Lecture 6. Applications of Metal Nanoparticles

The purpose of the lecture: to familiarize students with applications of metal nanoparticles.

Expected results: students getting information about applications of metal nanoparticles.

Environmental Applications

Surface-modified nanoparticles are used for removal of arsenic and other toxic metals, as well as setting up a chemical reactive barrier to treat deep groundwater contaminants. In some cases, such as groundwater remediation, bimetallic catalyst nanoparticles may be more effective than monometallic nanoparticles. Palladiumon-gold nanoparticles (Pd/Au NPs) are more effective than Pd-nanoparticles or Au nanoparticles in catalyzing the dechlorination of trichloroethene in water at room temperature. Hydrophobic nanoparticles called submarines effectively removed oil from water sources. Modified magnetically enhanced separation technology separated the target contaminants from a sediment matrix or wastewater streams. These particles have a magnetic core, a shell that provides stability and protection from oxidation, and a surface to which contaminant-specific ligands are attached. These observations suggest that metal nanoparticles may play a key role in environmental remediation.

Biomedical Applications

Metal nanoparticles are used in biomedical imaging, drug delivery, and high-throughput sensors.

IMAGING

Monomodal imaging using monofunctionalized nanoparticles (particles containing dyes, QDs, or guanidinium-functionalized nanoparticles and super-paramagnetic iron oxide) are common in diagnostic imaging. However, multifunctional imaging allows the combined diagnosis and therapy of cancer, thus visualizing the tumor to assess recovery in vivo. Huang and Hainfeld (2013) have described a biodegradable nanopolymer, poly (lactic-co-glycolic acid) (PLGA), functionalized with the following groups:

• Magnetic nanoparticles and doxorubicin for multimodal imaging and drug delivery

• Galactosylated chitosan (GC) that selectively targeted the hepatocarcinoma-selective glycoprotein receptors of hepatocarcinoma and allowed the nanoparticles' endocytosis within the carcinoma

• EGFP-N2 (green fluorescence protein plasmid) that acted as contrast agent for fluorescence imaging

The engineered nanoparticles allowed multimodal resonance imaging, hyperthermiainduced cancer cell destruction, and selective degradation of the nanoparticles for on-site drug release. Cheng et al. (2013) developed amultimodal ultrasoundtriggered phase transition nanoparticles called DiR-SPIO-ND (Figure 12) that exhibited significant ultrasound-triggered phase transition due to the vaporization of the pentafluoropentane (PFP) layer. The in vivo T2-weighted images of

MRI as well as the fluorescence images showed an enhancement in contrast in the liver and spleen of rodents after intravenous injection of DiR-SPIO-NDs. Furthermore, the ultrasound imaging in mice tumor as well as MRI and fluorescence imaging in liver of rats and mice showed that the DiR-SPIO-NDs had longlasting contrast ability in vivo. This suggests that DiR-SPIO-NDs could potentially be a great MRI/fluorescence multimodal imaging contrast agent in the diagnosis of liver tissue diseases.

Earlier studies have described Gd3ю-doped upconversion nanoparticles (UCNPs) that converted near-infrared (NIR) radiations with lower energy into visible radiations with higher energy via a nonlinear optical process. Some of the commonly used UCNPs are the following:

1. Gd2O3: Thulium (Tm) ю Ytterbium (Yb) that upconverts NIR wavelength to 455 nm
2. Gd2O3: Erbium (Er) ю Yb that upconverts NIR to 564 nm

3. Er3ю in Gd2O3: Er ю Yb that upconverts NIR to 661 nm designed an upconversion nanoparticle coupled to a dual-functional PEG and two layers of poly(ethylenimine) (PEI) as a gene-delivery vector for the transfection of plasmid DNA encoding enhanced green fluorescent protein. When serum is added during transfection, it shows remarkably enhanced transfection efficiency, possibly due to enhanced receptor-mediated endocytosis via the binding of serum proteins.

The PEG-PEI2 upconversion nanoparticles may be a promising gene vector that works well in the presence of serumproteins. The nanoparticles enter the cells via endocytosis and then deliver the plasmid into the nucleus, where the plasmid integrates into the cells' genome and expresses the encoded protein. The cells can be imaged via upconversion fluorescence imaging.

Traditional fluorescence imaging using fluorescent dyes or QDs is a downconversion technique in which the emitted wavelength is of lower energy than the excitation wavelength. The NIR-tovisible upconversion methods have a number of advantages. Autofluorescence, a serious problem associated with the traditional imaging, is no longer an issue for upconversion imaging. This allows improved signal-to-noise ratios and imaging sensitivity. NIR irradiation with better tissue penetration ability is used as the excitation source, facilitating in vivo imaging. However, UCNPs are resistant to photobleaching and have excellent photostability.

Drug Delivery

The traditional allopathic drugs, although highly effective, have certain disadvantages, such as nonspecific binding to blood cells and proteins, rapid diffusion into the healthy tissues, short half-life in the bloodstream, and high overall clearance rate. This reduces their efficacy in the body because relatively small amounts of the administered drug reach the target site. Distribution into healthy tissues may lead to severe side effects that often make many excellent drugs undesirable.

Nanoparticles can be designed to circumvent the disadvantages of traditional drug formulation by improving their bioavailability, transporting them to the target site, and then releasing them as needed. The nanoparticles' performance as drug vectors depends on the size and surface functionalities of the particles, drug release rate, and particle disintegration.

A transporter selective ligand may allow the drug carrier systems to pass through organ barriers, such as the bloodebrain barrier. One of the unique characteristics of certain transition metals, especially gold, is their strong affinity for thiol groups, which provides a simple means to load the drug-coupled PEG or drug-loaded dendrimers onto the metal nanoparticles.

As an alternative approach, studies have described a photothermal modulated drugdelivery system consisting of hollow metal nanocapsules covered by a thermosensitive hydrogel matrix. These nanocapsules strongly absorb NIR light and release multiple amounts of many soluble materials held within the hydrogel matrix.

Metal Nanoparticle-Based Sensors

Metal nanoparticle-based biosensors exhibit high sensitivity for nucleic acids, proteins, antibodies, enzymes, and other biological molecules. The key detection procedures are localized surface plasmon resonance (LSPR), fluorescence enhancement/quenching, surface-enhanced Raman scattering (SERS), and electrochemical activity. The colorimetric approaches, due to their simplicity and portability, are one of the most promising methods for diagnosis at the point-of-care. Gold, silver, and platinum nanoparticles have been extensively used in biosensors.