obtained in sea water after 120 days of exposure.

Key words: Cu₂O, synthesis, performance, agricultural application.

INTRODUCTION

It is witnessed that fouling is a destructive natural phenomenon that affects almost every economic sector, causing annually billions of dollars in damage and disorder [1-3]. The most common and efficient antifouling method was painting antifouling coatings containing biocides like TBT (tetra-*n*-butyl tin) which often had detrimental non-target environmental effects during its application, particularly in marine water. As soon as the environmentally disastrous effect of TBT coatings was noticed by the following research, the UN International Maritime Organization had decided to ban the use of TBT in antifouling coatings by the end of Jan. 1, 2008 [4]. Consequently, there still exists a desperate need for high-effective and environment-friendly alternatives [5-7]. Considering environmental protection, many researchers had developed two ways to resolve the matter by the end of last decade: one was constructing micro/nano-surfaces like low energy surface and superamphiphobic surface that physically released the accumulated fouling. The other was applying environmentally friendly biocides like Cu₂O that chemically inhibited most of marine organisms by leaching some biocides [8-11]. In order to unite these advantages and simplify the operation, our present work aimed at studying the synergistic performance of environmental biocides with sub-micro cuprous

oxide and functional acrylic resin. It was reported that Cu₂O was still the dominant biocide in antifouling coating. But seldom papers disclosed the relationship between crystal morphology, particle size, functional acrylic resin and antifouling performance. Fortunately, there were lots of papers about the synthesis of particles of different size and morphology. The Cu₂O particles with cubic, octahedral and spherical structures were interesting not only because excellent antibacterial properties could be investigated with great certainty, but also because synthetic conditions of controlling the particle morphology could be achieved. Generally speaking, templates were universally applied during micro/nano-particles synthesis. Yu *et al.* [12] reported the synthesis of Cu₂O nano-whiskers by using cetyl-trimethyl ammonium bromide (CTAB). Zeng *et al.* [13] reported Cu₂O nanocrystals with size of 70 nm produced at 160-220°C by using hexadecylamine. Dong *et al.* [14] reported the synthesis of micro/nano Cu₂O by using NH₂-NH₂ as a reducing agent. Huang *et al.* [15] synthesized eight nanocrystals of different morphology by changing the quantity of NH₂OH. All these suffered from the use of either high temperature, random morphology or toxic reducing agents.

According to atom economy, it would be desirable to develop a simple synthetic approach at mild conditions to synthesize Cu₂O of different morphology like cubic, octahedral and spherical structures without waste disposal or high temperature. Recently, the common fact was accepted that the template played an important role in nanocrystal synthesis and stability. The β-

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cyclodextrin (β -CD) derivative, α -1,4-linked D-glucopyranose polymer, was selected as a promising template. It is funnel shaped with hydrophilic groups outside, and lipophilic alkyl groups inside. There was little information about β -CD and its derivatives as soft templates to synthesize Cu₂O nanocrystals. This kind of hydrophilic-lipophilic template not only realized proper molecule-cages, but could improve the stability of nano-particles. In this paper, a typical Cu₂O biocide of various size and particle morphology was synthesized by direct reduction with fructose. Then, the novel coating containing acrylic resins copolymerized with VTMS (containing $-\text{Si}(\text{OCH}_3)_3$ as a cross-linking group) with Cu₂O was produced. Furthermore, the synergistic antifouling performance of the coating was investigated in Qingdao offshore.

EXPERIMENTAL

Material

The algae of *Nitzschia flosterium* were provided by the laboratory of alga at the Ocean University of China. The algae were cultivated in a biological culture box and prepared for the following anti-alga experiments. All nutrient salts were purchased from Alfa. Methyl methacrylate (MMA), butyl acrylate (BA) and vinyltrimethoxysilane (VTMS) were obtained from Qingdao Haida Chemical Co. Ltd (CN). All these materials were industrial grade products, which were used as received without further purification. Copper sulfate (CuSO₄), β -cyclodextrin (β -CD), fructose and toluene were obtained from BASF (CN). 2,2'-Azobis (2-methylpropionitrile) (AIBN) was obtained from Changzhou Watson Fine Chemical Co. Ltd. (CN). Deionized water (17.8 M Ω) was used for all solution preparations.

Synthesis of Cu₂O by "one-pot" reduction reaction

It is known that continuous efforts have been made to focus on efficient approaches for the synthesis of Cu₂O nanocrystals because of their remarkable antifouling and antibacterial properties. The multi-component reaction was one of the most efficient methods because it was a synthetic operation without the need for isolation of the intermediates [16,17]. The one-pot reaction was highly effective for the synthesis of Cu₂O nanocrystals with different shapes of cubic, octahedral and spherical structures via multi-component reaction of fructose, CuSO₄ and NaOH in β -CD solution. The raw material solutions were placed in a water bath at 45-75°C. Then 0.04g soft

templates like β -CD, cellulose and PG-200, were added to 10 mL of 1M CuSO₄ under stirring. Five minutes later, 30 mL of 1M NaOH and 2M fructose solutions were added to the former solution. The total solution volume was about 40 mL. The solution was kept in the water bath for half an hour in order to promote the reaction and then was centrifuged at 3000 rpm for 4 min. After the top solution was decanted, the precipitate was washed with 10 mL of a 1:1 volume ratio of C₂H₅OH and H₂O. The precipitate was centrifuged and washed at least three times using the former solution to remove the remainders. The precipitate was dispersed in 10 mL of absolute C₂H₅OH for storage and analysis.

Synthesis of acrylic resin copolymerized with VTMS

The free radical copolymerization of multi-monomers represents a versatile tool for the formation of copolymers. In the current study n-butyl acrylate and methyl methacrylate were synthesized via high-temperature acrylate synthesis in a one-pot-one-step procedure with radicals [18].

A mixture of 0.71 g of 2,2'-azobisisobutyronitrile (AIBN), 0.63 mol of methyl methacrylate, 0.26 mol of butyl acrylate, and 0.037 mol of VTMS, was put into a conical flask to obtain a clear solution after ultrasonic oscillation. The toluene was deoxygenated by purging with nitrogen in a 250 ml round-bottomed flask for at least 10 min. A small amount of radicals (1%, w/w) was added before the reaction. Otherwise the copolymerization was blocked or out of control. Then, the mixture was fed by an injector into 100 mL of toluene with a motor stirrer at 80°C-86°C. These monomers were copolymerized at 550 - 600 rpm for 1 h. Once the reaction was completed, which was evident from the change in the appearance of the doped solution, additional 0.55 g of AIBN was added to enhance the polymerization rate for more 3 h. The final product was saved in dark environment without air and water vapor [19]. The product was transparent and glutinous. The formation of copolymer structure was evidenced by IR (KBr): appearance of absorption peaks at 1770 cm⁻¹, 1149 cm⁻¹ and 1387 cm⁻¹ confirmed the presence of C=O, $-\text{Si}-\text{O}-\text{Si}-$ and $-\text{Si}-\text{OCH}_3$, respectively.

Anti-algal activity test

Algae cultivation. The algae of *Nitzschia flosterium*, a typical fouling organism, were transferred to a conical flask containing NaNO₃: 14.96 g, NaH₂PO₄·2H₂O: 1.0 g, Na₂SiO₄·9H₂O: 10.1 g, and distilled water. The flask was sterilized

for 15 min at 120°C. The nutrient salts (with or without silicate, as appropriate) were weighed exactly by electronic analytical balance. The algae were cultivated in a biological culture box for seven days at 21±1°C. In order to accelerate alga growth, the flask was stirred at least three times during the day-time. The culture box was under continuous illumination of cool-white fluorescent tubes at 3000-4000 lux with a 12 h light/dark cycle, coinciding with alga growth law [20,21].

Anti-algal colonization. There were two coatings; one group (coating containing Cu₂O) and the other group (coating without Cu₂O). The coatings were prepared on glass (30mm×70mm×5mm) without any flaws like pinholes or uneven surface. Until the solvent volatilizes, every tested example was vertically put into the alga pool, in order to avoid deposition of alga. As soon as the tested examples were placed into the culture pool, some bacteria directly colonized the surface. A few hours later, *Nitzschia flosterium* was successively gathering onto the coating surfaces following the bacterial colonization. After seven days, the surface of every tested coating was washed at least 30 times with 10 mL of distilled water without addition of a nutrient by an adjustable air-displacement pipette. Then the anti-alga property was evaluated by the counting method under stereo microscope as soon as possible, in case the algae were getting dead in distilled water. All tests were conducted in triplicate in three different parallel experiments.

Antifouling property of the novel coatings

The antifouling property of the novel coating was investigated according to GB 5370-85 [22]. Uncoated panels (control panels) were used to assess the fouling resistance rating. The main bio-fouling organisms observed were green algae and encrusting species like hydroids, bryozoans and barnacles. The marine coating systems were exposed in vertical position to sea water for 5 months (June to October). At first, the low-carbon steel test plates (150mm×250mm×3mm) were polished with sandpaper and coated within 8 hours or before rusting occurred with the appropriate anticorrosive coatings. Two kinds of Cu₂O were tested, one was the traditional product, and the other was octahedral nanocrystalline product. Then we brushed the antifouling coatings following the formulation shown in Table 1.

These panels dried at least 7 days without direct sunshine during daytime and were fastened by nylon ropes. The tested samples were vertically immersed in sea water at 1 to 1.5 m depth at the

No.8 harbor of Qingdao, east of China. The examples were traced and photographed during the effective antifouling period.

Table 1. Composition of antifouling coating (unit: g).

No.	Acrylic resin	Cuprous oxide	Functional group	Assistant	Xylene
A	31	25 (nanocrystal)	0	2	12
B	31	25a (nanocrystal)	VTMS	2	11
C	31	25	0	2	12
D	31	25	VTMS	2	11

RESULTS AND DISCUSSION

One-pot synthesis of Cu₂O nanocrystals

Previously, Cu₂O nanocrystals were fabricated by mixing deionized water, CuSO₄, cetyltrimethyl ammonium bromide, fructose and NaOH in the listed order. We considered that this synthetic method was a good starting point to synthesize these particles. We had witnessed the role of soft templates during the nanoparticles synthesis in our previous work. Hydroxyethyl-β-CD was selected because of the strong interaction of hydroxyl groups with Cu²⁺, thus the OH⁻ groups had little chance to destroy the interaction. Then the following reduction reaction was confined in the molecule-cages of the hydroxyethyl-β-CD, thus the reunited nanoparticles were resolved. The proper templates not only were critical for the nano-confinement effect, but also effected electrostatic repulsion. At the same time, we tested the influence of the reaction temperature on the Cu₂O shape. A series of Cu₂O nanostructures of the cubic, octahedral and spherical type were synthesized. The products were conserved in alcohol. The XRD patterns of the one-pot reduction reaction composed of cubic, octahedral and spherical crystals showed that both Cu₂O (PDF 00-005-0667) crystals were highly crystalline after a post deposition procedure (Figure 1). No impurity peaks from CuO (PDF 00-045-0937) or copper metal (PDF 00-004-0836) are seen in the following figure.

The quantity of NaOH increased the particle size without templates. The reaction was conducted under vigorous stirring. The fructose solution was directly added to the reactor without keeping constant temperature. Figure 2 shows the SEM images of the Cu₂O nanocrystals synthesized with different NaOH quantities. Some different Cu₂O shapes appear in the picture, due to the changing reaction temperature because of the addition of fructose solution. The size of Cu₂O particles increased with increasing NaOH quantity. The average particle sizes for the octahedral structure

were about 0.2, 3, 5, and 8 μm (see Figure 2). The results showed that NaOH quantity hardly influences the {100} faces, so there was little change of the morphology, yet enlarged the size of the particle [23].

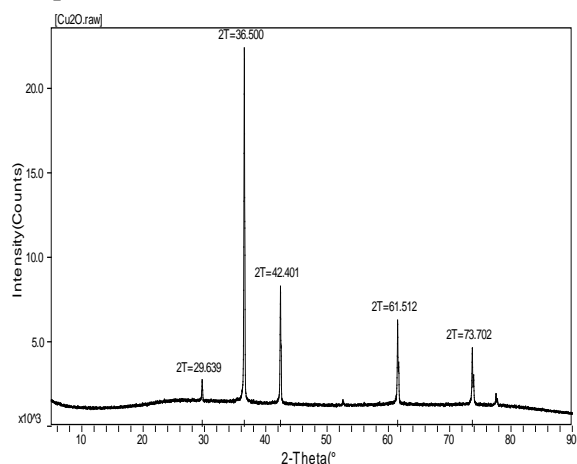


Fig.1. XRD pattern of Cu₂O of one-pot synthesis.

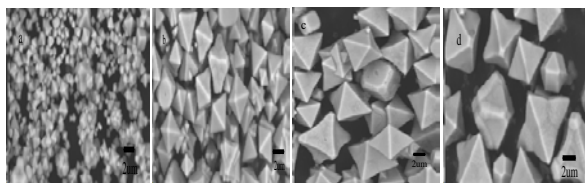


Fig. 2. SEM images of the Cu₂O nanocrystals synthesized at different NaOH concentrations: (a) 1 M, (b) 2 M, (c) 3M, (d) 4M.

In addition, it is known that the concentration of Cu²⁺ is getting lower with increasing NaOH quantity because of the equilibrium constant. So less Cu⁺ was produced and particle density was lower comparing to the control solution. Thus larger and larger crystals of Cu₂O were observed with the increase in NaOH concentration.

The different templates influenced the Cu₂O particles. After the same quantity of templates (0.4% w/w) was dissolved in water, the other constituents except the reducing agent were mixed in a thermostatic bath. In order to promote the reaction, the fructose solution was warmed-up before being poured into the mixture. The anticipated shapes of the octahedral nanocrystals were observed. The particle size is about 0.2 μm to 0.5 μm, as is seen from Figure 3.

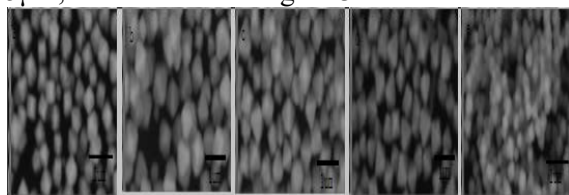


Fig. 3. SEM images of the Cu₂O nanocrystals.

It was realized that uniformity and stabilization of Cu₂O was achieved in hydroxyethyl-β-CD

solution. It contributed to the coordination complexes between Cu²⁺ and the hydroxyl groups surrounding its funnel structure; the Cu²⁺ was divided in the molecular space by the template, thus the chance of continuous crystal growth was blocked. As soon as the starch played its role, an amorphous mass of nano-Cu₂O was obtained through several rinses with alcohol and water. The HEC (hydroxyethyl cellulose) has poor solubility, thus it had weak effect to regulate the particle size. In terms of Cu₂O size, PEG-200 (polyethyleneglycol) and CMC (carboxymethyl cellulose) were inferior to the β-CD synthesized in different templates: (a) β-CD, (b) HEC, (c) PEG-200, (d) CMC, (e) starch.

The quantity of template influenced the particle shapes and size. In order to avoid changing the reaction temperature during the addition of fructose solution, all original materials were heated in a water bath. Figure 2 shows the octahedral nanocrystal synthesized when 0.04 g of hydroxyethyl-β-CD was added (the amount of Cu(OH)₂ was 0.01 mol). Figure 2a shows many crystal shapes and different sizes due to the non-templates controlling. When the template played its role, there was distinct evidence that uniform morphology appeared and the average particle sizes for the octahedra were about 300, 400, 200, 180 and 350 nm (see Figure 4). We could say that nanocrystals were synthesized by one-pot reduction reaction without bringing environmental burden like toxic reducing agents.

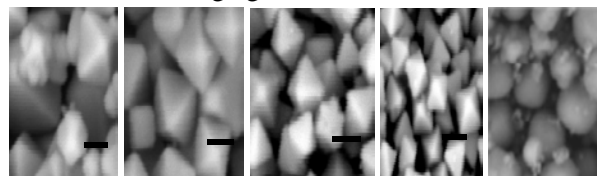


Fig. 4. SEM images of the Cu₂O nanocrystals synthesized with different β-CD quantities: (a) 0% (W/W), (b) 0.01% (W/W), (c) 0.02% (W/W), (d) 0.4% (W/W), (e) 0.08% (W/W).

With the increasing quantity of hydroxyethyl-β-CD, spherical particles were obtained and the template also was found in the image, probably because of the changing viscosity; this verified that templates imposed strong restrictions on crystal growth. Considering the particle size and nanocrystals morphology, the 0.4% (w/w) of hydroxyethyl-β-CD was screened out.

The reaction temperature influenced the particle morphology. Previously, cuprous oxide of different morphology like spherical, cubic, octahedral, polygonal nanostructures, was synthesized at random as shown in Figure 2. It was necessary that we control not only the particle morphology but the

particle size. Figure 3 shows the SEM images of Cu₂O synthesized under control in hydroxyethyl- β -CD solution. By progressively increasing the reaction temperature, spheres, cubes and octahedra were synthesized. The crystal growth rule gave that the final morphology depended on the growth velocity. It was authenticated that faster growth velocity of the crystal face is related to its faster disappearance. The following figure gives us clear explanation of the fact that the nanocrystals morphology is dependent on the growth velocity of {100} facets and {111} facets.

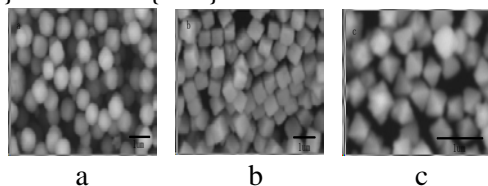


Fig. 5. SEM images of the Cu₂O nanocrystals synthesized at different reaction temperatures: (a) 45°C, (b) 55°C, (c) 65°C.

Once the two facets had the same or similar growth velocity, the spherical shape was observed at a temperature of 45°C. On the contrary, had they different growth velocities, the cubic shape appeared owing to the {100} facets being exposed, at a temperature of 55°C. So it was believed that the concentration of Cu⁺ was under control, that is to say, provided adjustable growth velocity of {111} facets, thus all kinds of nanocrystals morphology could be synthesized in theory [23]. As soon as the temperature reached 65°C, the octahedral shape appeared in the SEM image (see Figure 5 for the particle morphology). In fact, at least six different morphologies were found during our experiments, unfortunately these appeared irregularly. So there is still a lot of work needed to explore the field. The average particle sizes for the spheres, cubes and octahedra were 360, 450, and 270 nm, respectively (see Figure 4). The controlled release of Cu²⁺ and the nanocrystals stability was realized by the functional hydroxyethyl- β -CD template.

Coating performance

Table 2 shows the general information on the prepared tested coatings before the exposure in the ocean. It can be noticed that the performance of the

Table 2. General information on the prepared coatings.

	A	B	C	D	Inspection
Appearance	Red glutinous	Red glutinous	Red glutinous	Red glutinous	GB 1729
Dry to touch	1	1	1	1	GB1728-88
Impact strength/kg.cm ⁻¹	<10	20	<10	20	GB1732-89
Flexibility/mm	4	3	4	3	GB1731-79
Contact-angle/°	88	96	86	90	Contact-angle meter

coating B and coating D was superior to that of acrylic resin (coating C). As a result of the helix of Si-O- bond and reticular structure, the impact strength, flexibility and hydrophobicity were enhanced. The water contact angle of coating B containing nanocrystal Cu₂O increased to 96 \pm 1°, because the nano-structure had higher surface energy, the water was not inclined to spreading wetting. Comparing to the traditional coatings, that containing nanocrystals without functional monomer (VTMS) also gave the expected properties like water contact angles. We believe that the functional surface was constructed following the siloxane groups hydrolyzing with hydroxyl or other active groups. It is worth mentioning that the water contact angles were measured at least at five different points and the water droplet was not more than 1 μ l.

Anti-algal capacity. From Figure 6 it is evident that all tested coatings showed a good inhibition performance towards *Nitzschia flosterium* as expected.

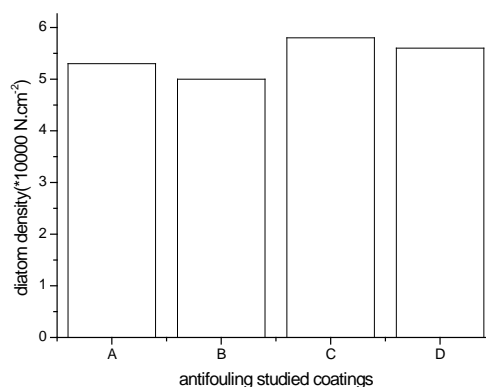


Fig. 6. Settlement density of *Nitzschia flosterium* on the tested coatings.

There was less *Nitzschia flosterium* on the B-board containing nanocrystals than on the other tested coatings. Believing that settlement of *Nitzschia flosterium* was by gravity, one would expect the same settlement density on all four surfaces [24, 25]. However, there were more diatoms adhering to the coating-C-surface, comparing to coating B and D owing to the microstructure of the surface.

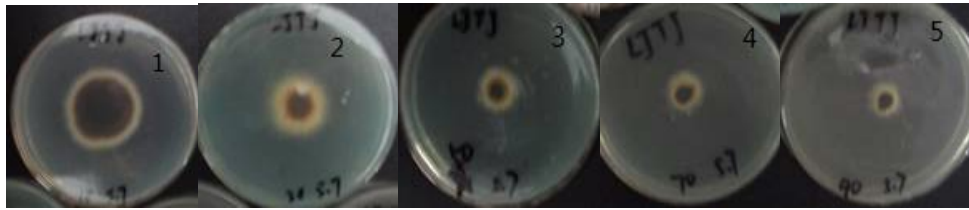


Fig. 7. Antibacterial images of Cu_2O towards *Colletotrichum capsici* (LJTJ) by the oxford cup method. The concentration of particles was 0.1 mg/L, 0.3 g/L, 0.5 g/L, 0.7 g/L, 0.9 g/L, corresponding to the number from one to five

The ingredient of VTMS was inclined to move to the surface in application, taking coating-B for instance, the low-surface-energy property was becoming evident, thus the alga hardly adhered to the constructed surface. The anti-alga performance of nano- Cu_2O was superior to the others, as shown in Figure 7. This is an evidence that the nanocrystals had a strong action with the cell walls of bacteria, once there was less bacteria; there was less alga-settlement.

Antibacterial activity. According to our former experiments, the nanoparticles were added into the culture media, which was scattered by sonic oscillator. *Colletotrichum capsici* was selected because it was common in north plantation. The following figures gave us the direct data and images about the novel particles in our experiment.

The antibacterial ability of the novel particles towards *Colletotrichum capsici* is shown in Fig. 7. The diameter of fungal zone was getting smaller and smaller with the increasing of Cu_2O . After 5 days, a concentration of 0.7 g/L Cu_2O was added, and the expected antibacterial activity was noticed.

Results for ocean plates of offshore platform. The four test plates covered with antifouling coatings were immersed in sea-water suspended under the offshore platform, and the experiment was carried out for about 120 days.

In this special period the marine organisms like algae and barnacles grow vigorously. The results of the periodic photographs are shown in Table 3.

Bio-fouling was considered to have four distinct stages according to their different attachment. The first step was that dissolved organic matter (DOM) and molecules such as protein fragments and polysaccharides accumulated onto the submerged substrates [26-28]. Then, bio-films were gradually obtained owing to the quantity of microorganisms, especially the bacterial colonies. They adhered to the surface of the under-water man-made engineering and shielded themselves in an extracellular matrix of polysaccharide, protein and nucleic acids. It was a typical step of the following fouling. As soon as the bio-film came into being, algae and macro-fouling organisms like bryozoans, mussels, barnacles, tunicates and tubeworms colonized the surface without hesitation where

perhaps the fouling organisms adapted themselves to adhere [27,29,30].

Table 3. Tracing pictures of ocean plates of offshore platform.

	30d	60d	120d
A			
B			
C			
D			
b l a n k			

Based on successive photographic records, we investigated the antifouling property of the novel coatings from the tested panels of surface-attached marine organisms under the experimental platform. Based on tracing pictures (Table 3), marine algae, barnacles and other marine organisms were invariably found to be the dominant fouling during about 150 days. The blank board was heavily covered with mud and marine fouling like green marine algae. Yet we could see no marine fouling on the other tested board for one month. Over a stretch of four months, there were less macro-organisms and mollusks accumulating on the surfaces of the tested coatings. Up to 150 days submerging under the platform, the last step was active. More barnacles had settled on most of the tested plates except coating-B. At the same time, we noticed that some parts of the tested coatings

had already been destroyed by these fouling organisms. Coating-B showed superior antifouling performance to the others owing to the interaction of VTMS and nano-Cu₂O. We reviewed the performance of the tested boards and analyzed the antifouling property of the coatings abiding by the bio-fouling mechanism. We gradually realized that the components interaction properly delayed the fouling-organisms accumulation. As we advanced our cognition of objectively explaining the antifouling performance with the experiments, a few doubts were gradually cleared. The functional monomer- VTMS containing the - Si(OCH₃)₃ was hydrolyzed into reticular structure. The acrylic polymerized with VTMS served as a warehouse to supply Cu₂O. When it came to sustained-release property, the reticular structure of -Si-O- links played as a compact net which made Cu₂O difficult to be quickly washed away by sea water. Furthermore, the nanocrystals had high effective and non-selective germicide effect owing to nano-Cu₂O which more easily adhered on the germ than the large particles. Once the bio-film was destroyed, fouling organisms had no chance of attachment. Therefore, the novel surface retarded the fouling organisms during five-month exposure. From the figures above we can clearly see that the novel coating containing VTMS and nano-Cu₂O had a good antifouling performance comparing to the traditional products, even during the peak vigorous growth period of barnacle and other marine fouling.

CONCLUSIONS

In this work, a series of Cu₂O nanocrystals were synthesized via one-pot reductive reaction. Different structures like cubes, spheres and octahedra with sizes of 180-450 nm were realized by adjusting the reaction temperature in β-cyclodextrin solution. At the same time, the related experiments with the novel coating containing nano-Cu₂O and VTMS showed significant antifouling performance around the offshore, especially in the peak growth period of marine macro-organisms. We witnessed a promising synergy towards antifouling and noticed that there is still a lot of work to do to find out the relationships between structure and antifouling, the components ratio, and so on.

Acknowledgement. This work was supported by the basis of the Qingdao science and technology plan (13-1-4-233-jch).

REFERENCES

1. M. E. Callow, J. A. Callow, *Biofouling*, **15**, 49 (2000).
2. P. Molino, R. Wetherbee, *Biofouling*, **24**, 365 (2008).
3. P. Y. Qian, S. Lau, H. U. Dahms, S. Dobretsov, T. Harder, *Mar. Biotechnol.*, **9**, 399 (2007).
4. S. M. Evans, A. C. Birchenough, M.S. Brabcat, *Mar. Pollution Bull.*, **40**, 204 (2000).
5. K. A. Dafforn, J. A. Lewis, E. L. Johnston, *Mar. Pollution Bull.*, **62**, 453 (2011).
6. P. Pagliara, C. Caroppo, *TOXICON*, **60**, 1203 (2012).
7. M. R. Mohammad, H. H. Chun, H. Park, *Macromol. Res.*, **19**, 8 (2011).
8. X. F. Yan, L. M. Yu, X. L. Jiang, *Periodical Ocean Univ. China*, **43**, 64 (2013) (in Chinese).
9. C. Bressy, A. Margailan, *Prog. Org. Coat.*, **66**, 400 (2009).
10. L. Marlène, M. André, B. Christine, *Chem. Rev.*, **112**, 4347 (2012).
11. W. W. Cong, L.M. Yu, *Chemical Research in Chinese University*, **27**, 803 (2011).
12. Y. Yu, F. P. Du, C. Jimmy, *J. Solid State Chem.*, **177**, 4640 (2004).
13. L. Dong, L. M. Yu, X.H. Jiang, *Chinese J. Inorg. Chem.*, **12**, 2013(2008) (in Chinese).
14. W. C. Huang, L. M. Yu, Y. C. Yang, M. H. Huang, *J. Am. Chem. Soc.*, **134**, 1261 (2012).
15. K. X. Yao, X. M. Yin, T. H. Wang, H.C. Zeng, *J. Am. Chem. Soc.*, **132**, 6131 (2010).
16. S. L. Schreiber, *Chem. & Eng. News* **81**, 51 (2003).
17. P. Dalko, L. Moisan, *Angew. Chem. Int. Ed.*, **40**, 3726 (2001).
18. G. Odian, *Principle of polymerization* (4th ed.). New York: Wiley-Interscience, 2004.
19. Q. Wang, Z. N. Yu, L.M. Yu, *JBTE*, **10**, 1 (2011).
20. M. Beutler, K.H. Wiltshire, B. Meyer, C. Moldaenke, C. Lüring, M. Meyerhöfer, U.P. Hansen, H. Dau, *Photosynth. Res.*, **72**, 39 (2002).
21. F. Guo, L. J. Zhu, C. H. Ke, S. Q. Zhou, *J. Xiamen University (Natural Science)*, **44**, 831 (2005).
22. GB/T 5370-85, Antifouling panels in shallow submergence
23. T. Sugimoto, F. Shiba, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **164**, 205 (2000).
24. P. G. Verity, C. Y. Robertson, C. R. Tronzo, *Limnol. Oceanogr.*, **37**, 1434 (1992).
25. A. Nishida, K. Ohkawa, I. Ueda, H. Amamoto, *Biomol. Eng.*, **20**, 381(2003).
26. D. M. Yebra, S. Kiil, C.E. Weinell, K.D. Johansen: *Prog. Org. Coat.*, **57**, 56 (2006).
27. P. Stoodley, K. Sauer, D. G. Davies, J. W. Costerton, *Ann. Rev. Microbiol.*, **56**, 187 (2002).
28. B. Natalia, A. Beatriz, R. Romagnoli, *Prog. Org. Coat.*, **74**, 411 (2012).
29. M. R. Parsek, P.K. Singh, *Ann. Rev. Microbiol.*, **57**, 677 (2003).
30. Y. Bautista, M. P. Gomez, C. Ribes, V. Sanz, *Prog. Org. Coat.*, **70**, 358 (2011).

СИНТЕЗ НА НАНОКРИСТАЛИ ОТ Cu_2O И ТЯХНОТО ПРИЛОЖЕНИЕ В ЗЕМЕДЕЛИЕТО

Ванг Кианг

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Постъпила на 1 май, 2014 г.

(Резюме)

Синтезирани са различни нанокристали от купроокис(Cu_2O) с различна структура чрез редукционна реакция. Нанокристалите са получени от водни разтвори на CuSO_4 , фруктоза, натриева основа и шаблони при 45-75°C. Разработена е проста, едностадийна синтеза на Cu_2O чрез контролиране на количеството на шаблоните. Тези нови частици са изследвани чрез SEM и XRD. Потвърдено е, че средните размери за кубичните, октаедричните и сферичните структури са с размери съответно 450, 180 и 360 nm. Октаедричният Cu_2O е избран за следващи експериментални изследвания заради най-малките си размери. Експериментите са относно агрономически приложения (напр. против развитие на алги) по метода на зоната на инхибиране. Те показват, че на повърхността се забелязват около $4.9 \times 10^3 \text{ N.cm}^{-2}$ кремъчни водорасли. Степента на инхибиране е 90% спрямо *Colletotrichum capsici*, ако се добавят 70 mg нано- Cu_2O в 100 mL културална среда. Подобен резултат е получен в морска вода след 120-дневна експозиция.