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The Place and Importance of Cyclodextrins in Nano-Chemosensors

Siklodextrinlerin Nano-Kemosensörlerdeki Yeri ve Önemi

Elif Esra ALTUNER[1,*]

[1,*]Kocaeli Health and Technology University, European Vocational School, Medical Laboratuary and Techniques Programme, Kocaeli, Türkiye.

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ÖZET

Siklodekstrinler (CD'ler), çeşitli kimyasalları bağlayabilen doğal olarak oluşan halka şeklindeki oligosakkaritlerdir. Bu özelliklerinden dolayı nanokimyasal sensörlerde önemli bir rol oynarlar. CD'ler, hedef moleküllerin seçiciliğini artırdıkları, çözünürlüğü ve kararlılığı yükselttikleri ve sinyallere her zaman yanıt verdikleri için nanokimyasal sensörlerde tercih edilirler. Nanokimyasal sensörler ve CD'ler, çevresel kirleticilerin tespiti, gıda güvenliği ve ilaç analizi, biyolojik ve kimyasal savaş ajanlarının tespiti, tıbbi teşhis vb. alanlarda kullanılmaktadır. Bu derlemede, ilgili kaynaklara atıfta bulunularak, CD'lerin nanokimyasal sensörlerdeki kullanımı, alanı, önemi ve özellikleri ayrıntılı olarak ele alınmıştır. Gelecekte, CD'lerin nanokimyasal sensörlerde daha da yaygın olarak kullanılması ve yeni ve gelişmiş sensörlerin geliştirilmesine katkıda bulunması beklenmektedir.

Anahtar Kelimeler: Siklodekstrinler, Nanokimyasal Sensörlerin Özellikleri, Nanokimyasal Sensörlerin Önemi, Nanokimyasal Sensörler

***Sorumlu Yazar / Corresponding Author:** Elif Esra ALTUNER, Kocaeli Health and Technology University, European Vocational School, Medical Laboratuary and Techniques Programe, Kocaeli, Türkiye.
e-posta / e-mail: elifesraaltuner@gmail.com

ABSTRACT

Cyclodextrins (CDs) are naturally occurring ring-shaped oligosaccharides capable of binding various chemicals.expand_more Due to this property, they play an important role in nanochemosensors. CDs are preferred in nano chemo sensors because they increase the selectivity of target molecules, increase resolution and stability, and always respond to signals. Nano chemosensors and CDs are used in areas such as detection of environmental pollutants, food safety and drug analysis, detection of biological and chemical warfare agents, medical diagnosis, etc. In this review, the use, field, importance and properties of CDs in nanochemosensors are discussed in detail, with references to the relevant places. In the future, CDs are expected to be used even more widely in nanochemosensors and will contribute to the development of new and advanced sensors.

Keywords: Cyclodextrins, Features of Nanochemosensors, Importances of Nanochemosensors, Nano-chemosensors.

1. INTRODUCTION

Cyclodextrins (CDs) are degradation products of starch formed through enzymatic pathways (1). CDs were first discovered by Villiers in the 19th century (1–3). In the mid-20th century, Freudenberg et al. defined CDs as macrocyclic structures with a truncated cone-like structure composed of glucopyranose units connected by α (1,4) glycosidic bonds (4). It was isolated by Schrodinger in the early 21st century (5). These findings indicate that cyclodextrins are naturally occurring oligosaccharides (6). Glycosidic hydroxyl groups were located on the outside of the cone. There are hydroxyl groups (-OH) in the structure of CDs and the structure of CDs is cone-shaped (1). The conical structure of CDs is shown in Figure 1. Detailed information is given under subheadings on CDs. Cyclodextrins are important oligosaccharides preferred as drugs and in sensor systems due to their water-soluble hydroxyl groups and specific structure.

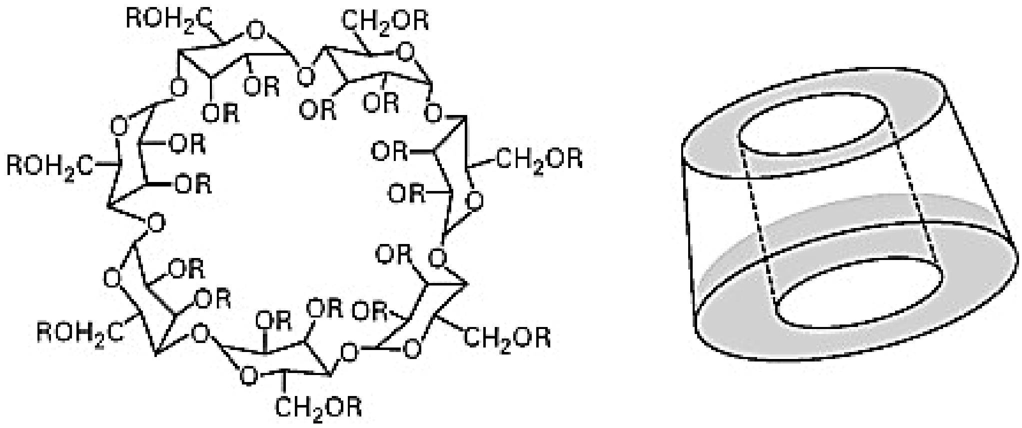

Figure 1. The scructure of cyclodextrine (a) and the shape of cyclodextrine (b) (7).

1.1. What are CDs?

As mentioned before, CDs are natural products formed by the enzymatic breakdown of starch (1). It has the ability to dissolve due to the hydroxyl groups in its structure and is cone-shaped (39–41). Pure cyclodextrins (CDs) have been edited with several functional groups, primarily to enhance their water solubility. (42,43). These are methylated CDs, hydroxypropylated CDs and sulfobutylated CDs (43–45). CDs are used to increase the solubility of natural CDs and inclusion complexes, to increase the effects between the guest compound and the CD, to form more durable complexes, to attach certain the CD structure compounds and to synthesize new compounds, to increase the permeability of CDs to facilitate passage by biological films and to modify drug release features. By the mid-1950s, the comprehensive inclusion-forming capacity of CDs emerged. The guest structure able to arise inclusion derivatives by fitting into the hydrophobic cavities of cyclodextrins. The new inclusion complex derivation is a dynamic process that involves non-covalent effects between the guest molecule and the cyclodextrin (CD) (47).

1.2. The Role of CDs in Biomedical Applications

After the emergence of their ability to form inclusion complexes, CDs have been used in many fields as molecular carriers (48). Targeting reduces the dose by ensuring that drugs act at the target site, which reduces side effects (1). CDs have been used to target the antimitotic docetaxel used in cancer treatment to macrophages (49). Beta-CD molecules were linked to the ring opening of docetaxel with a suitable coupling agent to form CD dimers (50). α-mannosidosis is sensitized to macrophage mannose receptors and is associated with CD dimers. Docetaxel molecule and CD dimers formed 1:2 inclusion complexes (51). Cell adhesion experiments showed that drug molecules and CD dimers bound to macrophage mannose receptors, ensuring their concentrated presence in the cell membrane (51). This increased the permeability of the drug (Figure 2). Although widely used in drug delivery, this targeting ability is also highly relevant for sensor applications, where selective recognition of analytes is essential.

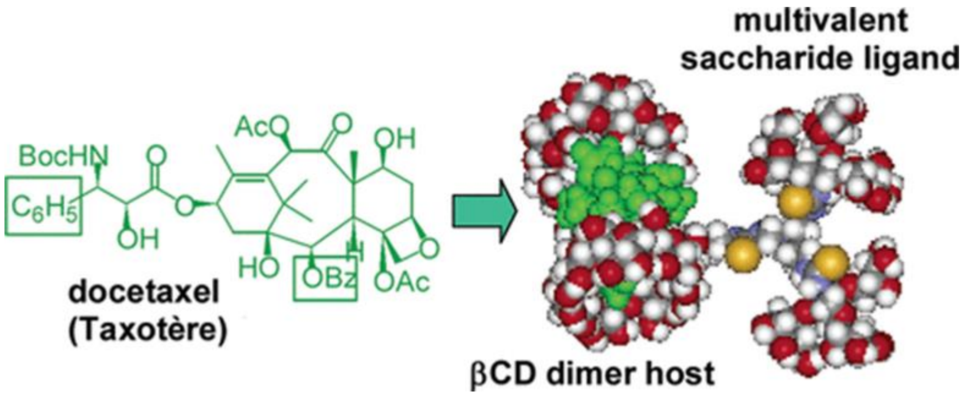

Figure 2. Schematic representation of targeting docetaxel with β-CDs (52)

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1.2.1. Increasing Drug Loading Capacity with Cyclodextrin Polymers

The drug-loading abilities of monomeric CDs depend on the formation of a 2-to-1 or 1-to-1 inclusion complex (1). The use of CD-based polymeric platforms can overcome this limitation (38, 53, 54). CDs can be in different locations within the polymeric structure (1, 2). Reports were indicated that the CDs drug-loading capacity can be enhanced using polymeric structures (2). A delivery system is required to improve this situation and deliver camptothecin to the target tissue (1, 2, 55). In a study using the CD:PEG copolymer mentioned above, camptothecin was incorporated into the system via amide bonds (55, 56). It has been observed that the system transforms into nanoparticles with an average size of 36 nm, which are not harmful per se and have a long half-life in vivo (1). These mechanisms can be translated into sensor systems to enhance analyte capture and improve detection sensitivity.

1.2.2. Cyclodextrin Based Polyrotaxanes

Rotaxanes, which have macrocyclic structures like CDs, contain a linear polymer and a terminator group in their structure (57). Surrounding polymeric chains by drug: CD conjugates plays an important role in the development of delayed drug delivery systems (1). For this purpose, polyrotaxanes were created using phenylalanine terminator groups (58–60). Polyrotaxanes were formed by wrapping hydroxypropylα-CD molecules (wheels) on PEG (axis) chains. Theophylline molecules, a bronchodilator drug, are bound to CD molecules (61). Theophylline remained inactive in the case of polyrotaxane due to steric hindrance and low membrane permeability (62). Active theophylline conjugates emerged via enzymatic cleavage of phenylalanine terminator groups (1). Polyrotaxanes contain intermolecular bonds between the wheel and the axis. Macrocyclic structure on the polyrotaxane axis; can slide on its axis; may rotate or come off axis (1, 69). Such dynamic supramolecular structures can also be adapted in smart sensor platforms for controlled signal modulation.

1.2.3. CDs in Nanotechnology

CDs are used as nanogels, nanofibers, nanoparticles, and in a wide variety of areas of nanotechnology (63,64). Gels are systems with solid and liquid properties. The three-dimensional structure of solids is formed by dispersing a small amount of solid material (polymer) in the liquid. The system is called organogel (liquid phase containing oil or organic solvents) and hydrogel (phase containing water) (65). Hydrogels can absorb a lot of water or biological fluid (66). In both physical and chemical hydrogels, it is very difficult to delay drug release from the system if the drug molecule has no affinity for the polymer network (67). If drug solubility is low or interaction with the polymer network does not occur, drug loading efficiency is low (1). Photosensitive CD-based hydrogels are also an important tool for the controlled release of drugs (68). Kros et al. encapsulated green fluorescent protein into hydrogel using CD or azobenzene-grafted dextran (1). An inclusion complex forms between the trans-azobenzene molecule and β-CD and a hydrogel is formed. Trans-cis isomerization occurred in azobenzene with UV irradiation. As a result, the hydrogel network was disrupted and the release of green fluorescent protein from the system accelerated because it could not form an inclusion complex with cis-azobenzene-CD (1, 68). CDs, which are generally considered inert, come into play by increasing the drug loading capacity of hydrogels and controlling drug release, which can change the physicochemical properties of hydrogels by taking all or part of the guest molecules into their internal cavities (Figure 3) (1).

Programmed drug release is achieved by the collaboration of CD chemistry and nanotechnology with each other (1). Mesoporous silica nanoparticles are an excellent choice for molecular encapsulation because they are non-toxic, easy to surface modify, and their pore and cavity sizes can be controlled (38). The biggest obstacle to the use of these materials as drug carrier systems is that the molecules in the system are cascaded as a kind of gatekeeper that will ensure the controlled release of drugs from the pores. At this stage, CDs can control drug release from mesoporous silica nanoparticles (1, 38).

Chemically, CD-based pH, reduction-oxidation reactions, and light- and enzyme-sensitive scavenger molecules have modified mesoporous silica nanoparticles (1).

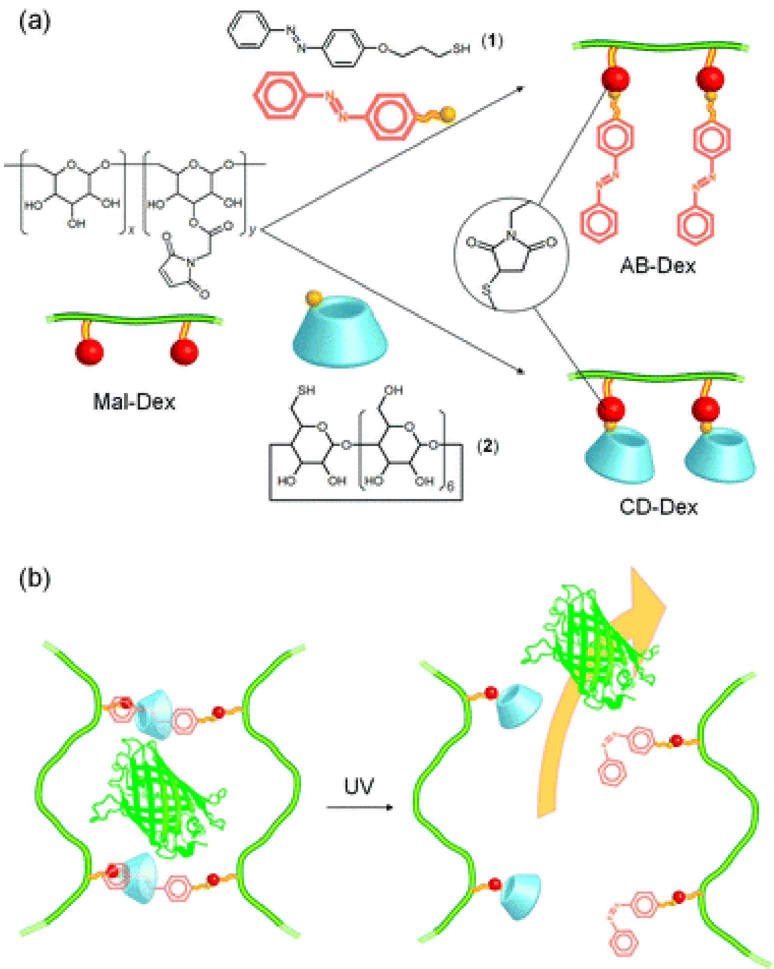

Figure 3. (a) Azobenzene-modified dextran (AB–Dex) and cyclodextrin-modified dextran (CD-Dex) are synthesized through a thiol–maleimide reaction. (b) The gel formed by trans-AB–Dex and CD–Dex exhibits photoresponsive protein release. When exposed to UV light, the azobenzene groups undergo isomerization from the trans to the cis form. This conversion disrupts the crosslinking points in the gel, enabling the entrapped protein to be released into the surrounding medium. (63).

1.2.4. Sensor importance of CDs

Cyclodextrins are a group of oligosaccharides that play important roles in the senses of taste and smell. They are detected by chemosensory cells in the tongue and nose and send taste and smell signals to the brain (69,70).

The importance of CDs regarding chemosensors is as follows:

• **These improve the sense of taste:** CDs enable us to perceive basic tastes such as sweet, sour, salty, and umami. They also increase the sensitivity and accuracy of the sense of taste (71,72).

• **These improve the sense of smell:** CDs improve the sense of smell by interacting with olfactory receptors. They also increase the sensitivity and accuracy of the sense of smell (73).

• **These connect the senses of taste and smell:** CDs act as a bridge connecting the senses of taste and smell. In this way, they enable us to perceive the taste of food and beverages better (73, 74).

• **These regulate appetite:** CDs can affect the secretion of hormones that regulate appetite. In this way, they can prevent overeating and help control weight (38, 75–79).

Some examples of the effects of CDs on chemosensors include:

• **Sense of taste:** CDs interact with sweet taste receptors and enable the perception of sweetness. For example, sweet sweeteners such as sucrose and fructose stimulate the taste receptors of CDs, creating the perception of a sweet taste (44, 75, 80).

In conclusion, CDs are a group of oligosaccharides that give a vital property for the smelling and tasting. They are detected by chemosensory cells and send taste and smell signals to the brain. Additionally, CDs are naturally found in many foods. Fruits, vegetables, grains and dairy products are good sources of cyclodextrins. CDs can also be used as food additives. They are used as sweeteners, texture improvers and flavorings.

Smart systems can reliably and quickly identify pathogens and allergens using CDs (54). Fragoso et al. attached adamantane (a molecule known to have an affinity for CDs) to the C6-thio-β-CD modified gold surface (1). The carboxymethyl cellulose structure decorated with gliadin, which is an antigenic molecule for antigliadin antibodies and a biological marker for gluten intolerance, was supramolecularly attached to the resulting system (1, 3). Using amperometers, the adsorption of a specific antibody onto the rope surface was measured. Techniques such as micro-plate reader can be preferred to detect the system's antigliadin antibodies sensitively and be much less costly (80). Seeberger et al. improved a probe for the observation of Escherichia coli using a supramolecular fluorescent probe, based on their lectin-carbohydrate interactions and their tendency to form adamantane: CD inclusion complexes (1). The system was obtained by grafting the adamantane unit onto the Ru (II) fluorescent core and forming an inclusion complex of α-D-mannopyranosyl-β-CD heptaconjugates with adamantane molecules (1, 80).

1.2.5. Cyclodextrins in Nano-Chemosensor Applications

The unique host-guest property of cyclodextrins (CDs) enables their efficient use as functional elements in the design of next-generation chemosensors at the nanoscale (79). Selective analyte binding is an essential feature of sensitive and selective detectors, thus enabling the use of CDs in nanotechnology applications (80). Electrochemical sensors benefit greatly from the use of CD-modified electrodes, which enable the concentration of analytes on the electrode surface. Fluorescence sensing is also positively impacted due to CDs' effect on signal generation, making them brighter and more stable (1). Also noteworthy is the development of hybrid sensors using CDs and nanomaterials, including graphene, carbon nanotubes, and metal nanoparticles. This approach helps to achieve low detection limits and high selectivity.

2. CONCLUSION

In this review, the role and growing importance of cyclodextrins (CDs) in sensing have been elaborated. Due to their distinct cavity structure, high compatibility with bio-relevant media, and ability to interact with various compounds via the formation of host-guest inclusion complexes, cyclodextrins can be used as highly efficient functional materials to enhance the sensitivity, selectivity, stability, and reliability of chemosensors.

Along with the progress in nanotechnology, the synthesis of nanostructures based on CDs and different combinations with them became the basis for the development of more advanced chemosensors. Notably, nanotechnology-based CD-based sensors can improve various physicochemical parameters of sensors and control interaction between sensors' components at the molecular level, providing higher efficiency of analyte detection. Furthermore, the application of CD-based nanostructures in bio-applications, in particular, as carriers for drugs delivery, development of controlled release systems, and biosensing, is very promising because of the possibility to provide selective interaction with different guests.

However, despite the numerous achievements, there are some challenges that should be overcome, including large-scale synthesis and improvement of sensors' stability and reproducibility. In the future, the efforts to resolve this issue should be undertaken together with the study of innovative functions of cyclodextrins. Summing up, it is clear that the use of cyclodextrins along with nanotechnology in the synthesis of sensors allows designing a new generation of innovative and highly efficient chemosensors due to high compatibility of their properties.

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