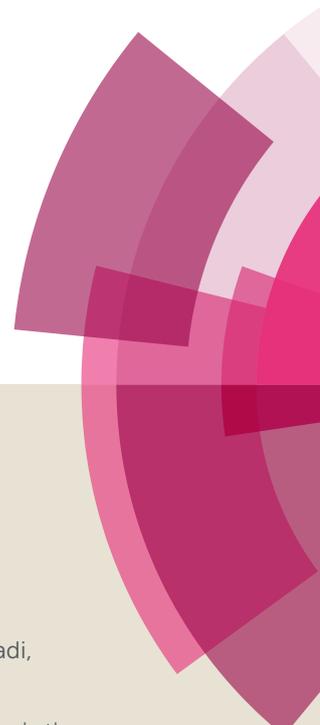


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Catalytic Applications of β -Cyclodextrin/Palladium Nanoparticles Thin Film Obtained from Oil/Water Interface in the Reduction of Toxic Nitrophenol Compounds and Degradation of Azo Dyes

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Abstract

The supramolecular catalyst of Pd/ β -cyclodextrin thin film is synthesized *via* a facile and one-pot procedure at oil-water interface. Macrocyclic oligosaccharides of cyclodextrins with glucose units exhibit wide range of applications due to their hydrophobic and chiral interior. Due to the ability of this supramolecular catalyst to form inclusion complexes with small organic molecules, the as-synthesized catalyst was applied for the reduction of toxic nitroaromatic compounds (*p*, *o*, *m*- nitrophenol and 4-Cl-2-nitrophenol) and degradation of harmful azo dyes (methyl orange and bismarck brown) with considerable results. This investigation illustrates the change of the catalyst properties in the presence of molecular receptors attached to the catalyst surface.

Keywords: Inclusion complex, Oil/water interface, Supramolecular catalyst, Thin film, Nitrophenol, β -cyclodextrin.

1. Introduction

Along with the rational design of catalytic approaches in industry, supramolecular chemistry (chemistry beyond the molecule) has attracted significant interest in recent years to improve the

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3 catalysts activity [1]. Cyclodextrins (CDs) are one of the main branches of polysaccharides that
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5 obtain from the starch degradation with various industrial applications since the end of 1980s in
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7 the field of medicine, supramolecular and catalysis chemistry [2,3]. Being biodegradable,
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9 nontoxic, available, producible in large scale amount, easily functionalized, having hydrophobic
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11 central cavity and hydrophilic outer surface and stability against chemical and photochemical
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13 degradation are some of the advantages of CDs that make them a good candidate for the above
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15 applications [4-6]. The special structure of CD molecules enables them to encapsulate small
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17 molecules and form inclusion complexes that control with the host-guest chemistry. Due to the
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19 chemical and physical modification and improvement of the guest molecules, formation of the
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21 inclusion complex is very important in industry [7]. Furthermore, these compounds can be
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23 applied as catalyst for pollution removal of water and air in order to their amazing chemical
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25 reactivity with the accelerated rate. One of the most commonly used noble transition metals
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27 applied in catalysis is palladium. The reaction rate can be increased in the presence of the
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29 nanoparticles (NPs) of Pd due to their high surface to volume ratio [8]. Pd NPs stabilized by
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31 graphene oxide, polymers or CDs have largely been used as catalysts in various applications
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33 [9,10]. In the case of CDs, supramolecular associations dictate a range of properties that is
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35 effective on the aqueous dispersion of Pd NPs, stability and growth in a controlled manner
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37 [11,12]. Pd NPs are applied as heterogeneous catalyst in various environmental problems such as
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39 water pollution [13]. One of the most important need of the day is the reduction of toxic
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41 nitrophenol compounds that obtain from the manufacture of pesticides and dyes to the
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43 corresponding non or less toxic amines which have a key role as an intermediate for antipyretic
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45 drugs (e.g. Paracetamol) [14] and corrosion inhibitors [15]. Different strategies have been
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47 developed to remove the organic pollutants [16,17a,b], but applying a facile way with a low cost
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3 catalyst is a challenge up to now. Recently, many research groups have studied the
4 transferhydrogenation of nitro compounds due to the importance of this subject. Ai *et. al.* have
5 used porous carbon frameworks encapsulated sub-3 nm Pd NPs for chemoselective
6 hydrogenation of nitroarenes to the corresponding anilines [17c]. Similar investigation was
7 reported by Hu *et. al.* using a magnetically separable 2D Rh/Fe₃O₄/g-C₃N₄ catalyst [17d]. A
8 multicomponent nanocatalyst system of Pd-CuFe was fabricated for the transfer hydrogenation
9 of nitrile compounds by Liu *et. al.* [17e]. Bao *et. al.* have reported a novel core-shell structured
10 nanocatalyst of Fe₃O₄@SiO₂- NH₂-FeCu with excellent activity and chemoselectivity for
11 hydrogenation of nitroarenes to corresponding anilines in the presence of hydrazine hydrate
12 [17f]. Like the nitrophenol compounds, azo dyes are another source of water pollution that
13 creates by textile industries [18] and is the result of uneconomic dyeing techniques. Decrease the
14 penetration of the oxygen and sun light to the water, risk of living for aquatic life and humans
15 and disturbing the photosynthesis process are some of the terrible hazardous of these
16 carcinogenic dyes [19]. So, efficient and economically manage of this kind of water pollution is
17 very important for industries. Ozonation and biological methods are some of the general water
18 treatments that are multi-step, time consuming and cost-effective [20] which reported by some
19 research groups using transition metal NPs synthesized in a harsh conditions [21,22]. One of the
20 facile techniques for the synthesis of transition metal nano catalysts with high catalytic activity
21 and low metal loading is liquid-liquid interface, the interface between oil and aqueous solutions,
22 that attracted a great interest due to the self-assembly of NPs at interface [23]. This defect-free
23 surface can be applied for the synthesis of nanostructures with special morphology due to the
24 low rate of nucleation and growth of crystals [24-28]. The obtained structures exhibited a wide
25 range of applications in catalysis and energy conversion [29-31]. With these issues in mind, we
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attempted to synthesize β -CD modified with Pd in the form of a thin film at the interface between the water and toluene as a supramolecular catalyst for the reduction of toxic nitrophenol compounds (*p*, *o*, *m*- nitrophenol and 4-Cl-2-nitrophenol) and degradation of harmful azo dyes (methyl orange and bismarck brown). In situ dye degradation and simultaneously catalyst formation in the mild reaction condition are some of the advantages of this strategy. This study exhibits the effect of the presence of molecular receptors attached to the surface of catalyst that can change the catalytic properties. Nitrophenols transformation is not only advantageous for pharmaceutical industry, but also in the pollutant-remediation field.

2. Experimental

2.1. Materials and methods

All of the chemical compounds and solvents were purchased from Merck and Sigma-Aldrich Companies. NaBH_4 was purchased from Panreac. Methyl orange ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$) with λ_{max} of 464 nm and bismarck brown ($\text{C}_{18}\text{H}_{18}\text{N}_8$) with λ_{max} of 460 nm were purchased from Aldrich. The crystal structure of the as-synthesized thin film was characterized by powder X-ray diffraction (XRD) patterns using a Bruker AXS (D8 Advance) instrument employing the reflection Bragg-Brentano geometry with Cu $K\alpha$ radiation. The energy dispersive analysis of X-ray (EDAX) was done applying a Philips XL30 instrument with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) image was obtained using a Philips CM-10 TEM microscope operated at 100 kV. The sputter-coated gold sample was characterized using scanning electron microscopy (SEM) analysis by a Philips XL30 instrument with an accelerating voltage of 20 kV. The loading amount of Pd NPs was examined by Inductively Coupled Plasma (ICP) analyzer (Varian, Vista-Pro). The UV-Vis spectra were carried out using a Lambda 25 spectrophotometer

(Perkin-Elmer) with a quartz cuvette to control and follow the reaction progress. Ultrasonication was done using a Soltec bath ultrasonic model. Atomic force microscopy (AFM) analysis was done using WITec alpha 300 A (Germany).

2.2. [PdCl₂(cod)] synthesis

[PdCl₂(cod)] (cod = *cis,cis*-1,5-cyclooctadiene), was synthesized according to reference [32a]. In brief, PdCl₂ (0.2 g) was dissolved in concentrated HCl (0.5-1 mL) and heated. After cooling to room temperature, ethanol was added (15 mL) followed by filtration and washed with ethanol (2 mL). cod (300 μL) was added to this stirred solution. The solution turned yellow from brown immediately. The obtained product was filtrated after 10 min and washed with diethyl ether (3-9 mL).

2.3. Synthetic procedure for the supramolecular catalyst of Pd/β-CD thin film

To prepare a supramolecular catalyst of Pd/β-CD thin film between the water and toluene interface, the following procedure is done: β-CD (0.02 g) was dissolved in distilled water (25 mL) and sonicated for 5 min. [PdCl₂(cod)] (0.0071 g) was dissolved in toluene (25 mL) followed by sonication for 5 min. The colorless aqueous solution of β-CD was transferred to the 100 mL beaker and the yellow toluene mixture was added. After the stabilization of two phases (by passing a few minutes), the aqueous solution of NaBH₄ (5 mL, 0.1 M) was added dropwisely using a syringe. The yellow toluene phase became pale and the thin layer formed at the interfaces simultaneously. The produced film was remained in this situation for 24 h to complete the nucleation, growth and self-assembly processes as illustrates in Figure 1.

2.4. General procedure for nitrophenol reduction

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3 The obtained thin film produced from sec. 2.3 was applied as a catalyst for the reduction of toxic
4 nitroaromatic compounds. In the first step, the catalyst was removed from the reaction medium
5 using a dropper to remove the top toluene layer. Ethanol (10 mL) was added to the catalyst
6 mixture followed by centrifugation. In a quartz cuvette, the aqueous solution of NaBH₄ (15 mM,
7 0.7 mL) was added to the aqueous solution of *p*-nitrophenol (0.2 mM, 1.7 mL). The color change
8 from light yellow to deep yellow was obvious in this step. In the next step, the thin film catalyst
9 was added using a syringe (The loading of a metal in the thin film was measured using ICP). To
10 monitor the reaction progress, UV-Vis spectrometer was used. The reaction mixture became
11 colorless when the reduction completed. Similar procedure was continued for *o,m*- nitrophenol
12 and 4-Cl-2-nitrophenol (Figure 2).
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2.5. *In situ* dye degradation and catalyst formation

1 For this *insitu* catalyst formation and dye degradation, the following procedure was done at room
2 temperature: In a quartz cuvette (3 mL), aqueous solution of methyl orange and β -CD (1.25 mL)
3 was used as the bottom aqueous phase (orange color) which stand in contact with the toluene-
4 [PdCl₂(cod)] solution as a top organic phase (1.25 mL) (yellow color). NaBH₄ aqueous solution
5 (250 μ L, 0.001 M) was added as a reducing agent to form a thin film. Catalyst formation was
6 begun simultaneously with methyl orange degradation. The reaction progress was studied using
7 Lambda 25, Perkin-Elmer UV-Vis spectrophotometer. When the reaction completed, the top and
8 bottom phases became colorless with a thin black layer of Pd/ β -CD catalyst between the water
9 and toluene phases. Similar procedure was continued for bismarck brown azo dye (brown color).
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3. Results and discussion

3.1. Mechanism of catalyst formation

Supramolecular catalyst of Pd/ β -CD thin film was prepared *via* a facile procedure as shown in Figure 1. [PdCl₂(cod)] complex was dissolved in toluene and β -CD compound was dissolved in distilled water and transferred to a beaker after sonication (Figure 1a,e). [PdCl₂(cod)] from the top phase and β -CD from the bottom phase were moved toward the interface. The driving force for this movement is the tendency to reduce the energy which is occurred at the interface. At this time, the (cod) ligand was folded to form a boat conformation and placed itself in the β -CD cavity and produced an inclusion complex (Figure 1b). NaBH₄ was added dropwisely and formed Pd(0) NPs (Figure 1c,d,f). Depending on the reaction conditions, the product may be with the morphology in Figure 1c or 1d. If the reduction take place fast, [PdCl₂(cod)] will reduce in the cavity of β -CD and form Pd(0) NPs (Figure 1c), but if the reduction takes place in a low rate, the morphology will change to Figure 1d. In this study, we have a liquid-liquid interface strategy which is famous for the low rate of nucleation and growth. So, the produced NPs can self-assemble at the interface and finally, we have a thin film of Pd/ β -CD with morphology like Figure 1d at toluene-water interface. Also, the wide separation of NPs in TEM image is another reason that confirms the most probable existence of Figure 1d. Figure 1g shows the top view of the as-synthesized thin film with the surface area of 16.6 cm².

The obtained thin film (Figure 1d,f) was removed from the reaction mixture and applied for the reduction of toxic nitrophenol compounds to useful aminophenols and degradation of carcinogenic dyes by formation of inclusion complexes [32b] with these toxic compounds (Figure 2).

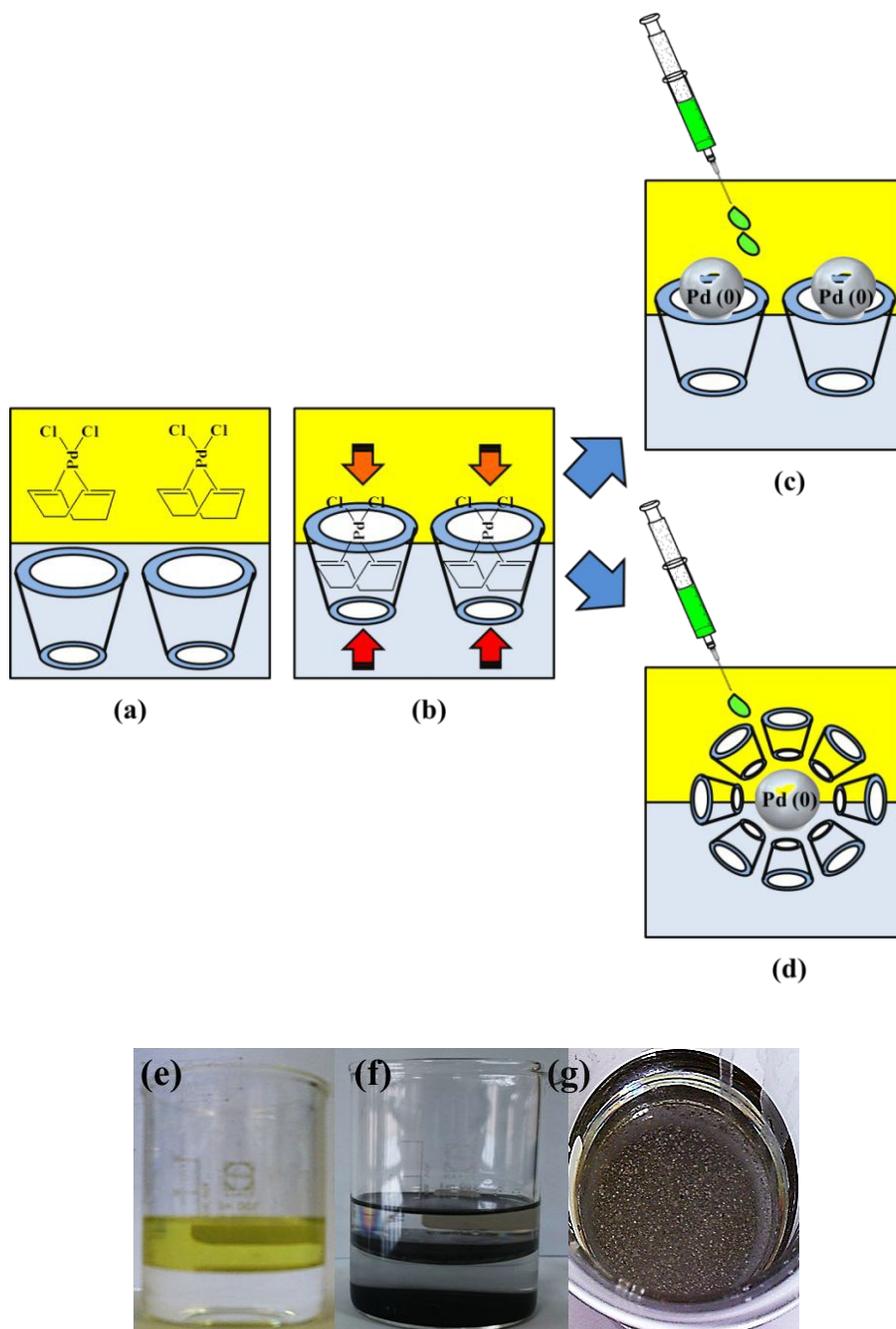


Figure 1. Schematic illustration for the formation of Pd/ β -CD at aqueous/ organic interface, (a,e) dissolving the precursors in H₂O (bottom phase) and toluene (top phase), (b) organic and aqueous phases stand in contact with each other and form an inclusion complex, (c,d,f) formation of Pd/ β -CD NPs thin film at the interface depend upon the reaction process, (d) self-assembly of NPs at toluene-water interface, (g) top view of the as-synthesized thin film

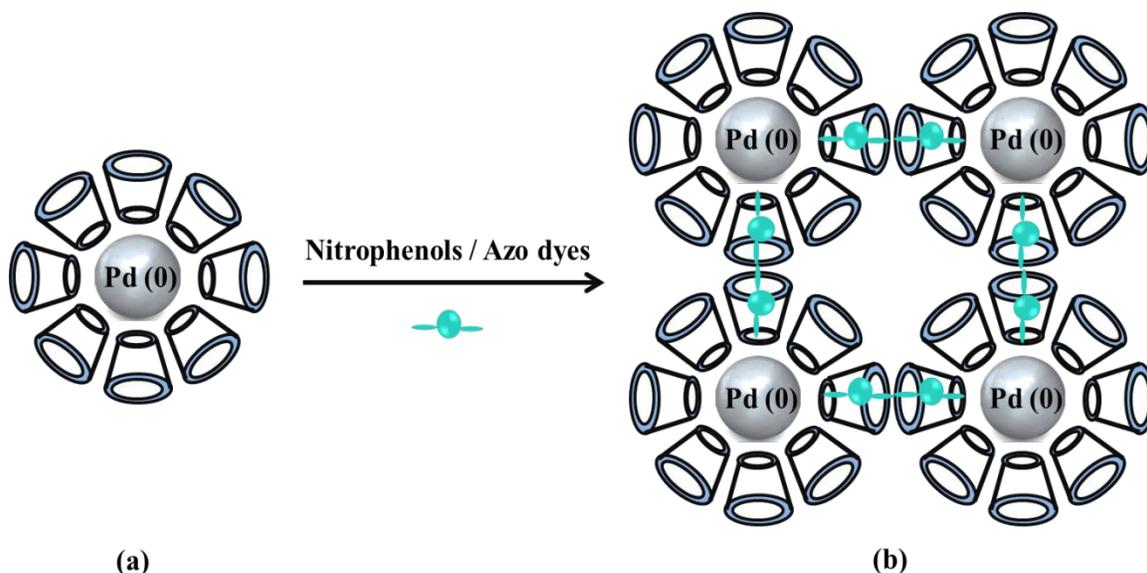


Figure 2. Schematic of host-guest recognition for Pd/ β -CD thin film in the presence of nitrophenols or azo dyes as guest molecules

3.2. Catalysts Characterization

The as-prepared Pd-based thin film was characterized first using XRD analysis. This analysis was done on the glass surface. As is observable in Figure 3a, five main diffractions corresponding to the [(111), (200), (220), (311) and (222)] planes can be seen in $2\theta = 40^\circ, 48^\circ, 68^\circ, 82^\circ$ and 86° and confirms the presence of Pd(0) with face-centered-cubic (*fcc*) structure [29].

The composition of the Pd/ β -CD thin film was examined using EDAX (Figure 3b) and elemental mapping analysis (Figure 4) and confirms the presence of C, O and Pd in the film.

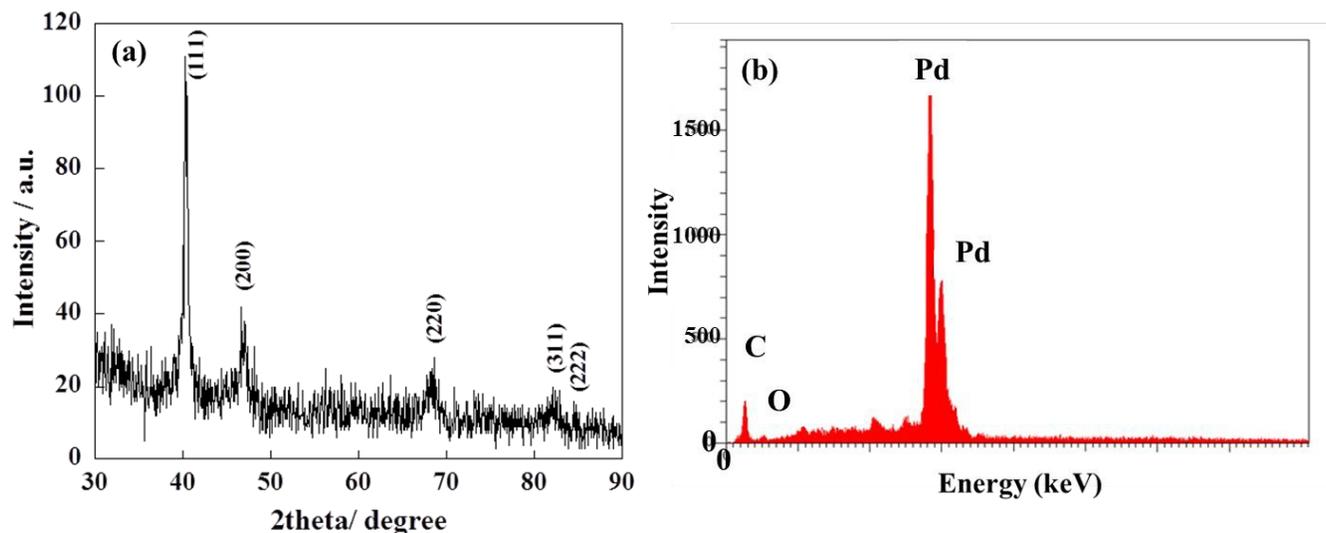


Figure 3. (a) XRD and (b) EDAX patterns of Pd/ β -CD thin film

FT-IR analysis was performed to confirm the presence of β -CD in the Pd/ β -CD thin film catalyst using KBr. Figure 5a shows the FT-IR spectrum of β -CD itself and Figure 5b is related to the Pd/ β -CD thin film. Comparing Figure 5b with 5a shows that all the peaks of β -CD are present in the FT-IR spectrum of Pd/ β -CD thin film but with a little shift. Table 1 shows the details for the FT-IR spectra [33].

Also, thin film was characterized using FE-SEM analysis. As is shown in Figure 6(a-d), the product has the connected spherical particle shape.

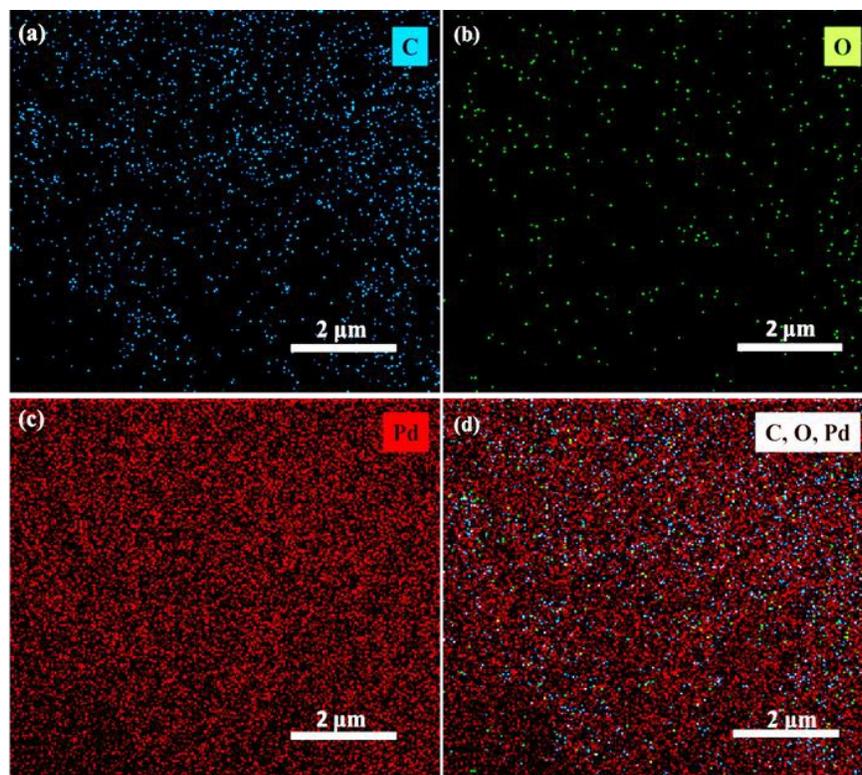


Figure 4. EDAX elemental mapping analysis of (a) C, (b) O, (C) Pd and (d) C, O, Pd for Pd/ β -CD thin film

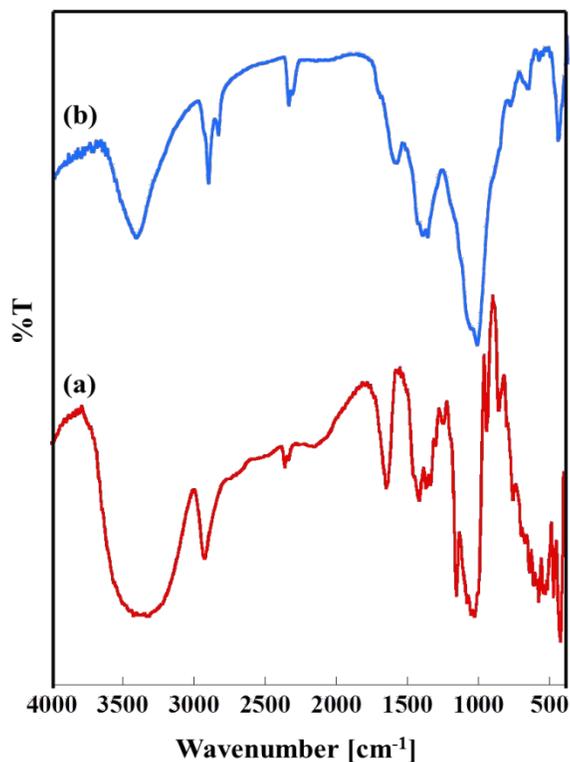
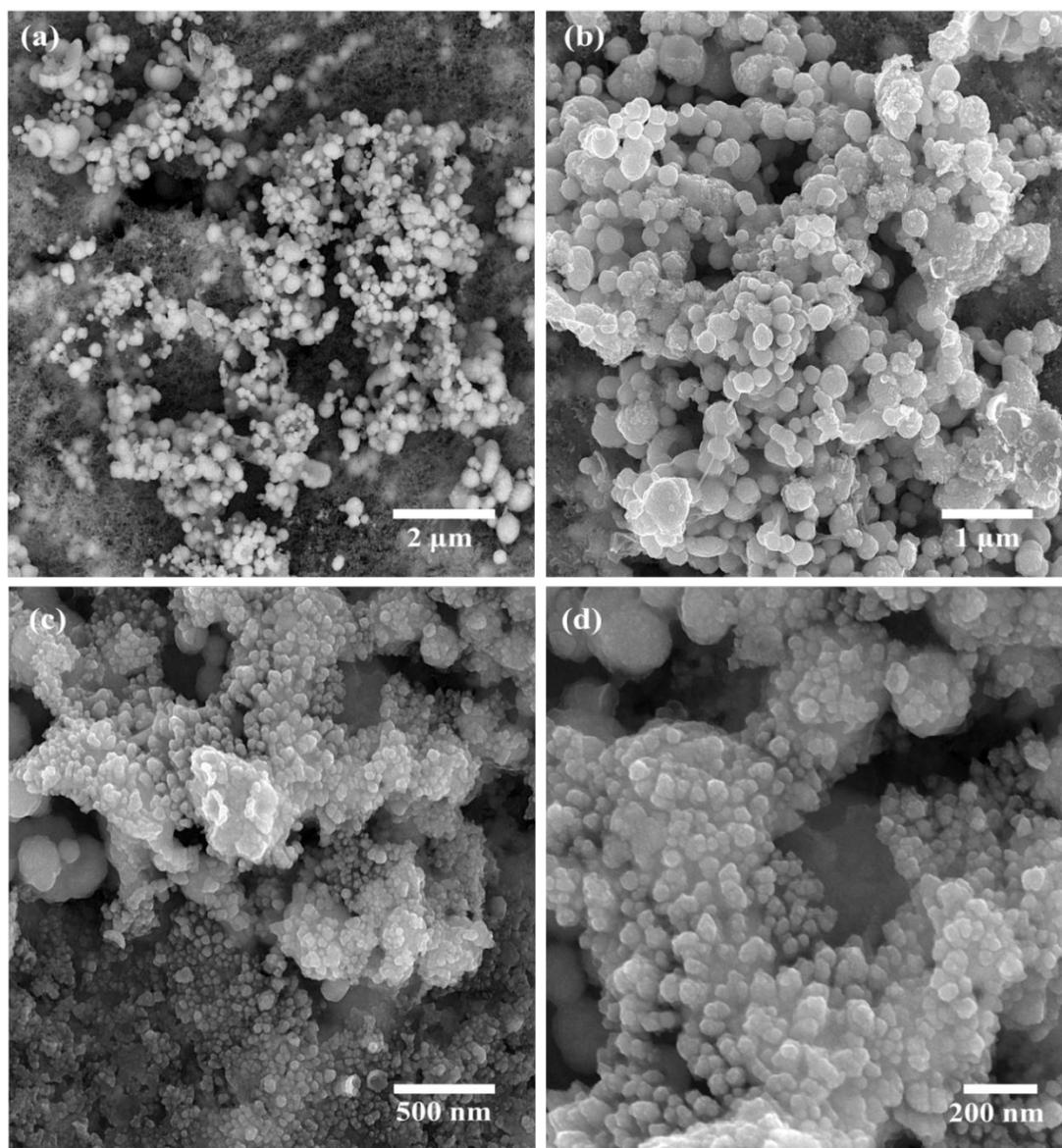


Figure 5. FT-IR spectra of (a) β -CD and (b) Pd/ β -CD

Table 1. Details of FT-IR spectra

Functional group	Wavenumber [cm ⁻¹]		Changes $\Delta\delta$
	β -CD	Pd/ β -CD	
ν [OH] symmetric and antisymmetric	3370	3430	+ 60
ν [CH ₂]	2930	2920	+ 10
ν [C-C]	1160	1110	+ 50
ν [O-H] bending vibration	1040	1040	-----

**Figure 6.** (a-d) FE-SEM images of Pd/ β -CD thin film obtain from toluene-water interface

To investigate the exact morphology and size of the as-prepared catalyst, TEM analysis was done. The thin film was sonicated in ethanol for 30 sec. and transferred to a cu-grid. Spherical particles with 6 nm mean diameter was observed (Figure 7a, b).

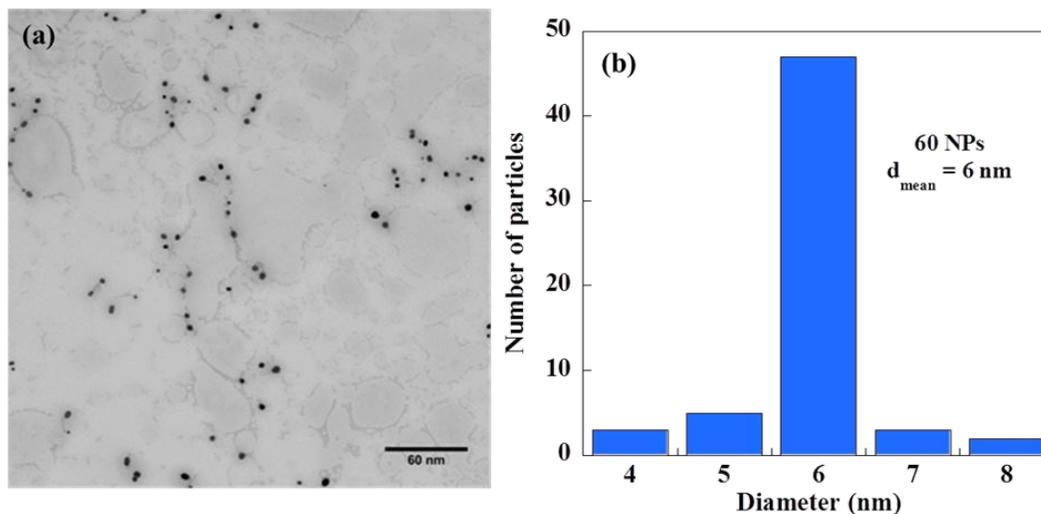


Figure 7. (a) TEM image of Pd/ β -CD thin film and (b) histogram of particles size distribution

Figure 8a shows the AFM image acquired at the edge that the film shared with the substrate to measure the thickness of the thin film. Figure 8b shows the related height profile which estimates the thickness to be ~ 210 nm.

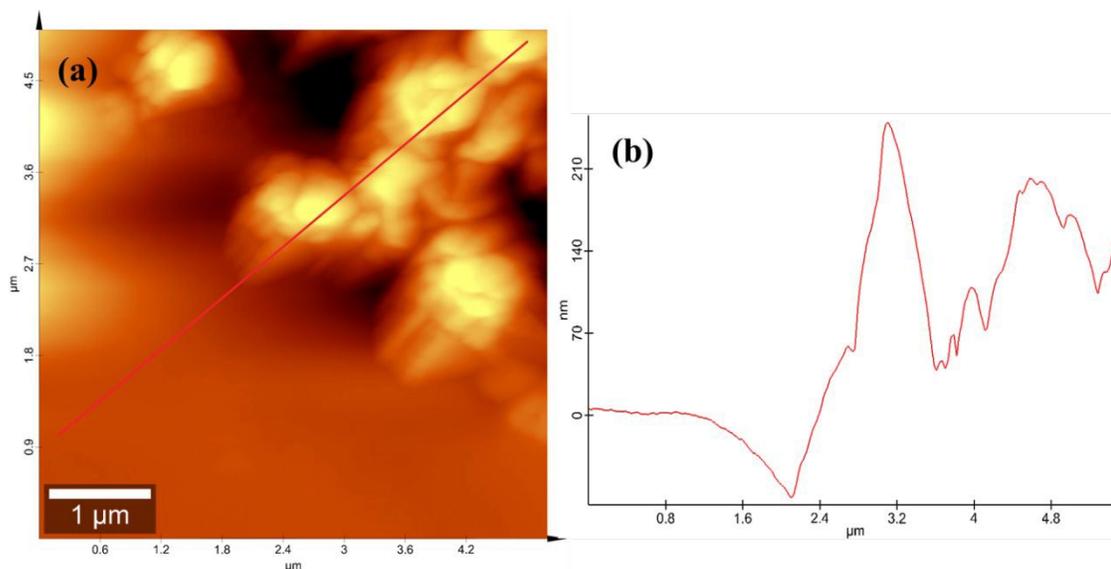


Figure 8. (a) AFM image and (b) the related height profile

3.3. Catalyst applications

3.3.1. Reduction of nitrophenol compounds

The efficiency of the as-prepared catalyst was examined in the reduction of nitrophenol compounds. The reaction progress was followed using UV-Vis spectrometer. In the case of *p*-nitrophenol aqueous solution, it has an absorption peak at 317 nm. After the addition of NaBH₄ reducing agent, it shifts to 401 nm (Figure 9b,c) and confirms the formation of *p*-nitrophenolate in aqueous solution but it does not show any decrease in the absorption peak. So, the reaction is not progressed in the presence of NaBH₄ even by passing a long time. This observation is similar in the case of 4-Cl-2-nitrophenol (Figure 9a, b), *o*-nitrophenol (Figure 9e, f) and *m*-nitrophenol (Figure 9 g, h). In the case of *o*-nitrophenol, as is observable in Figure 9 (e, f), the two peaks centered at 278 and 351 nm are shifted to 283 and 415 nm, respectively after the addition of NaBH₄.

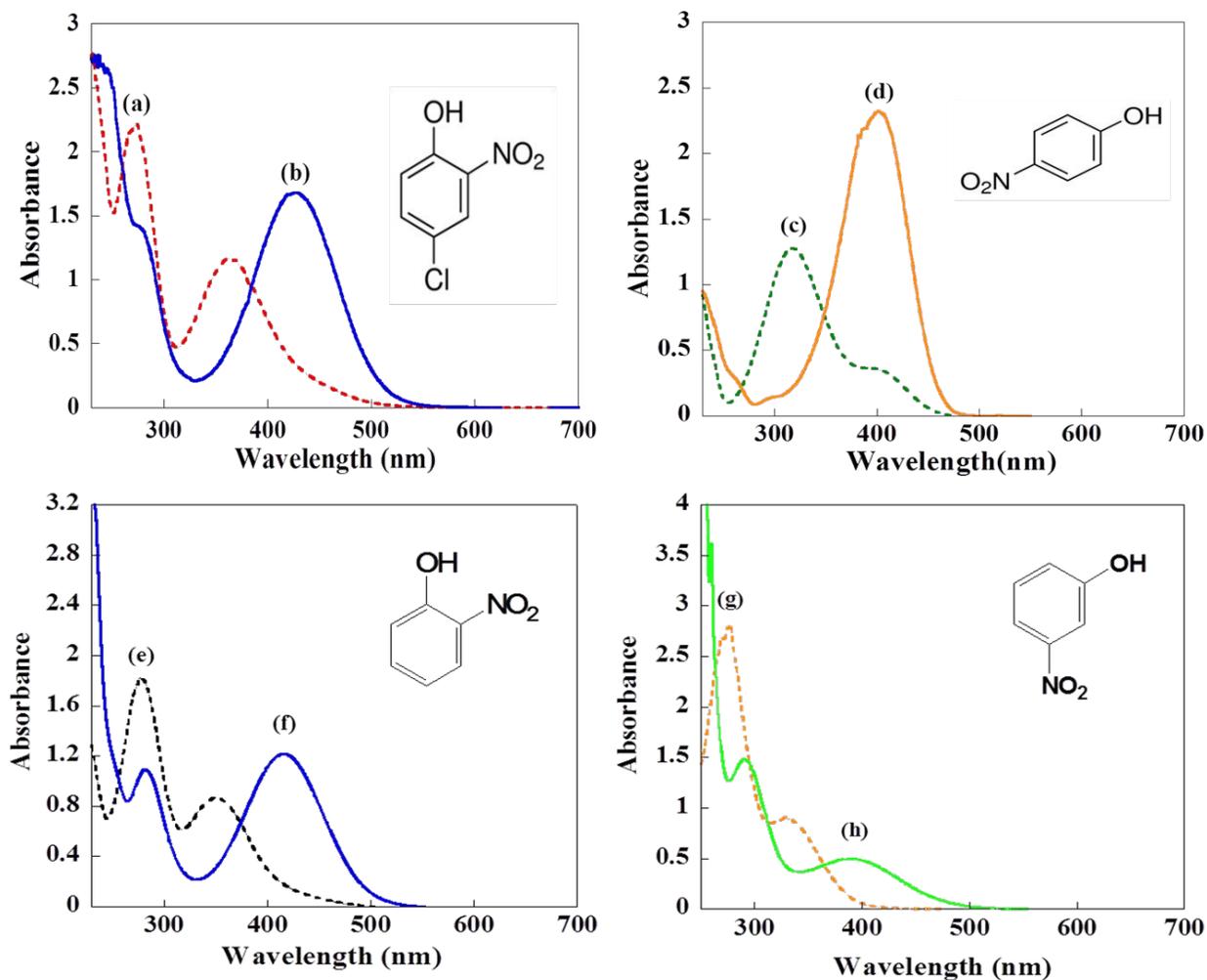


Figure 9. UV-Vis spectra of (a) 4-Cl-2-nitrophenol, (c) *p*-nitrophenol, (e) *o*-nitrophenol, (g) *m*-nitrophenol in water, (b, d, f, h) related nitrophenolate formation by adding NaBH_4

In the next step, after the addition of Pd/ β -CD NPs thin film as a catalyst, the reduction reaction was investigated using absorption *versus* wavelength curves that show a reduction of the absorption peaks related to the nitrophenolate (Figure 10a, c, e, g).

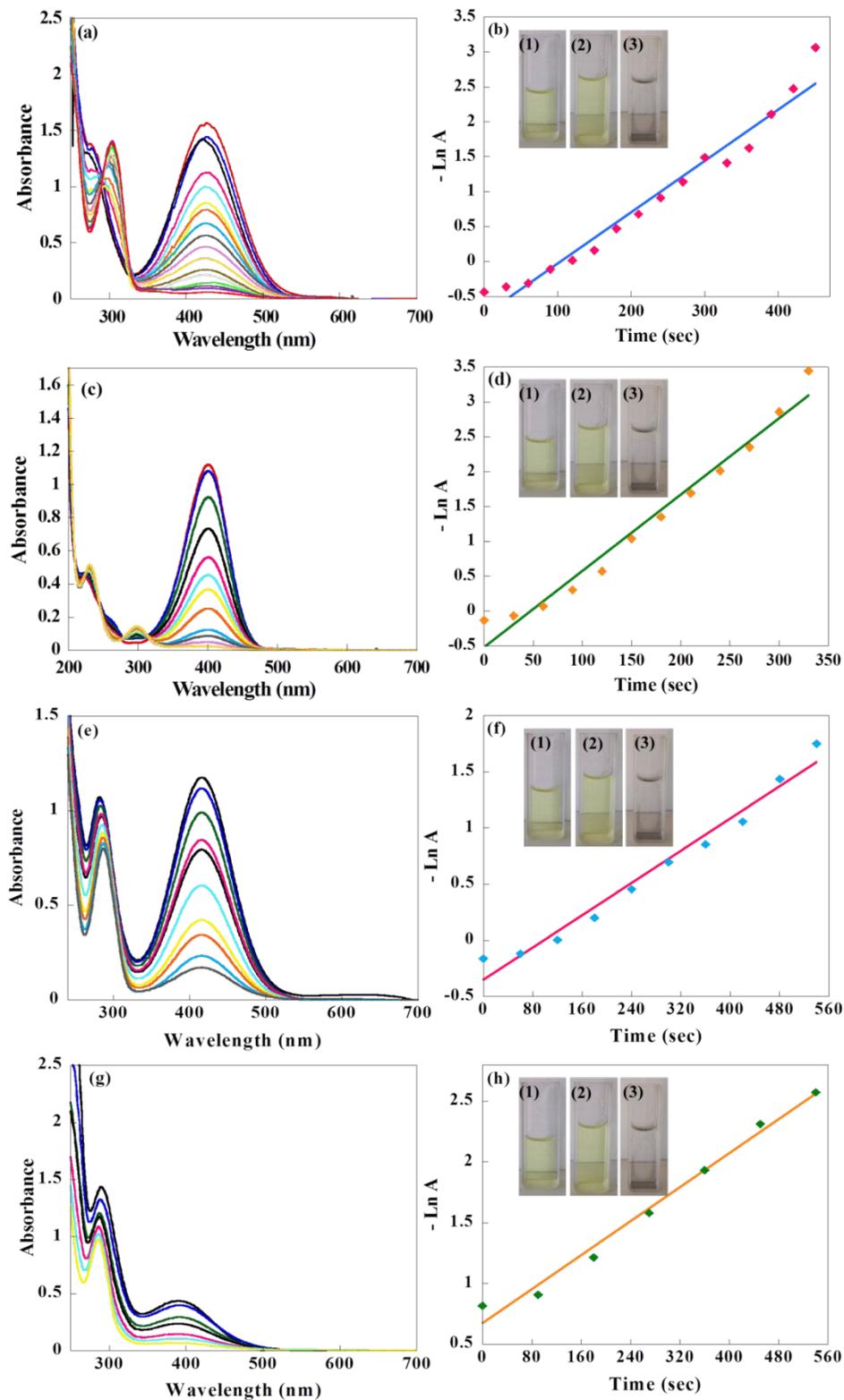


Figure 10. UV-Vis absorption spectra for the reduction of (a) 4-Cl-2-nitrophenol, (c) *p*-nitrophenol, (e) *o*-nitrophenol, (g) *m*-nitrophenol (0.2 mM) using aqueous solution of NaBH₄ (15 mM) in the presence of Pd/ β -CD thin film at 25 °C, (b, d, f, h) Plot of $-\ln A$ versus time for the related nitroaromatic compounds

Due to the high concentration of NaBH₄, the pseudo first-order kinetics can be used to evaluate the rate constants for the reduction of nitrophenols. Furthermore, the absorptions at λ_{\max} versus time were collected (Figure 10b, d, f, h) to obtain the apparent rate constants. These amounts were compared with the reported data for other catalysts (Table 2).

Table 2. Comparing the apparent rate constants in the presence of different catalysts

Entry	Catalyst	Apparent rate constant (s ⁻¹)	Metal loading (μg) ^a	Reference
1	Pd/β-CD thin film ^b	7.36 × 10 ⁻³	2.0	This work
2	Pd/β-CD thin film ^c	1.09 × 10 ⁻²	2.0	This work
3	Pd/β-CD thin film ^d	3.60 × 10 ⁻³	2.0	This work
4	Pd/β-CD thin film ^e	3.49 × 10 ⁻³	2.0	This work
5	Pd thin film ^c	1.02 × 10 ⁻³	3.1	[31a]
6	Pd NPs @ black tea	5.90 × 10 ⁻⁴	2000	[34]
7	PtNi ^d	2.56 × 10 ⁻³	2.1	[31a]
8	PtNi ^b	1.87 × 10 ⁻³	2.1	[31a]
9	PtNi ^e	1.00 × 10 ⁻²	2.1	[31a]
10	PtNi ^c	2.70 × 10 ⁻³	2.1	[31a]
11	Au/PMMA ^{c,f}	7.90 × 10 ⁻³	----	[35]
12	SPB-Au ₇₅ Pd ₂₅ ^{c,g}	8.54 × 10 ⁻³	----	[36]
13	SPB-Pd ^{c,g}	1.40 × 10 ⁻⁴	----	[36]
14	Pt	1.98 × 10 ⁻³	3.2	[37]

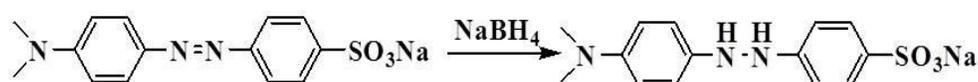
^a Obtain from ICP measurement ^b In the presence of 4-Cl-2-nitrophenol; ^c in the presence of *p*-nitrophenol; ^d in the presence of *o*-nitrophenol; ^e in the presence of *m*-nitrophenol, ^f PMMA: poly(methyl methacrylate), ^g SPB: spherical polyelectrolyte brushes

From Table 2, we concluded that Pd/β-CD NPs thin film was more effective catalyst for nitrophenol reduction than other reported catalysts. This better efficiency is the result of formation of the inclusion complex in the presence of the unique structure of β-CD. Figure 12 shows the detailed mechanism.

3.3.2. Azo dye degradation

To investigate the catalytic effect of the as-synthesized Pd/β-CD NPs thin film, we selected methyl orange and bismarck brown azo dyes. In the case of methyl orange toxic dye, the solution became colorless (-N=N cleavaged) from orange (due to the interaction of azo function and two

aromatic species) simultaneously with the formation of a thin film. This colorless solution contains N,N-dimethyl-1,4-phenylenediamine and sodium sulfanilate. The degradation progress in the presence of catalyst was investigated using UV-Vis spectrometer (Figure 11a,c). In the case of methyl orange, it has an absorption peak at 464 nm which is reduced and vanished when the reaction progressed. This is due to the (-N=N-) cleavage and decrease of conjugation. Increase in the intensity of the absorption peak at 280 nm is related to the formation of hydrazine derivatives that show in Scheme 1 [38]:



Scheme 1. Formation of a hydrazine derivative as a side product

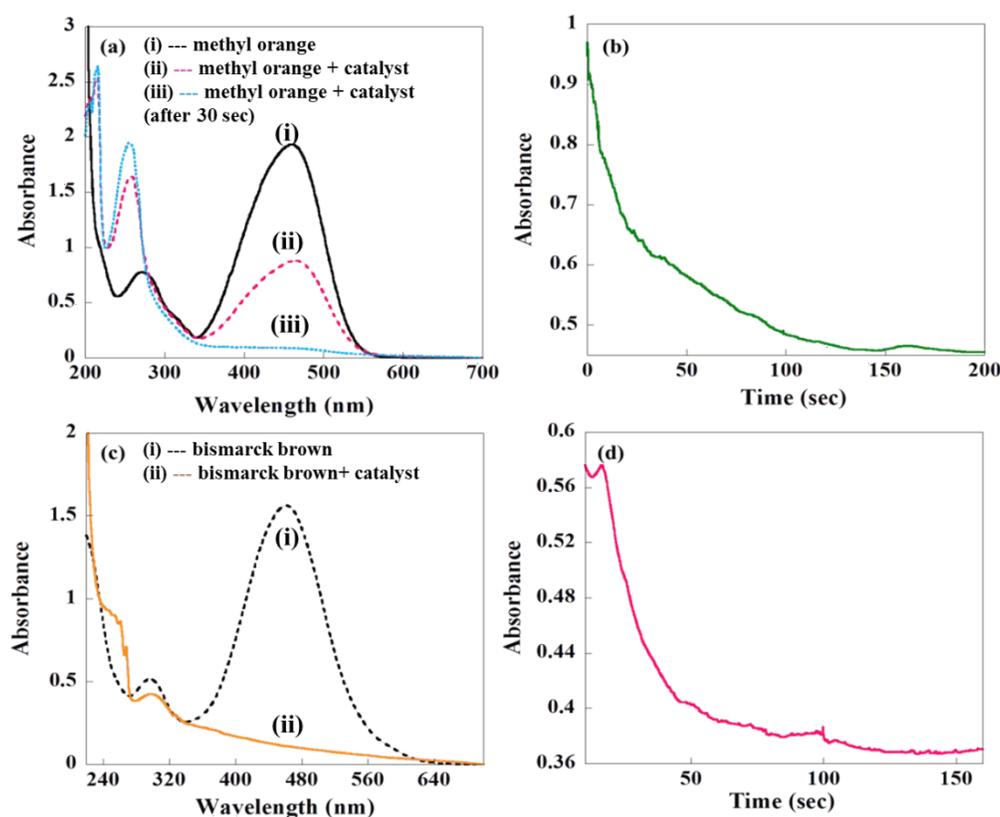


Figure 11. UV-Vis absorption spectra for the (a) methyl orange and (c) bismarck brown degradation by NaBH_4 (0.001 M) in the presence of Pd/ β -CD thin film, time interval = 30 sec; Plot of A versus time for the kinetic study of the reaction of (b) methyl orange and (d) bismarck brown

To obtain the apparent rate constants, absorbencies at λ_{\max} were collected with time for both methyl orange and bismarck brown dyes (Figure 11b,d). Also, in this case, similar to nitrophenol reduction process, the pseudo-first order kinetic could be used due to the high concentration of NaBH_4 . Table 3 shows the rate constants for this investigation and compares these values with some reported data.

Table 3. Comparing the apparent rate constants in the presence of different catalysts

Entry	Catalyst	Apparent rate constant (s^{-1})	Reference
1	Pd/ β -CD thin film ^a	1.85×10^{-2}	This work
2	Pd/ β -CD thin film ^b	3.60×10^{-2}	This work
3	Pt thin film ^a	1.09×10^{-2}	[38]
4	PtAu thin film ^a	1.70×10^{-2}	[38]
5	Pt/ TiO_2 ^a	1.17×10^{-4}	[39]
6	Pd/ TiO_2 ^a	4.00×10^{-5}	[39]
7	(0.4:0.1)PtPd/ TiO_2 ^a	1.06×10^{-4}	[39]
8	(0.1:0.4)PtPd/ TiO_2 ^a	9.60×10^{-5}	[39]

^a in the presence of methyl orange, ^b in the presence of bismarck brown

As is observable from Table 3, Pd/ β -CD thin film shows a better catalytic activity than other catalysts for dye degradation which is related to the ability of β -CD to form an inclusion complex. Figure 12 shows the general reaction mechanism.

The right view of Figure 12 is represented the mechanism for the reduction of nitrophenol molecules (guest) on Pd/ β -CD NPs thin film (host). The main driving force for the formation of this inclusion complex is hydrogen bonding with β -CD hydroxyl groups that is reversible. This means that the guest molecule can leave the hydrophobic inner cavity of β -CD after completion of the reaction. The same strategy is happened in the case of azo dyes in the left view of Figure 12. β -CD (host) formed an inclusion complex with azo dyes (guest molecules) on the surface of Pd NPs thin film. This orientation leads to increase the electron transfer between the azo dye and

NaBH₄ on the metal surface that in turn leads to the reduction of the activation energy. So, the reaction progressed easier and faster.

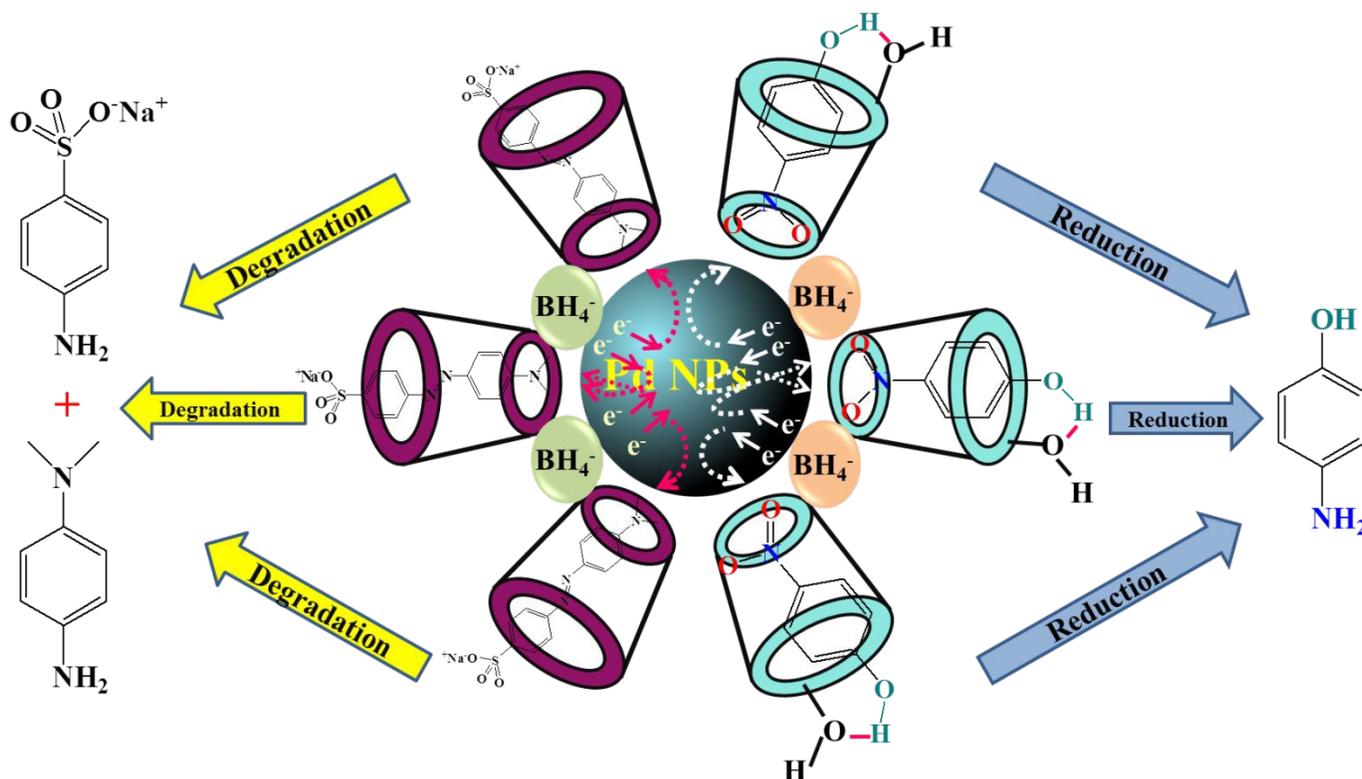


Figure 12. Mechanism for the reduction of nitrophenol (guest) on Pd/ β -CD NPs thin film (host) (right view), Forming an inclusion complex with azo dyes (left view)

Conclusions

In this study, the effect of the presence of molecular receptors attached to the surface of catalyst is investigated that can change the catalytic properties. This molecular receptor is β -CDs with its interesting structure, hydrophobic and chiral internal cavity, and the ability to form inclusion complexes with small molecules. We investigated the synthesis of Pd/ β -CD NPs thin film at the interface between water and toluene. This supramolecular catalyst was applied for the reduction

of toxic nitroaromatic compounds (*p*, *o*, *m*- nitrophenol and 4-Cl-2-nitrophenol) and degradation of harmful azo dyes (methyl orange and bismarck brown) with high rate constants which is due to the ability of β -CD to form an inclusion complexes and controls by the host-guest chemistry. In situ dye degradation and simultaneously, catalyst formation in one hand and the mild reaction condition in the other hand are some of the advantages of this strategy. Also, nitrophenols transformation and its benefit for pharmaceutical industry and also pollutant-remediation field are advantageous. The metal loading in this catalyst is very low so we can reduce the cost of the catalyst in this way despite improving the catalyst ability.

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There are no conflicts to declare.

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Graphical Abstract

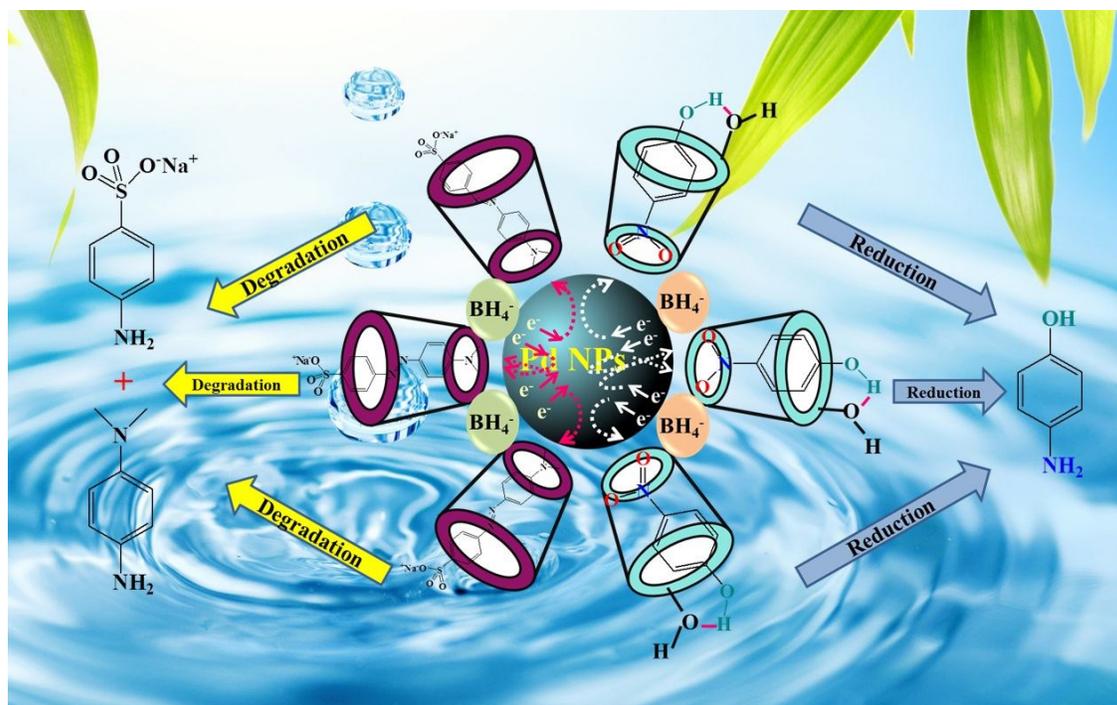
Catalytic Applications of β -Cyclodextrin/Palladium Nanoparticles Thin Film Obtained from Oil/Water Interface in the Reduction of Toxic Nitrophenol Compounds and Degradation of Azo Dyes

Azam Zare Asadabadi,^b S. Jafar Hoseini,^{*,a,b} Mehrangiz Bahrami^{a,b} and S. Masoud Nabavizadeh^a

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The supramolecular catalyst of Pd/ β -cyclodextrin thin film is synthesized *via* a facile and one-pot procedure at oil-water interface and applied for the reduction of toxic nitrophenol compounds and degradation of harmful azo dyes with considerable results. Nitrophenols transformation is not only advantageous for pharmaceutical industry, but also in the pollutant-remediation field.



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