

# A Study of the Conjugation of CdSe Nanoparticles with Functional Polyoxometalates Involving Aminoacids

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**Abstract** — CdSe nanoparticles (CdSe NPs) are regarded as nanomarkers and an important component for biomedical applications. In this study, CdSe NPs and polyoxometalates were synthesized; surface modification with 1-thioglycerol and ( $\beta$ -Ala) was carried out. Polyoxometalates, which cause an inhibitory effect on cancer cells, were conjugated to the nanoparticles. UV- VIS, IR, XRD, and TEM studies were performed to characterize the resulting CdSe NPs, polyoxometalates, and conjugates.

**Index Terms** — polyoxometalates, CdSe nanoparticles, aminoacid, absorption spectrum, conjugates.

## I. INTRODUCTION

Nanoparticles (NPs) are a class of particles that, because of their unique optical properties, show great potential for incorporation into numerous consumer, industrial, and medical products. NPs are semiconductor fluorescent nanocrystals whose unique chemical, physical, and optical properties make them ideal for use in a variety of applications in electronics, computing, and biomedical research [1].

Various polyoxometalates (POMs) exhibit an inhibitory effect on the cancer cell lines [2]. We have found an inhibitory effect in selenium-containing POMs with respect to SH-SY5Y cell line [3]. The conjugation of the active form of POMs with photoluminescent CdSe nanoparticles (nanomarkers) would make it possible to study the mechanism of the inhibitory effect of POMs.

## II. METHODS

**Chemicals.**  $\beta$ -Ala (alanin) (Aldrich, 90%), 1-thioglycerol(TG), tetramethylammonium hydroxide pentahydrate (TMAHP) (Aldrich, 99.999%), were used as purchased without further purification. Anhydrous, hexane, chloroform, acetone, 1,4-dioxane, methanol (Aldrich, 90%), were purchased from different companies and used without further purification. CdSe nanoparticles were prepared according to the moderate stirring technique described in [3]. Synthesis  $\text{Na}_7[\text{Cu}_3\text{Na}_3(\text{H}_2\text{O})_9(\alpha\text{-SeW}_9\text{O}_{33})_2] \cdot 11.5\text{H}_2\text{O(I)}$  was described in [4].

### Synthesis

$\text{Ala}_2\text{Na}_5[\text{Cu}_3\text{Na}_3(\text{H}_2\text{O})_9(\alpha\text{-SeW}_9\text{O}_{33})_2] \cdot 10 \text{H}_2\text{O(II)}$

Complex  $\text{Na}_7[\text{Cu}_3\text{Na}_3(\text{H}_2\text{O})_9(\alpha\text{-SeW}_9\text{O}_{33})_2] \cdot 11.5\text{H}_2\text{O(I)}$  (0.8 g, 0.2 mmol) was dissolved in  $\text{H}_2\text{O(II)}$  (40ml, pH 4.5).  $\beta$ -Ala (0.2 mmol) was added to the solution (1:4).

The solution changed color from green to blue. Blue crystals approached in several hours.

Yield, %: W 60,00; Cu 3,58; Se 4,02;  $\text{H}_2\text{O}$  7,45.

Found, %: W 60,65; Cu 3,51; Se 4,68;  $\text{H}_2\text{O}$  7,58. N; C;

### Synthesis of Thiol-Coated Nanocrystals CdSe. Ligand exchange and water solubilization.

Cadmium selenide nanoparticles were prepared by the colloidal method [5].

CdSe QDs were water-solubilized by replacing the initial hydrophobic surfactants (OA) with 1-thioglycerol(TG)<sup>(9)</sup>. A 10 mg amount of TG and 5.0 mg of QDs were dissolved in 30 mL of solvent. Two solvent systems were compared: methanol and a 1:1 mixture of 1,4-dioxane and methanol. The solution was adjusted to pH10 with TMAHP.

The flask was purged with  $\text{N}_2$ , and the temperature was raised to 70 °C. Samples were removed from the reaction at specific times during the exchange. Hydrophilic QDs were purified from hydrophobic QDs and the exchanged OA and TG ligands by adding ethyl acetate to the solution. TG-capped QDs aggregated, and the solution was centrifuged at 3 000 rpm for 45 min. The supernatant was discarded, and the pellet was redissolved in water (adjusted to pH 6.87 with phosphate buffer). This procedure was repeated at least three times.

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To conjugate POMs to NPs, we conducted a special reaction between an aqueous solution of thioglycerol-modified cadmium selenide and a solution of the complex in a water medium. The absorption spectrum was measured. The solution maintained stability for 1 month.

### Nanocrystalline sample characterization.

High-resolution transmission electron microscopy (HRTEM), powder X-ray diffraction (XRD), and infrared absorption spectroscopy (IR) were used to characterize the size, shape, structure, and composition of the CdSe nanocrystals and polyoxometalates. The powder XRD data were recorded with CuK  $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) using Scintag and PAN analytical X'Pert Pro diffractometers, both operating in the Bragg–Brentano geometry. Samples for the XRD measurements were prepared by the deposition of concentrated CdSe colloidal solutions in chloroform or trichloroethylene onto a glass substrate. The  $2\theta$  range was scanned from  $20^\circ$  to  $80^\circ$ . A Philips CM 30 transmission electron microscope (TEM) equipped with a Super-Twin lens and LaB<sub>6</sub> emitter was used for HRTEM measurements. TEM were prepared by the deposition of a drop of a dilute colloidal solution in chloroform, hexane, or trichloroethylene on a carbon-coated copper grid (200 mesh), allowing slow evaporation at room temperature. X-ray powder diffraction by depositing the colloidal solution onto a glass substrate drop wise.

### III. RESULTS AND DISCUSSION

The crystal structure of  $\text{Na}_7[\text{Cu}_3\text{Na}_3(\text{H}_2\text{O})_9(\alpha\text{-SeW}_9\text{O}_{33})_2] \cdot 11.5\text{H}_2\text{O}$  (I) has been synthesized and determined by single-crystal X-ray analysis. Compound I crystallizes in monoclinic space group  $P2_1/c$  with  $a=17.8386(7)$ ,  $b=19.6118(6)$ ,  $c=26.8254(13) \text{ \AA}$ ,  $\beta=117.905^\circ$ ,  $V=8293.6(6) \text{ \AA}^3$ . The structural analysis reveals that the anions  $\{[\text{Cu}(\text{H}_2\text{O})]_3[\text{Na}(\text{H}_2\text{O})_2]_3[\text{X}_2\text{W}_{18}\text{O}_{66}]\}^{7-}$ ,  $\text{X} = \text{Se}$  are the basic building units in both compounds. Each polyoxoanion consists of two  $[\alpha\text{-XW}_9\text{O}_{33}]^{8-}$ , where ( $\text{X} = \text{Se}^{\text{IV}}$ , , moieties linked by three  $(\text{CuO}_5)^{2+}$  and three  $(\text{NaO}_8)^{1+}$  units resulting in a sandwich-type structure  $\{[\alpha\text{-XW}_9\text{O}_{33}]^{8-}-(\text{Cu}^{\text{II}}\text{O}_5)^{2+}_3(\text{Na}^{\text{I}}\text{O}_8)^{1+}_3-[\alpha\text{-XW}_9\text{O}_{33}]^{8-}\}^{7-}$ . The sandwich-belt consists of three edgesharing tetrahedral pyramids of  $\{\text{CuO}_5\}$  and three  $\{\text{NaO}_8\}$  octahedrons which condensed together and linked through common edges the  $[\alpha\text{-XW}_9\text{O}_{33}]$  hemispheres. Three Cu atoms in I form the isosceles triangle with distances  $\text{Cu1}-\text{Cu2}=\text{Cu1}-\text{Cu3}=4.84(1) \text{ \AA}$  and  $\text{Cu2}-\text{Cu3}=4.80(1) \text{ \AA}$ .

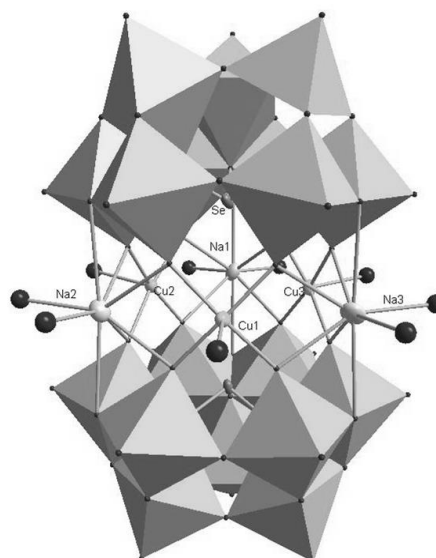


Fig.1 Polyoxoanion  
 $\{[\text{Cu}(\text{H}_2\text{O})]_3[\text{Na}(\text{H}_2\text{O})_2]_3[\text{Se}_2\text{W}_{18}\text{O}_{66}]\}^{7-}$

IR spectrometric study of complex (1) showed the presence of the following absorption bands: 3550 – 3200, 1630, 960, 880 – 870, 830, 770, 720, 630, 550, 470, 370, 325  $\text{cm}^{-1}$ , which are characteristic of polyanion  $[\text{Cu}_3\text{Na}_3(\text{H}_2\text{O})_9(\alpha\text{-SeW}_9\text{O}_{33})_2]^{7-}$ .

Complex (2) exhibit absorption bands characteristic of both polyanion  $[\text{Cu}_3\text{Na}_3(\text{H}_2\text{O})_9(\alpha\text{-SeW}_9\text{O}_{33})_2]^{7-}$  and beta-alanine molecules. The peaks at 1328 and 1131  $\text{cm}^{-1}$  are attributed to  $\gamma$  (C-H) and  $\gamma$  ( $\text{NH}_3^+$ ) pertaining to  $\beta$ -Alanine molecules, respectively.

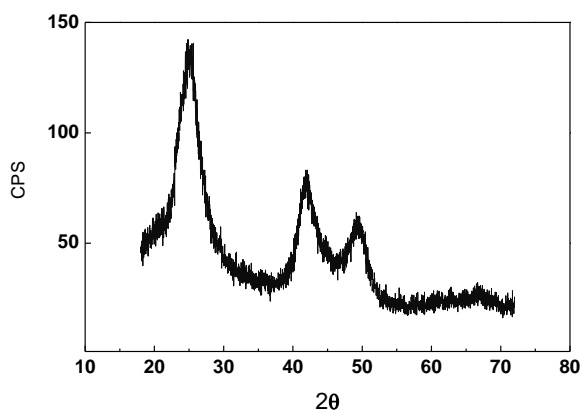


Fig.2. Typical powder diffraction pattern of CdSe QDs

A typical powder diffraction pattern of the produced CdSe nanocrystals is shown in Fig. 2. XRD revealed three broad peaks positioned at  $2\theta = 25.37,$

42.04, and 49.63° with corresponding interplanar spacing of 3.51, 2.15, and 1.83 Å, respectively. These peaks are assigned to the (002), (110), and (112) planes of the wurtzite structure of CdSe. The brodening of the diffraction pattern for CdSe implies a reduction in particle size. An average size of 3–3.5 nm for the CdSe nanoparticles was estimated from the X-ray powder diffraction data using the Scherrer equation

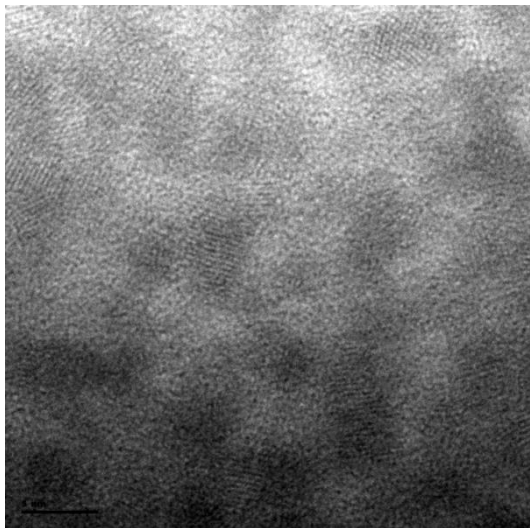


Fig. 3. High-resolution transmission electron microscopy image of low aspect ratio CdSe NPs.

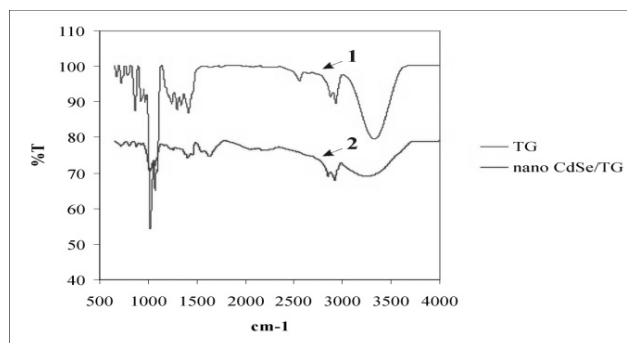


Fig. 4. FTIR transmission spectra of (1) thioglycerol, (2) typical CdSe/TG dots sample.

Figure 4 compares the IR spectra of 1-thioglycerol and theas-prepared CdSe QDs sample. 1-thioglycerol (1) has characteristic peaks at 2560 and 3400 cm<sup>-1</sup>, which are assigned to the SH and OH stretching vibrations, respectively. The IR spectrum of the as-prepared QDs in (2) shows the main bands due to 1-thioglycerol, except for the SH stretching band at 1360 cm<sup>-1</sup>. The disappearance of the -SH vibration of 1-thioglycerol clearly indicates that this reagent is chemisorbed onto the QDs, and that the OH functional groups remain intact on the particles. The QDs are thus hydrophilic and water soluble and the OH functionalities are available on the surface for further chemical modification.

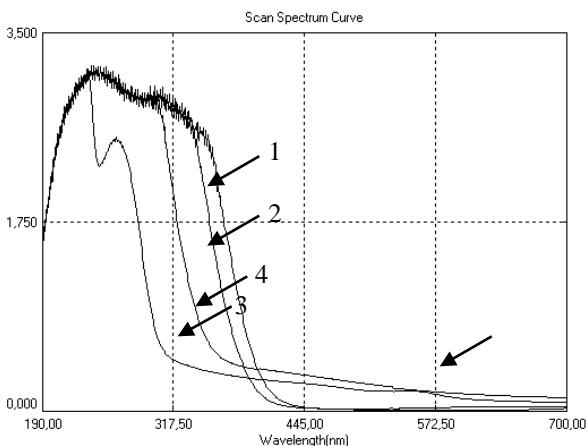


Fig.5. The absorption spectra of hidrig solution colloidal solution CdSe/TGNPs with 3,5nm; 1- POM(1) and 2- β-AlaPOM(2), 3- hydric colloidal solution CdSe/TGNPs with 3,5nm 4- CdSe/TG@β-AlaPOM

Complex (2) exhibit absorption bands characteristic of both polyanion [Cu<sub>3</sub>Na<sub>3</sub>(H<sub>2</sub>O)<sub>9</sub>(α-SeW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>7-</sup> and beta-alanine molecules. The peaks at 1328 and 1131 cm<sup>-1</sup> are attributed to γ (C-H) and γ (NH<sub>3</sub><sup>+</sup>) pertaining to β-Alanine molecules, respectively. Ala molecules were coordinated to on isolated Cu<sup>2+</sup> cation and thus formed a [Cuβ-Ala)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> two such complexes were covalently linked to the [Cu<sub>3</sub>Na<sub>3</sub>(H<sub>2</sub>O)<sub>9</sub>(α-SeW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>7-</sup> by two μ– oxygen atoms [6]

The UV spectra 199nm -350nm are indicated in Fig4. Bond the UV-spectra hare two absorption bands 210 and 230nm for (1), 350 and 360nm for (2).

The strong band at ca.200-250 is attributed to the harde transfer of Ot → W, and the weak band at.a. 300-350nm is due to that of Ob/Oc → W ,typocal for polyoxometalates. UV spectra CdSe/TG@β-AlaPOM is placed in in the absorption spectru of polyoxometalates and colloidal solution quantum dots CdSe /TGNPs (3). Typical absorption of polyoxometalate with alanine, quantum dots CdSe and conjugated system CdSe / TG @ β-AlaPOM is situated in the visible fild of the spectrum.

Possibility to exist of the alanine group in acid media is protonated, and an electrostatic interaction with CdSe/TG NPs can occur, as evidenced by the formation of a stable color solution.

#### IV. CONCLUSIONS

CdSe NPs and polyoxometalates were synthesized surface modification with 1-thioglycerol and (β-Alan) was carried out. Polyoxometalates were conjugated to the nanoparticles.

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