Immobilisation of organic agents on the surface of inorganic substrates

P. Exnar

Department of Chemistry, Faculty of Science, Humanities and Education,
Technical University of Liberec, Studentská 2, 461 17 Liberec, Czech Republic,
E-mail: petr.exnar@tul.cz

The article focuses on the immobilization of organic agents (antibiotics and other drugs, enzymes, antidotes, polypeptides or cells) on inorganic substrates (glass, ceramics, metals, special and combined materials like composites and nanocomposites, nanopowders and nanofibers). Principles of physical or chemical immobilisation of organic agents are described.

Immobilisation is binding of corresponding agents on the surface of a substrate. In this case, by organic agents we mean simple chemicals such as organic molecules and macromolecules (antibiotics and other drugs) or biological agents (enzymes, antidotes, polypeptides or cells).

The term of inorganic substrates includes not only common constructional materials such as glass, ceramics and metals, but also various special and combined materials like composites and nanocomposites, nanopowders and nanofibers prepared from inorganic oxides or organic materials with a suitably modified surface. In case of organic substrates, the presence of coating (nanocoating) prepared from inorganic materials, or at least locally protruding inorganic nanoparticles (nanocomposites) from the surface is important.

Inorganic coatings deposited on the organic materials are currently possible to be prepared via a variety of methods, for example sputtering, plasma deposition or the sol-gel method. Free access of environment (liquid or gas) on the surface with the inorganic coating is necessary for immobilisation of an organic substrate.

Many procedures describing the immobilisation of organic agents can be used in the case of purely organic substrates. The surface of organic substrates must contain suitable reactive functional groups (mainly -OH, -NH₂ or -COOH), or be modified for example with plasma (formation of surface -OH groups). Reactivity, especially of -OH groups bonded to a carbon atom, is in comparison to the reactivity of -OH groups bonded to other atoms (silicon, aluminium or titanium) lower and it is therefore appropriate to use other methods.

Immobilisation can be either physical or chemical. Purely physical immobilisation is generally characterised by weak Van der Waals forces of immobilised agents, which can be relatively easily desorbed. Physical adsorption is usually highly non-selective and due to a slight change of conditions (e.g. pH or the addition of a chemical with greater affinity to the surface) the organic agents can be deimmobilised. To this category belongs also surface treatment by depositing thin coatings mainly of organic chemicals on the surface of the substrate with the aim to modify the physical character of the surface (hydrophobic, hydrophilic or oleophobic treatment).

Deposited coatings can be only adsorbed on the surface, or they can be chemically bonded, for example by silanization (surface modification of glass with -C₆H₃ groups after the reaction with hexadecyltrimethoxysilane). These reactions are widely used in chromatography to modify the surface of the separating columns or to modify the surface of materials (hydrophobic treatment of materials).

Chemical immobilisation is based on creation of a chain of chemical bonds between the surface of the substrate and the organic agents. In exceptional cases, it is possible to use direct chemisorption of organic agents on the active centres of the surface of inorganic substrates. But in most cases, it is necessary to selectively modify the surface by chemical reactions so that the surface of the substrate will contain particular reactive groups.

In most cases, relatively simple molecules containing a suitable reactive group (alkylalkoxysilanes) and forming nanometer-thin coatings are chemically bonded on the surface of selected materials. A common connecting rod between the reactive groups of alkylalkoxysilanes and the organic agents are bifunctional crosslinker molecules, which are bonded to the alkylalkoxysilane by one group and to the organic agents by the second group (glutaraldehyde or glyoxal can be used as bifunctional molecules). The organic agents is thus immobilised on the surface of the substrate (Fig. 1).
Another possibility is the application of a thicker coating (from tens to hundreds nanometers) with alkylalkoxysilanes containing required functional groups by the sol-gel method. The organic bond of the organic agents is provided directly with the functional groups or through the bifunctional molecules.

A certain transition between chemisorption and purely physical adsorption is provided by organic groups with a defined cavity or porous materials. The example of an organic group with a defined cavity is cyclodextrin, which is a cyclic oligosaccharide composed of 6-8 units of glucopyranose. Cyclodextrins are described as conical frustums with a hydrophilic exterior surface and a hydrophobic interior cavity. Cyclodextrins are known for their ability to form complexes with a combination of various organic molecules as guests, whose size corresponds to the size of their cavity [1] (Fig. 2).

Another type of these chemicals are calixarenes, which form calyxine-like structures. Lee et al. [2] used the modified calix[4]arene for the immobilisation of bovine serum albumin (BSA). They used calix[4]arene carboxylic acid and its ester and observed the amount of immobilised BSA (Fig. 3).

In addition to the enlarged surface, inorganic porous materials also enable a stronger immobilisation of organic agents (e.g. cells) in the pores of appropriate size by the steric effect. Similar effects with a stronger immobilisation of cells occur also in the nanofiber coatings. For a long time, much attention has been paid to immobilisation of organic agents (mainly enzymes) into organic polymers [3]. When these polymers are applied in the form of a thin coating on the inorganic substrates, they can also be used as nanocoatings.

The basis of immobilisation of organic agents on the majority of inorganic substrates is their surface chemical activity, manifested by the existence of -OH groups. Only surfaces of high purity noble metals such as gold and platinum, on which the oxide and hydroxide coatings are not created, can be considered chemically inert. Gold and platinum can react with some chemicals to form a chemical bond or on the basis of a very strong adsorption. The most widely used are the compounds with -SH group, which readily make bonds with gold and platinum. A typical example is the usage of (3-mercaptopropyl) trimethoxysilane for the preparation of the first monomolecular coating for immobilisation on these metals. -SH group is bonded to the surface of the metal and after the hydrolysis of methoxy groups, the Si-OH groups provide immobilisation by classical procedures of silanization or sol-gel method on the surface.

In other cases, the surface reactive groups containing M-O and M-OH (M = metal, metalloid or non-metal) are the basis. These groups are formed by oxidation of metals or by hydrolysis of the surfaces of other inorganic materials. In most cases, not only the chemical composition of the substrate, but also the processes the surface of the substrate was exposed to before are very important for the reactivity of the surface (mainly chemical and corrosive effects of oxygen, moisture, electrolytes,
acid or alkaline chemicals, temperature and the time of exposition).
By these effects the number of active -OH groups is given (in case of contamination of the surface and reactions with other chemicals even other groups such as –SH, -NH₂ may appear). These are able to further react with used immobilisation chemicals.
Generally, when a substrate is heated to high temperatures, the number of -OH groups on its surface is reduced by the transition to less reactive oxides. Therefore, for successful immobilisation of different agents, the surface of a substrate should always be perfectly clean or chemically activated to achieve the optimal surface conditions.
Immobilisation of organic agens on the inorganic substrates is very important for many areas. Considerable attention is paid to the development of biosensors for rapid analysis of the presence of antigens and enzymes. Immobilisation of drugs, especially antibiotics, on textile materials for using as bandages can be very interesting. The possibilities greatly expanded with the development of nanotechnologies. Very promising is also the application of drugs to the nanoparticles for controlled therapy or growing of cells in the nanofiber materials.

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prof. RNDr. Petr Špatenka, CSc.
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Ing. Petra Prokopčáková, Ph.D.

Contact Address
Technical University of Liberec
Department of Material Science
Studentská 2
46 117 Liberec
Czech Republic

Tel.: (+420) 485353518
Fax: (+420) 485353631
E-mail: panms@seznam.cz
Web: http://nanocontact.cz

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