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CdSe nanometerials: kinetics, thermodynamics, antioxidant activity and application to Denim fabric

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For the first time in this study, the kinetics and thermodynamics of the CdSe nanomaterials were determined by spectral measurements. In addition, as a contrubution to the literature, antioxidant activity, application to denim fabric and testing of finished fabric for antimicrobial activities of CdSe nanomaterials were investigated. According to absorbance measurements, the activation energy (Ea) and other activation thermodynamic parameters (ΔS, ΔH and ΔG) were determined. The study showed that the process was endothermic and was a nonspontaneous process during activation. The presence of nanoparticles on denim fabric surfaces was confirmed by Scanning Electron Microscope (SEM).The nano CdSe impregnated denim fabric (100% cotton) showed excellent antibacterial activity against *Staphylococcus aureus* and *Escherichia coli.* Additionally, the CdSe nanomaterials demonstrated significant antioxidant activity.

Keywords: CdSe Nanomaterials, Kinetics, Thermodynamics, Antioxidant Activity, Antibacterial Activity

INTRODUCTION

Nanotechnology is regarded as a key technology which will not only influence technological development in the near future, but will also have economic, social and ecological implications. The technology can be used in engineering desired textile attributes, such as fabric softness, durability, breathability, water repellency, fire retardancy and antimicrobial resistance [1]. With the advent of nanotechnology, a new area has developed in the realm of textile finishing. Nano coating on the surface of textiles and clothing enhances the UV blocking, antimicrobial and self clening properties of the material [2].

The inherent properties of textile fibers provide room for the growth of micro-organisms. Besides, the substrate structures and chemical processes may induce growth of bacteria. Infestation by bacteria causes cross infection by pathogens and development of odor where the fabric is worn next to skin. With the use of nano sized particles, the number of particles per unit area is increased, and thus antibacterial effects can be maximized [3].

Nanomaterials are tiny particles with particle size mainly below 20 nm, as the optimum size quantity can be attained below this range. It is reported that optimum size variation in CdSe nanocrystals due to quantum confinement is from 1 to 11 nm, which means it contain 10-10.000 atoms. As the size decreases, number of atoms on the surface may result in loss of optical properties and shift in absorption frequency to the red region of the visible spectrum due to increase in particles [4-6].

CdSe has attracted great interest due to its high photosensitivity, its attractive application to photo conducting cells and the dependence of its properties on size [7]. Traditionally, CdSe nanomaterials have been prepared through a solid-state reaction between elemental cadmium and selenium at relatively high temperatures [8, 9]. Various chemical methods have been introduced to synthesize CdSe nanomaterials, such as solvothermal synthesis [10],laser ablation[11] and hard template [12].

In the previous studies, the effect of CdSe nanomaterials on humans are reported, such as cytotoxic [13], toxic [14], genotoxic [15]. For example, in the study by Young and colleagues [15], the genotoxic effect of CdSe/ZnS nanomaterials is measured in human cancer cells by comet and micronucleus assays. Treatment with CdSe/ZnS nanomaterials resulted in the most severe extent of cell death.

The main of this research study is kinetics, antioxidant activity, application to denim fabric and testing of finished fabric for antimicrobial activities of CdSe nanomaterials. In addition, as a contrubution to the literature, for the first time in this study, the kinetics and thermodynamics of the CdSe nanomaterials are determined by spectral measurements.

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EXPERIMENTAL

Material and measurements

All reagents were purchased from commercial sources and used as supplied. UV/Vis spectra were measured with a Shimadzu UV-1700 Pharma spectrophotometer in the 200-800 nm range. Bruker X Flash XRD-6110 and Shimadzu XRD-6000 were employed for the XRD analyses. For the SEM analysis, nano finished samples were mounted on a specimen stub with double sided adhesive tape coated with gold in a sputter coater and examined with a Scanning Electron Microscope (SEM) model ZEIS LEVO LS 10.

Synthesis of the CdSe nanomaterials [16]

30 mg Se and 5 mL of 1-octadecene were mixed and 0.4 mL of trioctylphosphine was added. The solution was stirred. It was warmed as necessary to speed up the dissolution of Se. The stock solution was storred at room temperature. Then, 17.4 mg cadmium acetate and 0.6 mL oleic acid were added in 10 mL octadecene and heated. When the temperature reached 225 °C, 1 mL of selenium solution at the room temperature was transferred into the cadmium solution. The orange- red-brown reaction mixture was cooled to room temperature followed by addition of 10 mL of toluene and and was stirred at room temperature for half on hour. The reaction mixture was then centrifuged and washed with the same solvent to obtain orange or brown povder.

Yield (%): 88, UV-Vis (λ/nm): 431 and 458, IR (cm^{-1}/KBr): 2923(sym $–CH_2$), 2854 (asym $–CH_2$), 1450 ($\delta_{as}$$–CH_3–$), 1600 (=CH), 1700-1720 (C=O), TGA (°C, a rate of 10 °C / min under nitrogen atmosphere): 250-330 (organic capping), 800 (CdSe), XRD (2θ): 23.89473, 25.39343, 41.98555, 45.80425 and 49.67800.

Kinetics and thermodynamics procedure

There is no paper in the literature on the kinetics of the synthesis reaction of CdSe nanomaterials [17-21]. Rate formulas are derived from the experimental data. The rate formula is [22],

$$\ln C / C_0 = - k\, t \text{ , (1)}$$

where t is the time, C is the concentration at the time t, C_0 is the concentration t = 0, and k is the rate constant.

According to the Beer-Lambert law [23], because absorbance is proportional to the concentration, equation 1 can be rearranged as follows,

$$\ln A / A_0 = - k\, t \text{ , (2)}$$

where A is the absorbance at time t, A_0 is the absorbance at t = 0.

The activation energy can be determined by the Arrhenius equation [22]:

$$k = A\, e^{-Ea / RT} \text{ , (3)}$$

where k is rate constant, A is the frequency factor or the Arrhenius Arrhenius constant, Ea is the activation energy, R is the universal gas constant (8.314 $JK^{-1}mol^{-1}$) and T is absolute temperature.

According to transition state theory, thermodynamic parameters are assigned an activated complex as follows [24]:

$$A = RT / Nh\, e^{\Delta S / R} \text{ , (4)}$$

$$\Delta H = Ea – RT \text{ , (5)}$$

$$\Delta G = \Delta H – T\Delta S \text{ , (6)}$$

where N is the Avogadro constant (6.022 x 10^{23} mol^{-1}), h is the Planck constant (6.626 x 10^{-34} Js), ΔS is the activation entropy, ΔH is the activation enthalpy, and ΔG is the activation energy or the Gibbs energy of activation.

Antioxidant activity procedure

The antioxidant activity [25-28] of the CdSe nanomaterials was determined in vitro as described with slight modifications as follows: The compounds were serially diluted in DMSO to obtain a concentration range of 1.25–20 mM on a 96 well plate. The reaction mixture consisted of 100 μL of 0.5 mM 2,2-diphenyl-1-picrylhydrazyl radical (DPPH), and 100 μL of each concentration of the test compounds using DMSO as the solvent. For positive control, 2,6-di-tert-butyl-4-methylphenol (BHT) was used at a concentration range of 0.0625–2 mM in methanol. The solvents, DMSO and methanol, were used as blanks. Duplicate experiments were performed. The plates were covered with aluminum foil and kept in the dark for 20 minutes after which the absorbance was read on a Tecan-PC infinite M 200 Pro Plate reader at the absorbance wavelength of 517 nm. The percent antioxidant activity was calculated as follows:

$$\text{Antioxidant (\%)} : 100 \times (A_0 – A_1 / A_0) \text{ , (7)}$$

where A_0 is the absorbance of the blank and A_1 is the absorbance in the presence of the sample or positive control.

General procedure for application to denim fabric

The denim fabric used in the experiments was 100 % cotton, weight was 247 g/m^2, the warp was dyed blue and the weft yarn wasn't dyed. CdSe nanomaterials were sprayed on denim fabric by using a spray gun [29, 30].

Nanomaterials were applied on the face side of the fabric with concentration 1%, material to liquor ratio 1:20, and acrylic binder 1%. The 100 % cotton denim fabric was cut to a size of 30 x 30 cm. This fabric was coated with CdSe nanomaterials by using a spray gun. The hand spray gun was filled with a dispersion of nanomaterials. The fabric substrate was fixed on a vertical board. The nanomaterials solution was evenly sprayed over the fabric by maintaining a constant distance between the fabric and spray gun nozzle. The excess solution was squeezed using a padding mangle. After padding, the fabric was dried naturally.

Antibacterial activity procedure

To investigate the in vitro antibacterial activity, denim fabric impregnation was done with CdSe nanomaterials separately. Antibacterial test AATCC-100 [31-33] was carried out against *Staphylococcus aureus* (Gram positive bacteria) and*Escherichia coli* (Gram negative bacteria). The percentage reduction of bacteria by the 100 % cotton denim fabric is reported as R,

$$R (\%) = 100 \times (A-B / A) , (8)$$

where R is % reduction, A is the number of bacteria on the untreated fabric after 24 hours and B is the number of bacteria on the antibacterial treated fabric after 24 hours.

RESULTS AND DISCUSSION

Kinetics and thermodynamics results

During the measurements of the absorbance, The orange- red-brown reaction mixture was cooled to room temperature followed by addition of 10 mL of toluene and was stirred at room temperature for half an hour. Then, all kinetic experiments were carried out at temperatures of 60, 70, 80 and 90 °C. The absorbance values determined are tabulated in Table 1. Decreasing absorbance values show that the the particle growth is a logaritmic function of time and temperature. At first, the particles grow fast, but then, the growth rate slows down.

Rate formulas are derived from the experimental data. If ln A vs. t is plotted according to equation (2), the slope gives k (Fig. 1). The values of the rate constant k in equation (2) are as follows [t (°C), k (min^{-2})] : 60 °C, 5.11×10^{-3}, 70 °C, 5.29×10^{-3}, 80 °C, 5.45×10^{-3}, and 90 °C, 5.60×10^{-3}. According to Fig. 1., reaction is first order.

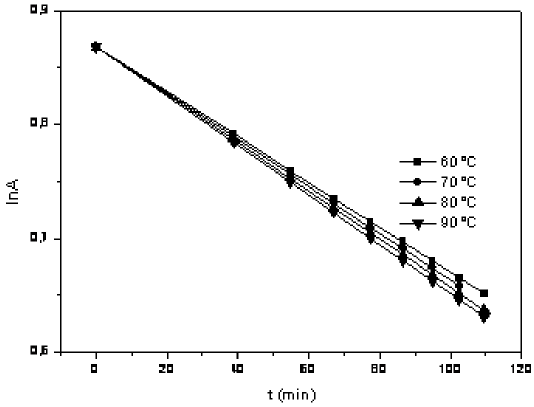

Fig. 1. The plot of ln A vs, t for the CdSe nanomaterials.

Where ln k is plotted against the reciprocal of the temperature (1/T), -Ea/R represents the slope, and the intercept gives ln A (Fig. 2). The values of Ea and A were calculated as 3289 J and 1.676×10^{-2} min^{-1} = 2.79×10^{-4} s^{-1}, respectively.

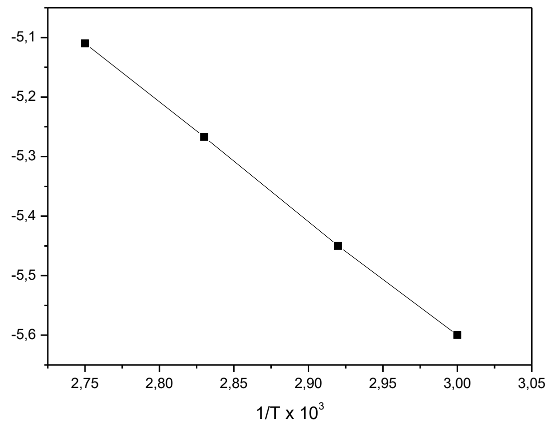

Fig. 2. The plot of ln k vs, 1/T for the CdSe nanomaterials.

Table 1. Absorbance values of CdSe nanomaterials at different temperatures

	Absorbance(nm)			
t (min)	T = 60 (°C)	T = 70 (°C)	T = 80 (°C)	T = 90 (°C)
0	2.383	2.383	2.383	2.383
15	2.207	2.201	2.196	2.191
30	2.137	2.130	2.123	2.116
45	2.086	2.077	2.068	2.060
60	2.043	2.033	2.024	2.014
75	2.007	1.996	1.985	1.975
90	1.974	1.962	1.951	1.939
105	1.944	1.932	1.919	1.908
120	1.917	1.904	1.891	1.879

Thermodynamic parameters at 60, 70, 60 and 90 °C were calculated by means of equations (4), (5,) and (6). These values are given in Table 2.

Table 2. The thermodynamic parameters for the CdSe nanomaterials.

T (°K)	ΔH ($J\ mol^{-1}$)	ΔS ($J\ mol^{-1}K^{-1}$)	ΔG ($J\ mol^{-1}$)
333	520.818	-148.022	49812.144
343	437.678	-147.775	51124.503
353	354.538	-147.540	52436.158
363	271.398	-147.307	53743.839

The positive value of ΔH shows that the process is endothermic and a certain amount of energy is received during activation. The negative value of ΔS and the positive value of ΔG show that the process is a nonspontaneous process from a physicochemical respect. The enthalpy and entropy values decrease with increasing temperature while Gibbs free energy values increase, as can be seen from Table 2.

Antioxidant Activity

The antioxidant results of the CdSe nanomaterials are given in Fig.3. According to Fig. 3, the antioxidant activity increased significantly. As reported, the increased antioxidant activity is a result of the electron withdrawing effect of the metal ion which facilitates the release of hydrogen to reduce the DPPH radical. CdSe nanomaterials also show significant free radical scavenging ability when tested against DPPH.

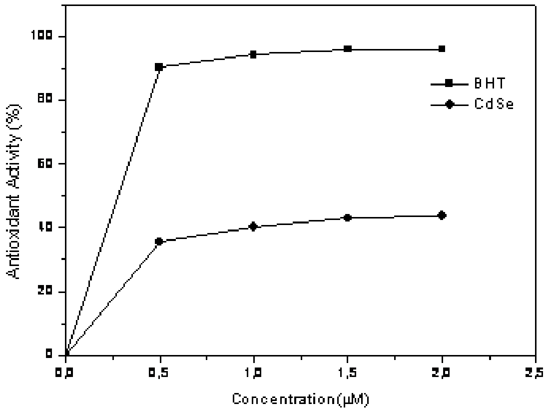

Fig. 3. Percent antioxidant activity of CdSe nanomaterials.

Analysis of the finished denim fabric with CdSe nanomaterials using SEM

The surfaces of the treated fabric were observed by SEM microscopy. Fig. 4 and Fig. 5 the SEM micrographs show SEM image of the untreated 100 % cotton denim fabric and the nano scaled CdSe nanomaterials on 100 % cotton denim fabric samples, respectively. In Fig. 5, the nanoparticles are well dispersed on the fabric surfaces, although some aggregated CdSe nanomaterials are still visible. The particles size plays a primary role in determining their adhesion to the fabric. It is reasonable to expect that the largest particle agglomerates will be easily removed from the fabric surface, while the smaller particles will penetrate deeper and adhere strongly into the fabric matrix.

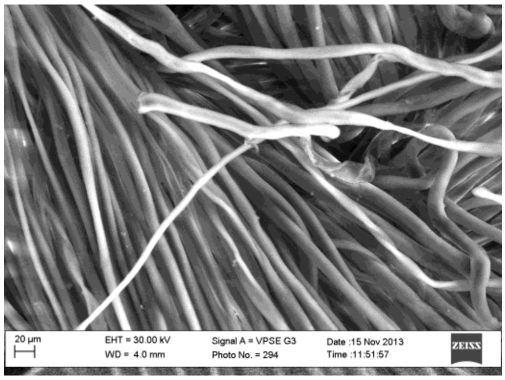

Fig. 4. SEM image of the untreated 100 % cotton denim fabric.

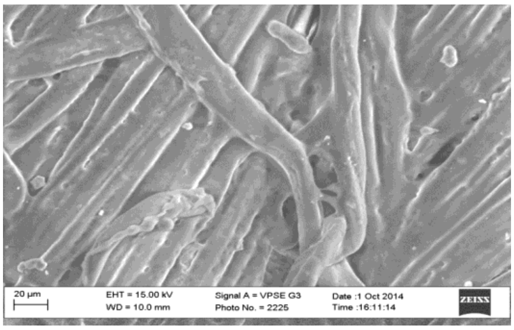

Fig. 5. SEM image of 100 % cotton denim fabric treated with CdSe nanomaterials.

Also in Fig. 6 and Fig. 7 SEM micrographs show that the presence of Cd and Se metals on the denim fabric. Red and green points demonstrate that the presence of Cd metal and Se metal, respectively.

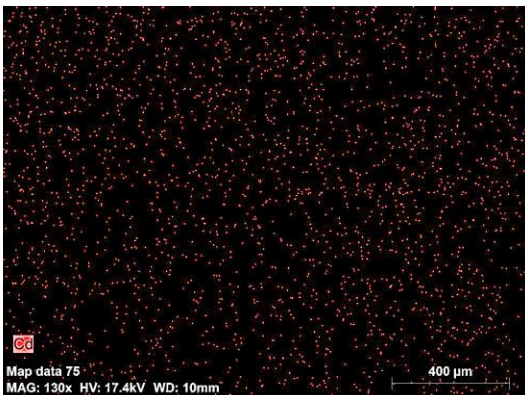

Fig. 6. Colorful SEM image of 100 % cotton denim fabric treated with CdSe nanomaterials. Red points demonstrate that the presence of Cd metal.

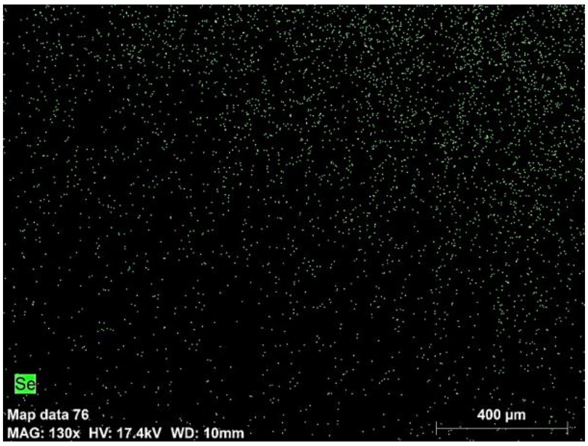

Fig. 7. Colorful SEM image of 100 % cotton denim fabric treated with CdSe nanomaterials. Green points demonstrate that the presence of Se metal

Antibacterial Activity

The results for the AATCC-100susceptibility tests recorded in Table 2 show that the CdSe nanoparticles have significant antibacterial activity against Staphylococcus aureus and show moderate activity against *Escherichia coli.* As a result, CdSe nanomaterials are preferable to other inorganic forms of cadmium because of its higher efficiency in preventing infection.

Table 3. Antibacterial activity of CdSe nanomaterials treated denim fabric.

Fabric sample	*Staphlococcus aureus*	*Escherichia coli*
Untreated	No reduction	No reduction
Denim fabric	80.20 %	20 %

CONCLUSION

In the present study, the kinetic and thermodynamic parameters such as the activation energy (Ea), the activation entropy (ΔS), the activation enthalpy (ΔH), and the Gibbs energy (ΔG) of CdSe nanomaterials was determined by spectral measurements. The activation energy is found to be approximately 3289 J. The rate constant does not depend on temperature due to the lower activation energy. That is, lower activation energy signifies that the rate constant does not change rapidly with temperature. Finally, the reaction is entropy controlled and the enthalpy contribution changes slightly with change in temperature.

It was shown that the nano-CdSe impregnated on denim fabric showed excellent antibacterial activity against two representative bacteria *Staphlococcus aureus* and *Escherichia coli*. This work provides a simple method for CdSe nano composites and their application onto denim fabric to impart antibacterial function. Additionally, the nano CdSe demonstrates significant antioxidant activity.

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НАНОМАТЕРИАЛИ ОТ CdSe: КИНЕТИКА, ТЕРМОДИНАМИКА, АНТИОКСИДАНТНА АКТИВНОСТ И ПРИЛОЖЕНИЕ В DENIM-ТЪКАНИТЕ

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(Резюме)

За пръв път са изследвани кинетиката и термодинамиката на наноматериали от CdSe с помощта на спектрални методи. Допълнително са изследвани антиоксидантната и антимикробната активност на CdSe – наноматериалите нанесени върху denim-текстил. Определени са активиращата енергия (Ea) и дрги термодинамични параметри (ΔS, ΔH и ΔG) с помощта на измервания на абсорбционни спектри. Изследванията показват, че процесът е ендотермичен и не е спонтанен по време на активирането. Наличието на наночастици върху denim-тъканитее потвърдено със сканираща електронна микроскопия (SEM). Импрегнираните с наночастици от CdSe denim-тъкани (100% памук) показват отлична антибактериална активност спрямо бактериите *Staphylococcus.*