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Luminescent cadmium(II) (8-hydroxyquinoline) chloride (CdqCl) complex nanowires are synthesized via a sonochemical solution route. The results of X-ray photoelectron spectroscopy, energy dispersive X-ray analysis, infrared spectroscopy, elemental analysis (EA), and atomic absorption spectroscopy demonstrate that the chemical composition of the product is Cd(C9H6NO)Cl. Transmission electron microscopy and scanning electron microscopy images show that the CdqCl product is wire-like in structure, with a diameter of approximately 50 nm and an approximate length of 2–4μm. The morphology and composition of the product can be transformed from Cdq2 micrometer-scaled flakes to CdqCl nanowires by increasing the ratio of CdCl2/q. A new fluorescent sensing strategy for detecting H2O2 and glucose is developed and is based on the combination of the luminescent nanowires and the biocatalytic growth of Au nanoparticles. The quenching effects of Au nanoparticles and AuCl4− on the fluorescence of CdqCl nanowires are investigated. The dominant factor for the fluorescence quenching of CdqCl nanowires is that the Stern–Volmer quenching constant of Au nanoparticles is larger than that of AuCl4−.

1. Introduction

Metal 8-hydroxyquinoline (Mq₈) chelates have been the focus of many studies because of their wide range of applications in photoluminescence, electroluminescence, and field-emission. Anzenbacher and co-workers recently reported the synthesis of a series of emission-color-tunable Alq₃ complexes with arylethynyl substituents.[1] The substituents were found to affect the emission color and fluorescence quantum yield of the resulting Al³⁻ complex. A new δ-phase of Alq₃ was identified and its blue luminescence studied.[2,3] Brett and co-workers fabricated chiral thin films, consisting of sub-micrometer scaled helical Alq₃ structures that generate circularly polarized photoluminescence.[4] As electroluminescent materials, Mq₈ and its derivatives have been widely used in organic light-emitting devices (OLEDs).[5–10] Alq₃ has been used frequently because of its good electronic conductivity and strong electroluminescence emission.[11,12] Many other Mq₈ chelates have also been demonstrated to be useful emitter materials. For instance, the Gaq₃ devices have a power efficiency that is approximately 50% higher than Alq₃ structures, suggesting that Gaq₃ might be a superior emitter material for display applications. The operating voltage of (Znq₂)₃-based OLEDs is lower than that of identical devices made with Alq₃.[6] Due to the unique optoelectronic properties of nanostructured organic materials, more attention is, therefore, turning to nanostructured Mq₈ chelates. For example, the electroluminescent device fabricated by Alq₃ nanowires showed an obvious size-dependent performance.[13] In addition, Alq₃ nanostructures, such as nanowires, nanorods, and nanometer-scaled crystalline films, exhibited field emission with a relatively low turn-on voltage.[14,15] Currently, most research work has focused on the nanostructure of Alq₃ and Znq₂. Only a few investigations of other metal 8-hydroxyquinoline nanostructures have been carried out, partly because it is not easy to synthesize a well-defined nanostructure.

Recently, luminescent Cdq₂ has received much attention. As most-frequently reported in the literature, Cdq₂ can be synthesized by the reaction of the cadmium ion with excess 8-hydroxyquinoline.[16,17] For instance, Cdq₂ nanorods and nanoflowers were synthesized in an oleic acid/sodium oleate/ethanol/hexane/H₂O system at a Cd²⁺/q ratio of 1:2.[18] The reaction time, temperature, and reagent concentrations are the key factors in controlling the morphology of the Cdq₂ nanostructure at a q-excess condition. However, it is interesting to investigate the situation where q reacts with excess cadmium salt. A new structure might be obtained because of the effect of the cadmium-salt anion on the formation of Cdq₂.

Herein, we report a sonochemical route to synthesize well-defined CdqCl nanowires in the presence of a highly excessive amount of cadmium salt (CdCl₂), while Cdq₂ flakes were obtained at a q-excess condition. By increasing the ratio of CdCl₂/q, the morphology and composition of the products could be transformed from Cdq₂ micrometer-scaled flakes to CdqCl nanowires. Furthermore, the prepared CdqCl nanowires can be developed into a fluorescence sensor for H₂O₂ and...
glucose, based on biocatalytic growth of Au nanoparticles. The quenching effects of Au nanoparticles and AuCl₂/C₄ on the fluorescence of CdqCl nanowires were investigated. Accordingly, a model was proposed to describe the mechanism of the fluorescence quenching of CdqCl nanowires. The results demonstrate that the difference in the respective Stern–Volmer quenching constants of the two quenchers (AuCl₂ and generated Au nanoparticles) plays the most important role in the change of total fluorescence intensity.

2. Results and Discussion

2.1. Product Composition and Morphology

The composition of the CdqCl nanowires was confirmed by elemental analysis (EA), atomic absorption spectroscopy (AAS), and energy dispersive X-ray (EDX) spectroscopy. The results of EA and AAS show that the content of C, H, N, and Cd is 37.11, 2.01, 4.81, and 37.84%, respectively. The EDX spectrum in Figure 1a shows very strong peaks for Cd and Cl. The atomic ratio of Cd/Cl is 1.09:1. These results are in good agreement with the theoretical values (calculated for Cd(C₉H₆ON)Cl: C: 37.02%, H: 2.07%, N: 4.80%, Cd: 38.49%; the Cd/Cl atomic ratio was 1:1).

The IR spectrum of the CdqCl nanowires in Figure 1b does not show any strong band in the region from 4000 to 2000 cm⁻¹, indicating no OH vibrations are detected. In the IR region between 1600 and 700 cm⁻¹, the peaks are attributed to the quinoline ligand vibrations. The vibrations of Cd–ligand and Cd–Cl bonds are observed in the region between 700 and 100 cm⁻¹. The detailed assignments are summarized in Table 1.[16,19–21]

Figure 1c shows X-ray photoelectron spectroscopy (XPS) of the CdqCl nanowires. Detailed spectra were taken at the Cd and Cl regions, as shown in the insets of Figure 1c. The binding energy values of Cd 3d₃/₂, Cd 3d₅/₂, and Cl 2p₃ are 412.7, 405.7, and 199.2 eV, respectively.

The morphology of the CdqCl nanowires was studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Figure 2 shows that the typical CdqCl nanowires are about 30–50 nm in diameter and about 2–4 μm in length. When the CdCl₂/q ratio was changed from 3:1 to 10:1, no significant changes in the diameter and length were observed. However, an increase of the reaction time from 50 to 120 min resulted in a slight increase in the diameter. Although an increase of the CdCl₂/q ratio from 3:1 to 10:1 showed quite limited effects on product morphology, significant changes were seen when the ratio was decreased from 1:1 to 1:5. The products synthesized at the 1:5 ratio have a flake-like morphology and a wide particle size distribution from hundreds of nanometer to thousands of nanometers, as shown in Figure 3a and b. The as-prepared products were characterized by EA, AAS, and XPS. The C, H, N, and Cd content is 53.97, 3.07, 6.86, and 29.73%, respectively. The results are in good agreement with the molecular formula for Cdq₂: Cd(C₉H₆ON)₂, C: 53.95%, H: 3.02%, N: 6.99%, Cd: 28.05%.

Furthermore, from the XPS result, no Cl peak was observed. Thus, the composition of prepared samples was confirmed as Cdq₂. An increase of the CdCl₂/q ratio to 1:3 and 1:1 led to observation of wire-like nanostructures in the TEM images. By further increasing the CdCl₂/q ratio to 3:1, the flake-like particles disappeared, and instead, a large number of nanowire structures were found. The wire-like morphology did not
Table 1. Wavenumbers and assignments of IR spectra of the CdqCl nanowires.

<table>
<thead>
<tr>
<th>Wavelength [cm⁻¹]</th>
<th>Assignment</th>
<th>Wavelength [cm⁻¹]</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>1599 and 1574</td>
<td>CC stretching vibration involving the quinoline group</td>
<td>783</td>
<td>out-of-plane CH wagging vibrations (quinoline groups)</td>
</tr>
<tr>
<td>1498 and 1464</td>
<td>CC/CN stretching and CH bending vibration</td>
<td>746</td>
<td>Ring breath/Cd–N stretching</td>
</tr>
<tr>
<td>1269</td>
<td>C–O, C–C stretching</td>
<td>731</td>
<td>Ring breath/Cd–N stretching</td>
</tr>
<tr>
<td>1039</td>
<td>CH bending and CC bending</td>
<td>578</td>
<td>CCC bending/Cd–N,Cd–O stretching</td>
</tr>
<tr>
<td>906</td>
<td>CH out-of-plane wagging</td>
<td>401</td>
<td>Cd–N stretching/CCC bending</td>
</tr>
<tr>
<td>821</td>
<td>CH wagging (phenyl)</td>
<td>280</td>
<td>Cd–Cl stretching</td>
</tr>
<tr>
<td>804</td>
<td>CH wagging</td>
<td>181</td>
<td>CCC twisting/butterfly</td>
</tr>
</tbody>
</table>

Figure 2. TEM images of CdqCl nanowires synthesized at CdCl₂/q ratios of a,b) 3:1, c,d) 5:1, e) 10:1. f) SEM image of CdqCl nanowires synthesized at a CdCl₂/q ratio of 3:1. The reaction times were a–e) 50 min and f) 120 min.

Figure 3. a) SEM image of the product synthesized at a CdCl₂/q ratio of 1:5. TEM images of the products synthesized at CdCl₂/q ratios of b) 1:5, c) 1:3, d) 1:1, e) 3:1, and f) 5:1. The reaction time was 50 min.

Figure 4. TEM images of the samples obtained at different reaction times: a) 2, b) 12, c) 20, d) 30, e) 50, and f) 120 min.
change even if the CdCl\textsubscript{2}/q ratio increased to 10:1. The experiments support the conclusion that the composition of the product synthesized at a CdCl\textsubscript{2}/q ratio of 1:5 is Cdq\textsubscript{2}. This is consistent with the reported result that Cdq\textsubscript{2} could be formed when ligand q is present in excess. However, when the CdCl\textsubscript{2}/q ratio was increased to 1:3 and 1:1, the products are a mixture of Cdq\textsubscript{2} and CdqCl, due to the coordination of Cl\textsuperscript{−} with Cd\textsuperscript{2+} to form CdqCl.

Time-dependent experiments were performed to investigate the formation process of the CdqCl nanowires. The samples obtained at a CdCl\textsubscript{2}/q ratio of 3:1 were characterized by TEM at different reaction times. Figure 4 shows the TEM images taken from the reaction mixture after the solution was exposed to ultrasound irradiation for 2, 12, 20, 30, 50, and 120 min. Figure 4a shows that the initial products are shuttle-like structures with a size of 200 nm × 1 μm at a reaction time of 2 min. As the reaction time increases, the shuttle-like particles become thinner and slender. When the reaction time reached 20 min, nanowires were observed (Fig. 4c). At a reaction time of 30 min, the main morphology was nanowires (Fig. 4d). The fact that the shuttle-like structures transform to nanowires supports the supposition that the products undergo a recrystallization process. After 50 min, the wire-like morphology did not change with an increase of reaction time. We also carried out the reaction with electromagnetic stirring instead of ultrasound irradiation. At the CdCl\textsubscript{2}/q ratio of 3:1, CdqCl nanowires were obtained without ultrasonic irradiation. However, using ultrasonic irradiation can obtain a more uniform morphology of CdqCl nanowires and can shorten the reaction time. TEM images of CdqCl nanowires obtained with and without ultrasonic irradiation are shown in Figure 5.

2.2. Fluorescence Sensing for H\textsubscript{2}O\textsubscript{2} and Glucose

We used the CdqCl nanowires, combined with biocatalytically grown Au nanoparticles, to develop a fluorescence sensing strategy for H\textsubscript{2}O\textsubscript{2} and glucose. Recently, Willner and co-workers developed an optical biosensor based on biocatalytically generated Au nanoparticles [22–27]. The excellent fluorescence properties of the CdqCl nanowires, when combined with biocatalytic growth of Au nanoparticles, allow us to develop a sensitive fluorescence sensing strategy for H\textsubscript{2}O\textsubscript{2} and glucose.

Figures 6 and 7 show the fluorescence sensing for H\textsubscript{2}O\textsubscript{2} and glucose by using CdqCl nanowires. The ways to generate Au nanoparticles for H\textsubscript{2}O\textsubscript{2} and glucose sensing are different. In the case of H\textsubscript{2}O\textsubscript{2}, AuCl\textsubscript{4} could be reduced by H\textsubscript{2}O\textsubscript{2} in the presence of Au nanoparticle seeds. In the case of glucose, the oxidase-biocatalyzed oxidation of glucose leads to the formation of H\textsubscript{2}O\textsubscript{2}, which acts

\[
F/F_0 = 1 - \frac{F}{F_0} = \frac{F}{F_0}
\]

as the quencher.
as a reducing reagent for the generation of Au nanoparticles. Whatever the growth process for Au nanoparticles, the concentration of generated Au nanoparticles is dominated by the concentration of \( \text{H}_2\text{O}_2 \) or glucose. After the generation of Au nanoparticles, CdqCl nanowires were added to the growth solution. When the nanowires was added into the growth solutions with differently generated Au nanoparticle concentrations, the fluorescence of CdqCl nanowires was quenched with increasing Au nanoparticle concentration, as shown in Figures 6a and 7a.

Figures 6b and 7b show the calibration curve derived from the changes in the fluorescence at \( \lambda = 508 \text{ nm} \) as the concentration of \( \text{H}_2\text{O}_2 \) and glucose, respectively, increases. The linear concentration ranges for \( \text{H}_2\text{O}_2 \) and glucose are from \( 8.33 \times 10^{-7} \) to \( 2.5 \times 10^{-4} \text{ m} \) and from \( 8.33 \times 10^{-7} \) to \( 2.33 \times 10^{-4} \text{ m} \), respectively.

For understanding the mechanism of the fluorescence quenching, the effects of \( \text{AuCl}_4^- \) and catalytically generated Au nanoparticles on the fluorescence of CdqCl nanowires were investigated. We synthesized Au nanoparticles by using \( \text{H}_2\text{O}_2 \) as a reducing reagent without glucose or glucose oxidase (GOx) in the growth solution, which contained \( 2.4 \times 10^{-4} \text{ m} \text{HAuCl}_4, 2.0 \times 10^{-3} \text{ m CTAC, } 47 \mu \text{g mL}^{-1} \text{ GOx (glucose oxidase), 15 \mu L cysteamine, 0.01 m PBS, pH 7.05} \), reacting with different concentrations of glucose. The fluorescence quenching of CdqCl nanowires by Au nanoparticles and \( \text{AuCl}_4^- \) nanoparticles are shown in Figures 8a and 8b, respectively, and are found to be linear. \( K_{SV} \) for the Au nanoparticles and \( \text{AuCl}_4^- \) are \( 8.84 \times 10^3 \) and \( 1.28 \times 10^4 \text{ m}^{-1} \), respectively. According to the results above, a model was proposed to explain the mechanism of the fluorescence quenching of CdqCl nanowires.

\[
\frac{F_0}{F} = 1 + K_{SV}[Q]
\]
by the biocatalytically grown Au nanoparticles. Assuming that the fluorescence quenching of CdqCl nanowires are due to two quenchers present in concentrations \([Q_a]\) for AuCl\(_4^-\) and \([Q_b]\) for generated Au nanoparticles, their contribution to the overall quenching process is given by:

\[
\frac{d(F_0)}{d[H_2O_2]} = \frac{d(F_0)}{d[Q_a]} + \frac{d(F_0)}{d[Q_b]} = aK_{SV} + bK_{SV}
\]

where \(F_0\) is the fluorescence intensity of CdqCl nanowires in the presence of the Au nanoparticles growth solution containing 2.4 \times 10^{-4} \text{ m AuCl}_4^- \text{, } 2.0 \times 10^{-3} \text{ m CTAC, } 1.8 \times 10^{-6} \text{ m Au seeds, } 0.01 \text{ m PBS, pH 7.05} \) but without the reducing reagent (H\(_2\)O\(_2\)). \(F\) is the fluorescence intensity of CdqCl nanowires in the presence of the Au nanoparticles in the presence of a blank solution with Au nanoparticles. The CdqCl complex was in the form of nanowires with diameter of about 50 nm and length of 2–4 \text{ m}. By controlling the ratio of CdCl\(_2\)/q, the morphology and composition of the products could be transformed from Cdq\(_2\) micrometer sized flakes to CdqCl nanowires. A new fluorescent sensing strategy for detecting H\(_2\)O\(_2\) and glucose was developed on the basis of the combination of the luminescent nanowires and the biocatalytic growth of Au nanoparticles. The quenching effects of Au nanoparticles and AuCl\(_4^-\) on the fluorescence of CdqCl nanowires were investigated. It was found that the Stern–Volmer quenching constant of Au nanoparticles is larger than that of AuCl\(_4^-\), and this is the dominant factor for the fluorescence quenching of CdqCl nanowires.

In this present work, we get the total quenching constant \(K_{SV} = aK_{SV} - bK_{SV} = 7.56 \times 10^4 \text{ m}^{-1}\). Mathematically, if \(d(F_0)/d[H_2O_2] > 0\), the value of \(F_0/F\) decreases with the increase of [H\(_2\)O\(_2\)]. In another word, the CdqCl nanowires fluorescence decreases with the increase of H\(_2\)O\(_2\) or glucose. From the S–V plot in Figures 5d and 6d, the total quenching constant for the case of H\(_2\)O\(_2\) and glucose were found to be 6.84 \times 10^3 and 6.77 \times 10^4 \text{ m}^{-1} \), respectively, which is in good agreement with the results of Equation 7 (\(K_{SV} = 7.56 \times 10^4 \text{ m}^{-1}\)).

### 3. Conclusions

Well-defined CdqCl complex nanowires were synthesized via a sonochemical route. TEM and SEM images showed that the CdqCl complex was in the form of nanowires with diameter of about 50 nm and length of 2–4 \text{ m}. By controlling the ratio of CdCl\(_2\)/q, the morphology and composition of the products could be transformed from Cdq\(_2\) micrometer sized flakes to CdqCl nanowires. A new fluorescent sensing strategy for detecting H\(_2\)O\(_2\) and glucose was developed on the basis of the combination of the luminescent nanowires and the biocatalytic growth of Au nanoparticles. The quenching effects of Au nanoparticles and AuCl\(_4^-\) on the fluorescence of CdqCl nanowires were investigated. It was found that the Stern–Volmer quenching constant of Au nanoparticles is larger than that of AuCl\(_4^-\), and this is the dominant factor for the fluorescence quenching of CdqCl nanowires.

### 4. Experimental

In a typical process for the synthesis of CdqCl nanowires, a certain amount of 8-hydroxyquinoline and CdCl\(_2\)-2.5H\(_2\)O was dissolved in an ethanol/water solution (50% v/v, 50 mL). The molar ratio of CdCl\(_2\)-2.5H\(_2\)O/8-hydroxyquinoline was 3:1. The solution was then mixed and exposed to ultrasonic irradiation in air for 50 min. Ultrasonic irradiation was accomplished with an ultrasonic probe (Xinzhi Co., Xinzhi, China; 1.2 cm diameter; Ti horn, 20 kHz, 100 W cm\(^{-2}\)) immersed directly in the reaction solution. When the reaction finished, a yellowish-green precipitate was obtained. The product was purified by centrifugation–redispersion cycles with water and ethanol and then dried in air at 60°C. The products were characterized by field-emission scanning electron microscopy (FE-SEM; LEO-1530VP), transmission electron microscopy (TEM; JEOL-JEM 200CX), infrared spectroscopy (IR, Nicolet Nexus 870 FT-IR), elemental analysis (EA, Heraeus CHN-O), atomic absorption spectroscopy (AAS, Hitachi 180-80), and photoluminescence spectroscopy (PL, Hitachi 850). All spectra were collected at room temperature.

Preparation of Au Nanoparticle Seeds: Au nanoparticle seeds were prepared by using KBH\(_4\) as reductant and stabilized with sodium citrate following the literature [30,31]. HAuCl\(_4\) (5 mL, 1%) and sodium citrate (10 mL, 0.03 M) were added into 250 mL of doubly distilled water and stirred. Then freshly prepared KBH\(_4\) (5 mL, 0.1 M) was added, and the mixture was stirred at room temperature for 24 h. The diameter of the Au nanoparticle seeds was about 4–7 nm.

Growth of Au Nanoparticles and Fluorescence Sensing for \(H_2O_2\) and \(\beta\)-Glucose: A 5 mL volume of the Au nanoparticles growth solution consisted of 2.4 \times 10^{-4} \text{ m AuCl}_4^- \text{, } 2.0 \times 10^{-3} \text{ m cetyltrimethylammonium chloride (CTAC) in 0.01 \text{ m phosphate-buffered saline (PBS), pH 7.05, and different concentrations of either H}_2\text{O}_2\) or glucose. From the S–V plot in Figures 5d and 6d, the total quenching constant for the case of H\(_2\)O\(_2\) and glucose were found to be 6.84 \times 10^3 and 6.77 \times 10^4 \text{ m}^{-1} \), respectively, which is in good agreement with the results of Equation 7 (\(K_{SV} = 7.56 \times 10^4 \text{ m}^{-1}\)).
together with 47 μg mL⁻¹ GOx. For the catalytic growth of Au nanoparticles, 20 μL of Au nanoparticle seeds (4.5 × 10⁻⁴ m) were added to the growth solution. The growth of Au nanoparticles was performed at a temperature of 5 °C for 5 h in the case of H₂O₂, or 37 °C for 5 h in the case of β-glucose with GOx. Then 15 μL of cysteamine was added to terminate the reaction. Subsequently, 1 mL of Cd(qCl)₂ nanowires (12 mg dispersed in 60 mL doubly distilled water, containing 600 μL of CTAC, 2.4 μL 3-mercaptopropionic acid (MPA)) was added into the solution and the fluorescence spectra were recorded after 5 min at room temperature.

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