We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists



International authors and editors 122,000 135M





Our authors are among the

most cited scientists TOP 1%

Countries delivered to **Contributors** from top 500 universities contributors from top 500 universities 12.2%



**WEB OF SCIENCE** 

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

# Interested in publishing with us? Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected. For more information visit www.intechopen.com



# **The Development of Smart, Multi-Responsive Core@Shell Composite Nanoparticles**

Bo Sang Kim and T. Randall Lee

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/61262

#### **Abstract**

The unique optical, magnetic, and electronic properties of metal nanoparticles (NPs) give rise to photothermal, therapeutic, and electronic device applications, correspond‐ ingly. On the other hand, the limited range of the properties of simple spherical metal NPs has complicated their ability to function in many of these applications. Therefore, this chapter starts by reviewing a specific type of NP that can be classified into three main groups: silica coated with metal (silica@metal) NPs, metal coated with silica (metal@silica) NPs, and other similar forms of core@shell structures. The objective of this review is to introduce the concept of multi-responsive core@shell nanoparticles. More specifically, this chapter highlights "smart" core@shell composite NPs having multiple response mechanisms (e.g., temperature, light, and/or an applied magnetic field) due to the ability of these systems to perform a task by remotely responding to stimuli. Additionally, hydrogel-coated metal@silica NPs, with the ability to store drugs in a mesoporous silica (m-silica) interlayer, are examined because these nanomaterials potentially provide substantial advantages for carrying cargos to targeted sites. To demonstrate this capability, we examine recent research that provided initial tests of composite NPs with a pH- and temperature-responsive hydrogel coating, in‐ cluding the application of an underlying m-silica interlayer to improve the capacity of these NPs to load and release small molecules.

**Keywords:** Nanoshells, core@shell nanoparticles, surface plasmon resonance, smart multi-responsive nanoparticles

# **1. Introduction**

Metal nanoparticles (NPs) provide optical, magnetic, and electronic properties which are different from the corresponding bulk metal materials, leading to photothermal, therapeutic, and electronic device applications, respectively. Recent research efforts have explored NPs



© 2015 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

having complex compositions with controllable sizes and morphologies. Special attention has been given to metal NPs for use as optical materials (i.e., using palladium [1, 2], silver [3-12], copper [13-18], and particularly gold [19-31]). This is due to the ease of fabrication of these metal nanoparticles and their unique physical properties [32-34], such as the ability to absorb or scatter light [25, 35, 36]. However, the narrow scope of simple spherical metal NPs' optical properties has limited their use in practical applications. Thus, investigators have pursued new classes of nanostructured materials such as triangular prisms [37-40], disks [41, 42], nanorods [43-46], nanocubes [47-51], and NPs coated with a shell (core@shell NPs) [52-58], to overcome the restrictions on the optical properties associated with simple spherical metal NPs. Among these, core@shell NPs represent a promising nanoscale tool for biomedical research [59-63]. A number of metals have been used as the shell for these NPs (as detailed in Table 1), but silica has proven to be the favorite core for such structures [64-76].



**Table 1.** References for core@shell nanoparticles with silica cores and metal shells.

Recent research has also centered on the capacity of core@shell NPs containing metal/metal oxide cores to respond to an external stimulus (e.g., a magnetic field or near IR light) and to affect their local surroundings, resulting in their use in diagnostic, therapeutic, and drug delivery applications utilizing either a polymer coating or a more complex shell design [77-80]. The development of these more sophisticated NP structures has been presaged by a number of simpler particle architectures.

# **2. Types of Core@Shell nanoparticles**

Core@shell NPs can be categorized according to their material properties (e.g., dielectric, semiconductor, etc.) and form (e.g., single-layered shell, multilayered shell, etc.). In this chapter, the core or shell materials in a core@shell NP are considered in terms of their constitution or shape. For this report, the core@shell NPs of interest are classified into three main groups: (i) silica@metal NPs; (ii) metal@silica NPs; and (iii) other forms of core@shell NPs.

*Silica@Metal Nanoparticles.* Since the publication of the "Stöber Method" of preparing silica particles, various metals and metal oxide shell materials have been deposited on silica spheres [81]. Because of the unique qualities of gold, silica-based core@shell NPs with gold as the shell material became the focus of efforts to produce the first of these structures in the late 1990's [64, 68, 82]. A gold coating on the silica core provides improved biocompatibility, photonic energy absorption, catalytic properties, chemical stability, bio-affinity (through greater diversity in the functionalization of the surface), and tunable optical properties [64]. Similar to the sizedependent color of pure gold NPs, the optical response of gold nanoshells (GNSs) depends dramatically on the relative size of the core NP as well as the thickness of the gold shell [67, 83]. Importantly, the surface-enhanced Raman scattering (SERS) activity of GNSs can be increased or decreased by decreasing or increasing the thickness of the gold shell material [84, 85]. By adjusting the relative core size and shell thickness, an intense light absorption associated with the gold in the GNSs can be varied across a broad range of the optical spectrum, spanning the visible and the near-infrared spectral regions. This phenomenon is known as surface plasmon resonance (SPR) and its impact upon the extinction spectra of GNSs is illustrated in Figure 1 with regards to changes in shell thickness.



**Figure 1.** Illustration of the optical resonances of various sizes of silica@gold composite particles (gold nanoshells) as a function of their shell thickness. Reproduced with permission from reference [67].

The development of these gold shells has been followed by a number of alternative metal and metal oxide coatings, broadening the number of applications for such core@shell structures [53, 54, 69, 74]. These data indirectly indicate that GNSs with a silica core (SiO<sub>2</sub>@Au NPs) may be useful for biomedical imaging, cancer treatment, and optical materials in future applications owing to the ability of certain wavelengths of light to penetrate human tissue.

*Metal@ Silica Nanoparticles.* Using a silica coating as the shell on a metal core to form NPs with core@shell architectures offers several benefits. First, a silica shell diminishes the bulk metal conductivity and improves the chemical and physical stability of the core component [86]. Second, silica particles produced via the Stöber Method have been shown to be chemically biocompatible [87, 88]. And silica can be used to block the core surface from making contact with a biological environment without disrupting key phenomena involving the core surface,

such as light absorption. This is an important feature for metals/metal oxides that have been shown to be cytotoxic. Third, the silica coating can be used to modulate the position and intensity of the surface plasmon absorption band due to both the optical transparency of silica at technologically important wavelengths of light and the shift in these bands associated with a small change in the metal's optical properties because of the material in contact with their surfaces [89]. And the fourth point is that an outer silica shell on a metal nanoshell can help stabilize the metal shell when it is generating intense localized heat in response to intense light absorption [90, 91]. Therefore, scientists have recently focused more on silica coatings as a shell for a variety of core materials such as metals [92-99] and metal oxides [100-103], than on any other material. Many research groups have investigated the use of silica on coinage metals such as gold [92, 93] and silver [98]. Silica-coated gold or silver NPs are synthesized by using a slightly modified Stöber (or sol-gel) Method. The resulting coating does not interfere with the intensity of the light absorption for targeted wavelengths, and only produces a minor shift in the absorption band toward the higher wavelength region, as compared to an uncoated NP, as shown in Figure 2 [104]. This coating method has been adjusted further to control the uniformity of the thickness of the silica layer on gold NP cores [105].



**Figure 2.** UV-visible absorption spectra of aqueous dispersions that contained gold@silica NPs with different shell thicknesses (t). The gold cores were 50 nm in diameter for all samples. Reproduced with permission from reference [104].

Figure 2 provides the absorption spectra of aqueous dispersions of gold@silica (Au@SiO $_2$ ) NP colloids with different shell thicknesses. The characteristic surface plasmon peak of the core of these NPs is ~528 nm before adding the silica coating to the gold cores. After coating with silica, the metal's plasmon peak red-shifted to ~540 nm. This is because the refractive index of silica ( $n = 1.52$ ) is slightly higher than that of water ( $n = 1.31$ ), the solvent used to suspend the

nanoparticles for collecting spectroscopic data [106]. The optical intensity of these  $Au@SiO<sub>2</sub>$ NPs was increased correspondingly when thicker silica shells were created. But the specific positioning of this peak was not sensitive to the change in the silica coating thickness.

In the report by Lu *et al.* referenced above, the silica-coated gold NPs were assembled into ordered arrays [104]. The transmission spectra collected from these lattices of  $\text{Au@SiO}_2$  NPs are shown in Figure 3. All samples were wet with the hollow spaces between NPs being completely filled with water, when these spectra were measured. The incident light was kept vertical to the (111) planes of these face-center-cubic lattices (Au).



**Figure 3.** Transmission spectra taken from the arrays produced from  $\text{Au@SiO}_2$  NPs with different shell thicknesses (t). The incident light was perpendicular to the (111) planes of these face-center-cubic crystalline lattices for all measurements. The gold cores were 50 nm in diameter for all samples. Reproduced with permission from reference [104].

These transmission spectra show two peaks resulted from the surface plasmon resonance of the gold core NPs around ~540 nm and the Bragg diffraction of each opaline lattice. Depending on the changes in the silica shell's thickness, the position of the Bragg diffraction peak varied. For example, the Bragg diffraction peak overlapped with the surface plasmon resonance band when the silica shell was 70 nm in thickness, as shown Figure 3. In this case, only one broad absorption peak was observed at ~540 nm.

Figure 4 demonstrates the reflection spectra acquired from the surface array of  $\text{Au@SiO}_2 \text{NPs}.$ All samples were wet with the hollow spaces between NPs being completely filled with water when these spectra were measured. The incident light was kept vertical to the (111) planes of these face-center-cubic lattices (Au).

For the reflectance spectra, the Bragg diffraction features were the only peaks detected, and they aligned with the features in the transmission spectra. Additionally, the peaks in Figure



**Figure 4.** Reflectance spectra taken from the arrays produced from  $\text{Au@SiO}_2$  NPs with different shell thicknesses (t). The incident light was perpendicular to the (111) planes of these face-center-cubic crystalline lattices for all measure‐ ments. The gold cores were 50 nm in diameter for all samples. Reproduced with permission from reference [104].

4 associated with particles that possessed various shell thicknesses, were narrow and wellresolved. This shows that such core@shell nanoparticle arrays provide two pathways for modulating their interaction with light. Liz-Marzan *et al.* also recently illustrated the fabrication of 3D crystalline lattices from  $Au@SiO_2$  NP colloids; however, these authors failed to provide similar optical characterization [95]. Above all, the spectra displayed in Figures 2, 3, and 4 provide perspective regarding the potential for utilizing the optical properties of  $Au@SiO<sub>2</sub> NP$  colloids, and their crystalline lattices.

To tune the shell thickness from 20 to 100 nm, the experimental parameters (e.g., coating time and concentration of reactants, catalyst, or other precursors) can be precisely and systematically controlled. Li *et al.* demonstrated how the shell thickness for Ag@SiO<sub>2</sub> NPs can be tuned by controlling certain parameters, the molar volume ratio of water to surfactant,  $R(R = [water]/$ [surfactant]), and the molar volume ratio of water to TEOS, H (H = [water]/[TEOS]) [98]. The manipulation of these parameters provides control over the availability of water molecules for the hydrolysis of TEOS (tetraethyl othosilicate).

Other researchers have developed the magnetic properties of alternative silica-coated cores (e.g., Fe, Ni, Co, and alloyed metal compounds) to be used in the presence of external magnetic fields for the improvement of bio-imaging, biological labeling, information storage, catalysis, etc. [101, 107-109]. Magnetic NPs can be easily synthesized by using wet chemical processes in aqueous systems, but there is a disadvantage; the difficulty of making a stable dispersion of these NPs for use in aqueous environments or biological systems. To resolve this restriction, a silica-coating on the magnetite core NPs offers excellent dispersion and improved biocom‐ patibility [110]. More recently, magnetic NPs formed from different core and shell magnetic

materials have been reported [111]. These unique core@shell structures allow the magnetic properties of the resulting assembly to be more precisely tuned through the choice of magnetic materials and the dimensions of the component parts.

*Other Forms of Core@Shell Nanoparticles.* Various shaped core@shell NPs have proven to be similarly important in research because of their potential applications in the fields of catalysis [112], nanoelectronics [113], information storage [114], and sensors [115]. To synthesize these variously shaped core@shell NPs, researchers have employed a soft or hard core NP template particle to establish the physical shape [116, 117]. The most familiar examples are the use of a firm core NP of a specific shape as the template. Therefore, a soft shell material on a rigid core NP is deposited evenly to present a core@shell NP resembling the shape of the template core. Researchers synthesize core NPs through careful control of the reaction parameters, a process that relies upon controlled crystal growth using surfactants to manipulate the resulting structure [113, 116]. Examples of the types of shapes that can be made (cubic, cuboctahedral, and octahedral) are shown in Figure 5 [113]. These specific examples are  $Cu@Cu<sub>2</sub>O$  NPs and such shaped NPs can be synthesized on a similarly formed core by electro-deposition with a free capping agent.



Figure 5. SEM images of Cu@Cu<sub>2</sub>O NPs in the form of a) cubic, b) cuboctahedral, and c) octahedral shapes. Reproduced with permission from reference [114].

The fitness of the coating of the shell material can be impacted by the shape of the core NP or the nature of the materials used. This means that the production of a uniform coating might be reduced with shape distortions from spherical or when the material used to form the shell reacts with the core material [118]. In the case of the octahedral gold@platinum NPs, the shell material is incompletely coated on the octahedral core because there is an incomplete reduction of the salt by the core material. Additionally, in some bimetallic "core@shell" structures, the shell is formed by a reduction-transmetalation process which fails to produce a distinguishable shell [119]. On the other hand, with the example given above, a spherical core can be more completely coated with a shell material due to a more perfect reduction of the salt and a more uniform exposure of the metal core surface in solution. These examples highlight the importance of the choice of materials used to prepare core@shell composite NPs.

# **3. Smart, multi-responsive Core@Shell nanoparticles**

The development of a stimuli-responsive composite nanoparticle requires an efficient trigger mechanism. One such trigger is the heat generated by the light absorption of metal nanostructures. The optical properties of GNSs can be specifically controlled to maximize the absorption/ scattering of light in the wavelength range of 700 to 1000 nm [64, 83]. This is advantageous because light at wavelengths between 800 nm and 1200 nm, a range called the "water window", can penetrate human tissue, enabling its use in biomedical applications [59]. Several studies have pursued the use of this technology in combination with mesoporous silica shells that can carry model drugs. This drug carrying capacity exists in part because of the large pore volume in the etched silica surface, a feature that is tunable to achieve a specific mesopore diameter (2-50 nm). However, mesoporous silica nanoparticles by themselves are not "smart" materials because these NPs cannot release drugs in a precise and controlled manner at a specific location (i.e., they have irreversible pore openings). To overcome this drawback, our research group has explored the growth of a stimuli-responsive hydrogel polymer coating on gold nanoshells that can release a model drug upon the collapse of the hydrogel matrix. These hydrogel polymers are very useful materials in a variety of applications such as drug delivery, chemical separations, and catalysis. But such polymers need an appropriate stimulus to initiate the release of a drug remotely. For many hydrogel applications, heat is used to initiate the collapse of the polymer hydrogel. Since specific frequencies of light can be used to generate heat at the surface of GNSs that are responsive to such light, the combination of a well-tuned nanoshell for specific light absorption and a thermally-responsive hydrogel provide the potential for remotely controlled drug delivery, a smart, multi-responsive core@shell nanoparticle system.

Additionally, core@shell composite particles that respond to magnetic stimuli can also be used to perform useful tasks in controlled drug delivery [77, 78], bio-separation [120], chemical catalysis [121, 122], and electronics [1, 3]. By integrating the application of both their physical and chemical properties, these magnetic core@shell materials can become multifunctional devices that enable a variety of advanced applications that cannot be accomplished by simple magnetic NPs alone. Recent examples of the application of magnetic NPs in research have demonstrated their usefulness because of their capacity to produce heat under an external oscillating magnetic field or to be manipulated remotely, allowing for their use as an antitumor treatment, cell tracking tag, or drug delivery vehicle [123-125]. These core@shell composite particles that respond to both a magnet and other external stimuli, typically consist of a magnetic core encapsulated in a stimuli-responsive hydrogel copolymer layer that responds rapidly to changes in temperature slightly above that of the body. And such a coating heightens the particles' biocompatibility and chemical stability in an aqueous medium [126-138].

Core@shell composite particles that respond to optical, magnetic, and other external stimuli (e.g., temperature, ionic strength, and pH), can be used to perform more useful tasks in research. For this project, we employed a biocompatible mesoporous silica interlayer between the magnetic core and the hydrogel copolymer outer layer to improve the composite particle's loading capacity and payload release effectiveness. The advantages that such porous struc-

tures provide is their high surface area (ca. 1000 m²/g), large pore volume (ca. 1 cm3/g), tunable mesopore diameter (2-50 nm) and biocompatibility [139, 140]. Thus, impregnation of these mesoporous silica and poly(N-isopropylacrylamide-co-acrylic acid; NIPAM-co-AAc)-coated magnetic NPs (or gold GNSs as the core) with drugs produces a nanoscale drug-delivery system that can be specifically targeted and magnetically (or phothermally) activated. We call them "smart" core@shell NPs.

# **4. Synthesis of smart multi-responsive Core@Shell nanoparticles**

To accomplish the research goals described above, hydrogel-based core@shell composite NPs were fabricated by encapsulating a mesoporous silica-coated GNS (or  $\text{Fe}_3\text{O}_4$  NP) as the core with a PNIPAM-*co*-AAc copolymer coating [141]. The oleylamine-functionalized mesoporous silica-coated GNS (or Fe $_{3} \mathrm{O}_4$  NP) was used as a nano-template for the shell layer growth of a hydrogel copolymer. Ammonium persulfate (APS) was used as a polymerization initiator to produce a hydrogel-encapsulated composite NP. The amount of NIPAM monomer was optimized for the hydrogel-encapsulated mesoporous silica-coated composite NPs [142]. The shell layer thickness was increased with an increase in polymerization time until no further increase in the shell layer thickness was clearly observed [143]. Hydrogel-encapsulated mesoporous silica-coated composite NPs exhibited systematic changes in particle size corresponding to the variation of temperature, which originates from hydrogen-bonding interactions between PNIPAM amide groups and water, as well as electrostatic forces attributed to the ionization of carboxylic groups in the acrylic acid.

#### **5. Long term research objectives**

Lee and co-workers recently reported the initial methodology to precisely control drug delivery by employing gold NPs and GNSs coated with a pH- and temperature-responsive hydrogel originating from the co-polymerization of NIPAM and acrylic acid [142-144]. These nontoxic composite NPs were designed to be loaded with drug molecules, providing the ability for the NP cores to be photothermally activated, initiating collapse of the hydrogel coating and releasing the drug molecules, as illustrated in Figure 6.

Furthermore, we have been working to employ a *m*esoporous silica interlayer between a goldcoated silica core and a hydrogel outer layer to prevent unwanted structural changes to the gold shell during photomodulation and to assist in the carrying of hydrophobic or hydrophilic drugs to targeted sites [141]. The advantages that such porous structures provide is their high surface area (ca. 1000 m²/g), large pore volume (ca. 1 cm $^3$ /g), tunable mesopore diameter (2-50 nm) and biocompatibility [139, 140]. By using smart hydrogel technology as an outer layer and a mesoporous silica coating as an interlayer, GNSs that are activated by tissue-transparent near-IR light can be more effectively used for advanced medicinal applications. With our initial investigation, once these nontoxic composite NPs were loaded with methylene blue (MB; a



Figure 6. Illustration of drug release by increasing the environmental temperature or by generating heat through an SPR response in these optically active composite particles to a near IR laser.

dye used as a model drug), and the NPs thermally activated, the hydrogel coating collapsed and released the test molecules. The potential for such smart, multi-responsive core@shell nanoparticles for use as drug delivery carriers, contrast agents, and therapeutic entities will clearly encourage the application of this new technology in future research projects.

# **Acknowledgements**

The Robert A. Welch Foundation (Grant No. E-1320) and the Texas Center for Superconduc‐ tivity at the University of Houston provided generous support for this research.

# **Author details**

Bo Sang Kim and T. Randall Lee<sup>\*</sup>

\*Address all correspondence to: trlee@uh.edu

Department of Chemistry and the Texas Center for Superconductivity, University of Houston, Houston, Texas, USA

# **References**

[1] Teranishi T, Miyake M. Size control of palladium nanoparticles and their crystal structures. Chem Mater. 1998;10:594-600. DOI: 10.1021/cm9705808.

- [2] Shen L, Luo M, Huang L, Feng P, Wu L. A Clean and General Strategy To Decorate a Titanium Metal-Organic Framework with Noble-Metal Nanoparticles for Versatile Photocatalytic Applications. Inorg Chem. 2015;54:1191-1193. DOI: 10.1021/ic502609a.
- [3] Quaroni L, Chumanov G. Preparation of Polymer-Coated Functionalized Silver Nanoparticles. J Am Chem Soc. 1999;121:10642-10643. DOI: 10.1021/ja992088q.
- [4] Wei L, Lu J, Xu H, Patel A, Chen Z-S, Chen G. Silver nanoparticles: synthesis, properties, and therapeutic applications. Drug Discovery Today. 2015;20:595-601. DOI: 10.1016/j.drudis.2014.11.014.
- [5] Fukuura T. Plasmons excited in a large dense silver nanoparticle layer enhance the luminescence intensity of organic light emitting diodes. Appl Surf Sci. 2015;346:451-457. DOI: 10.1016/j.apsusc.2015.04.044.
- [6] Zhan Z, Xu R, Mi Y, Zhao H, Lei Y. Highly Controllable Surface Plasmon Resonance Property by Heights of Ordered Nanoparticle Arrays Fabricated via a Nonlithographic Route. ACS Nano. 2015;9:4583-4590. DOI: 10.1021/acsnano.5b01226.
- [7] Ranjan M, Bhatnagar M, Mukherjee S. Localized surface plasmon resonance anisotro‐ py in template aligned silver nanoparticles: A case of biaxial metal optics. J Appl Phys. 2015;117:103106/103101-103106/103107. DOI: 10.1063/1.4914408.
- [8] Fojan P, Hanif M, Bartling S, Hartmann H, Barke I, Popok VN. Supported silver clus‐ ters as nanoplasmonic transducers for protein sensing. Sens Actuators, B. 2015;212:377-381. DOI: 10.1016/j.snb.2015.01.131.
- [9] Su Y-A, Lin W-C, Wang H-J, Lee W-H, Lee R-H, Dai SA, et al. Enhanced photovoltaic performance of inverted polymer solar cells by incorporating graphene nanosheet/ AgNPs nanohybrids. RSC Adv. 2015;5:25192-25203. DOI: 10.1039/c4ra16855k.
- [10] Yang Y, Matsubara S, Xiong L, Hayakawa T, Nogami M. Solvothermal Synthesis of Multiple Shapes of Silver Nanoparticles and Their SERS Properties. J Phys Chem C. 2007;111:9095-9104. DOI: 10.1021/jp068859b.
- [11] Temple TL, Mahanama GDK, Reehal HS, Bagnall DM. Influence of localized surface plasmon excitation in silver nanoparticles on the performance of silicon solar cells. Sol Energy Mater Sol Cells. 2009;93:1978-1985. DOI: 10.1016/j.solmat.2009.07.014.
- [12] Amendola V, Bakr OM, Stellacci F. A Study of the Surface Plasmon Resonance of Sil‐ ver Nanoparticles by the Discrete Dipole Approximation Method: Effect of Shape, Size, Structure, and Assembly. Plasmonics. 2010;5:85-97. DOI: 10.1007/ s11468-009-9120-4.
- [13] Chen S, Sommers JM. Alkanethiolate-protected copper nanoparticles: spectroscopy, electrochemistry, and solid-state morphological evolution. J Phys Chem B. 2001;105:8816-8820. DOI: 10.1021/jp011280n.
- [14] Chan GH, Zhao J, Hicks EM, Schatz GC, Van Duyne RP. Plasmonic Properties of Copper Nanoparticles Fabricated by Nanosphere Lithography. Nano Lett. 2007;7:1947-1952. DOI: 10.1021/nl070648a.
- [15] Yaduvanshi P, Mishra A, Kumar S, Dhar R. Enhancement in the thermodynamic, electrical and optical properties of hexabutoxytriphenylene due to copper nanoparticles. J Mol Liq. 2015;208:160-164. DOI: 10.1016/j.molliq.2015.04.030.
- [16] Zhang S, Peng B, Yang S, Wang H, Yu H, Fang Y, et al. Non-noble metal copper nanoparticles-decorated TiO<sub>2</sub> nanotube arrays with plasmon-enhanced photocatalytic hydrogen evolution under visible light. Int J Hydrogen Energy. 2015;40:303-310. DOI: 10.1016/j.ijhydene.2014.10.122.
- [17] Guo X, Hao C, Jin G, Zhu H-Y, Guo X-Y. Copper Nanoparticles on Graphene Sup‐ port: An Efficient Photocatalyst for Coupling of Nitroaromatics in Visible Light. An‐ gew Chem, Int Ed. 2014;53:1973-1977. DOI: 10.1002/anie.201309482.
- [18] Heo M, Cho H, Jung J-W, Jeong J-R, Park S, Kim JY. High-Performance Organic Op‐ toelectronic Devices Enhanced by Surface Plasmon Resonance. Adv Mater. 2011;23:5689-5693. DOI: 10.1002/adma.201103753.
- [19] Clark HA, Campagnola PJ, Wuskell JP, Lewis A, Loew LM. Second harmonic genera‐ tion properties of fluorescent polymer-encapsulated gold nanoparticles. J Am Chem Soc. 2000;122:10234-10235. DOI: 10.1021/ja002223v.
- [20] Zhou N, Polavarapu L, Wang Q, Xu Q-H. Mesoporous SnO<sub>2</sub>-Coated Metal Nanoparticles with Enhanced Catalytic Efficiency. ACS Appl Mater Interfaces. 2015;7:4844-4850. DOI: 10.1021/am508803c.
- [21] Lee K-S, El-Sayed MA. Gold and Silver Nanoparticles in Sensing and Imaging: Sensitivity of Plasmon Response to Size, Shape, and Metal Composition. J Phys Chem B. 2006;110:19220-19225. DOI: 10.1021/jp062536y.
- [22] Al-Azawi MA, Bidin N, Ali AK, Bououdina M. The effects of gold colloid concentra‐ tion on photoanode electrodes to enhance plasmonic dye-sensitized solar cells performance. J Mater Sci: Mater Electron. 2015;26:6276-6284. DOI: 10.1007/ s10854-015-3214-x.
- [23] Yockell-Lelievre H, Bukar N, McKeating KS, Arnaud M, Cosin P, Guo Y, et al. Plasmonic sensors for the competitive detection of testosterone. Analyst. 2015;140:5105-5111. DOI: 10.1039/c5an00694e.
- [24] Hwang JD, Wang FH, Kung CY, Chan MC. Using the surface plasmon resonance of Au nanoparticles to enhance ultraviolet response of ZnO nanorods-based Schottkybarrier photodetectors. IEEE Trans Nanotechnol. 2015;14:318-321. DOI: 10.1109/ tnano.2015.2393877.
- [25] Jain PK, Lee KS, El-Sayed IH, El-Sayed MA. Calculated Absorption and Scattering Properties of Gold Nanoparticles of Different Size, Shape, and Composition: Applica‐

tions in Biological Imaging and Biomedicine. J Phys Chem B. 2006;110:7238-7248. DOI: 10.1021/jp057170o.

- [26] Hu M, Chen J, Li Z-Y, Au L, Hartland GV, Li X, et al. Gold nanostructures: engineer‐ ing their plasmonic properties for biomedical applications. Chem Soc Rev. 2006;35:1084-1094. DOI: 10.1039/b517615h.
- [27] Liu Z, Hou W, Pavaskar P, Aykol M, Cronin SB. Plasmon Resonant Enhancement of Photocatalytic Water Splitting Under Visible Illumination. Nano Lett. 2011;11:1111-1116. DOI: 10.1021/nl104005n.
- [28] Nath N, Chilkoti A. Label-Free Biosensing by Surface Plasmon Resonance of Nanoparticles on Glass: Optimization of Nanoparticle Size. Anal Chem. 2004;76:5370-5378. DOI: 10.1021/ac049741z.
- [29] Reinhard BM, Siu M, Agarwal H, Alivisatos AP, Liphardt J. Calibration of Dynamic Molecular Rulers Based on Plasmon Coupling between Gold Nanoparticles. Nano Lett. 2005;5:2246-2252. DOI: 10.1021/nl051592s.
- [30] Tokareva I, Minko S, Fendler JH, Hutter E. Nanosensors Based on Responsive Polymer Brushes and Gold Nanoparticle Enhanced Transmission Surface Plasmon Reso‐ nance Spectroscopy. J Am Chem Soc. 2004;126:15950-15951. DOI: 10.1021/ja044575y.
- [31] Kowalska E, Mahaney OOP, Abe R, Ohtani B. Visible-light-induced photocatalysis through surface plasmon excitation of gold on titania surfaces. Phys Chem Chem Phys. 2010;12:2344-2355. DOI: 10.1039/b917399d.
- [32] Alivisatos AP. Semiconductor clusters, nanocrystals, and quantum dots. Science. 1996;271:933-937. DOI: 10.1126/science.271.5251.933.
- [33] Daniel M-C, Astruc D. Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology. Chem Rev. 2004;104:293-346. DOI: 10.1021/cr030698+.
- [34] Burda C, Chen X, Narayanan R, El-Sayed MA. Chemistry and Properties of Nanocrystals of Different Shapes. Chem Rev. 2005;105:1025-1102. DOI: 10.1021/cr030063a.
- [35] Bohren CF, Huffman DR. Absorption and Scattering of Light by Small Particles: John Wiley and Sons; 1983.
- [36] Qin Z, Bischof JC. Thermophysical and biological responses of gold nanoparticle laser heating. Chem Soc Rev. 2012;41:1191-1217. DOI: 10.1039/c1cs15184c.
- [37] Kim F, Song JH, Yang P. Photochemical Synthesis of Gold Nanorods. J Am Chem Soc. 2002;124:14316-14317. DOI: 10.1021/ja028110o.
- [38] Xue B, Wang D, Zuo J, Kong X, Zhang Y, Liu X, et al. Towards high quality triangular silver nanoprisms: improved synthesis, six-tip based hot spots and ultra-high local surface plasmon resonance sensitivity. Nanoscale. 2015;7:8048-8057. DOI: 10.1039/ c4nr06901c.
- [39] Sherry LJ, Jin R, Mirkin CA, Schatz GC, Van Duyne RP. Localized Surface Plasmon Resonance Spectroscopy of Single Silver Triangular Nanoprisms. Nano Lett. 2006;6:2060-2065. DOI: 10.1021/nl061286u.
- [40] Chan GH, Zhao J, Schatz GC, Van Duyne RP. Localized Surface Plasmon Resonance Spectroscopy of Triangular Aluminum Nanoparticles. J Phys Chem C. 2008;112:13958-13963. DOI: 10.1021/jp804088z.
- [41] Sun Y, Mayers B, Xia Y. Transformation of Silver Nanospheres into Nanobelts and Triangular Nanoplates through a Thermal Process. Nano Lett. 2003;3:675-679. DOI: 10.1021/nl034140t.
- [42] O'Brien MN, Jones MR, Kohlstedt KL, Schatz GC, Mirkin CA. Uniform Circular Disks With Synthetically Tailorable Diameters: Two-Dimensional Nanoparticles for Plasmonics. Nano Lett. 2015;15:1012-1017. DOI: 10.1021/nl5038566.
- [43] Hao E, Kelly KL, Hupp JT, Schatz GC. Synthesis of Silver Nanodisks Using Polystyr‐ ene Mesospheres as Templates. J Am Chem Soc. 2002;124:15182-15183. DOI: 10.1021/ ja028336r.
- [44] Hou H, Chen L, He H, Chen L, Zhao Z, Jin Y. Fine-tuning the LSPR response of gold nanorod-polyaniline core-shell nanoparticles with high photothermal efficiency for cancer cell ablation. J Mater Chem B. 2015;3:5189-5196. DOI: 10.1039/c5tb00556f.
- [45] Huang X, Neretina S, El-Sayed MA. Gold Nanorods: From Synthesis and Properties to Biological and Biomedical Applications. Adv Mater. 2009;21:4880-4910. DOI: 10.1002/adma.200802789.
- [46] Mayer KM, Lee S, Liao H, Rostro BC, Fuentes A, Scully PT, et al. A Label-Free Immu‐ noassay Based Upon Localized Surface Plasmon Resonance of Gold Nanorods. ACS Nano. 2008;2:687-692. DOI: 10.1021/nn7003734.
- [47] Jiang T, Wang B, Zhang L, Zhou J. Hydrothermal synthesis of silver nanocubes with tunable edge lengths and their size dependent SERS behaviors. J Alloys Compd. 2015;632:140-146. DOI: 10.1016/j.jallcom.2015.01.164.
- [48] Sherry LJ, Chang S-H, Schatz GC, Van Duyne RP, Wiley BJ, Xia Y. Localized surface plasmon resonance spectroscopy of single silver Nanocubes. Nano Lett. 2005;5:2034-2038. DOI: 10.1021/nl0515753.
- [49] Sun Y, Xia Y. Shape-Controlled Synthesis of Gold and Silver Nanoparticles. Science. 2002;298:2176-2179. DOI: 10.1126/science.1077229.
- [50] Im SH, Lee YT, Wiley B, Xia Y. Large-scale synthesis of silver nanocubes: the role of HCl in promoting cube perfection and monodispersity. Angew Chem, Int Ed. 2005;44:2154-2157. DOI: 10.1002/anie.200462208.
- [51] Wang C, Daimon H, Lee Y, Kim J, Sun S. Synthesis of Monodisperse Pt Nanocubes and Their Enhanced Catalysis for Oxygen Reduction. J Am Chem Soc. 2007;129:6974-6975. DOI: 10.1021/ja070440r.
- [52] Graf C, van Blaaderen A. Metallodielectric Colloidal Core-Shell Particles for Photonic Applications. Langmuir. 2002;18:524-534. DOI: 10.1021/la011093g.
- [53] Kim J-H, Bryan WW, Chung H-W, Park CY, Jacobson AJ, Lee TR. Gold, palladium, and gold-palladium alloy nanoshells on silica nanoparticle cores. ACS Appl Mater Interfaces. 2009;1:1063-1069. DOI: 10.1021/am900039a.
- [54] Kim J-H, Bryan WW, Lee TR. Preparation, characterization, and optical properties of gold, silver, and gold-silver alloy nanoshells having silica cores. Langmuir. 2008;24:11147-11152.
- [55] Kim J-H, Park J-S, Chung H-W, Boote BW, Lee TR. Palladium nanoshells coated with self-assembled monolayers and their catalytic properties. RSC Adv. 2012;2:3968-3977. DOI: 10.1039/c2ra00883a.
- [56] Mejac I, Bryan WW, Lee TR, Tran CD. Visualizing the Size, Shape, Morphology, and Localized Surface Plasmon Resonance of Individual Gold Nanoshells by Near-Infra‐ red Multispectral Imaging Microscopy. Anal Chem. 2009;81:6687-6694. DOI: 10.1021/ ac9007495.
- [57] Pham T, Jackson JB, Halas NJ, Lee TR. Preparation and Characterization of Gold Nanoshells Coated with Self-Assembled Monolayers. Langmuir. 2002;18:4915-4920. DOI: 10.1021/la015561y.
- [58] Jankiewicz BJ, Jamiola D, Choma J, Jaroniec M. Silica-metal core-shell nanostructures. Adv Colloid Interface Sci. 2012;170:28-47. DOI: 10.1016/j.cis.2011.11.002.
- [59] Simpson CR, Kohl M, Essenpreis M, Cope M. Near-infrared optical properties of ex vivo human skin and subcutaneous tissues measured using the Monte Carlo inver‐ sion technique. Phys Med Biol. 1998;43:2465-2478.
- [60] Khantamat O, Li C-H, Yu F, Jamison AC, Shih W-C, Cai C, et al. Gold Nanoshell-Decorated Silicone Surfaces for the Near-Infrared (NIR) Photothermal Destruction of the Pathogenic Bacterium E. faecalis. ACS Appl Mater Interfaces. 2015;7:3981-3993. DOI: 10.1021/am506516r.
- [61] Michalak GJ, Goodrich GP, Schwartz JA, James WD, O'Neal DP. Murine photople‐ thysmography for in vivo estimation of vascular gold nanoshell concentration. J Bi‐ omed Opt. 2010;15:047007/047001-047007/047005. DOI: 10.1117/1.3454374.
- [62] Jin Y. Multifunctional Compact Hybrid Au Nanoshells: A New Generation of Nano‐ plasmonic Probes for Biosensing, Imaging, and Controlled Release. Acc Chem Res. 2014;47:138-148. DOI: 10.1021/ar400086e.
- [63] Liu S-Y, Liang Z-S, Gao F, Luo S-F, Lu G-Q. In vitro photothermal study of gold nanoshells functionalized with small targeting peptides to liver cancer cells. J Mater Sci: Mater Med. 2010;21:665-674. DOI: 10.1007/s10856-009-3895-x.
- [64] Oldenburg SJ, Averitt RD, Westcott SL, Halas NJ. Nanoengineering of optical resonances. Chem Phys Lett. 1998;288:243-247. DOI: 10.1016/s0009-2614(98)00277-2.
- [65] Oldenburg SJ, Westcott SL, Averitt RD, Halas NJ. Surface enhanced Raman scatter‐ ing in the near infrared using metal nanoshell substrates. J Chem Phys. 1999;111:4729-4735. DOI: 10.1063/1.479235.
- [66] Oldenburg SJ, Jackson JB, Westcott SL, Halas NJ. Infrared extinction properties of gold nanoshells. Appl Phys Lett. 1999;75:2897-2899. DOI: 10.1063/1.125183.
- [67] Loo C, Lin A, Hirsch L, Lee M-H, Barton J, Halas N, et al. Nanoshell-enabled photon‐ ics-based imaging and therapy of cancer. Technol Cancer Res Treat. 2004;3:33-40. DOI: 10.1177/153303460400300104.
- [68] Averitt RD, Westcott SL, Halas NJ. Linear optical properties of gold nanoshells. J Opt Soc Am B. 1999;16:1824-1832. DOI: 10.1364/josab.16.001824.
- [69] Jackson JB, Halas NJ. Silver Nanoshells: Variations in Morphologies and Optical Properties. J Phys Chem B. 2001;105:2743-2746. DOI: 10.1021/jp003868k.
- [70] Jiang Z-J, Liu C-Y. Seed-Mediated Growth Technique for the Preparation of a Silver Nanoshell on a Silica Sphere. J Phys Chem B. 2003;107:12411-12415. DOI: 10.1021/ jp035060g.
- [71] Deng Z, Chen M, Wu L. Novel Method to Fabricate SiO2/Ag Composite Spheres and Their Catalytic, Surface-Enhanced Raman Scattering Properties. J Phys Chem C. 2007;111:11692-11698. DOI: 10.1021/jp073632h.
- [72] Wang K, Zhang X, Niu C, Wang Y. Template-Activated Strategy toward One-Step Coating Silica Colloidal Microspheres with Silver. ACS Appl Mater Interfaces. 2014;6:1272-1278. DOI: 10.1021/am405096z.
- [73] Peterson MSM, Bouwman J, Chen A, Deutsch M. Inorganic metallodielectric materials fabricated using two single-step methods based on the Tollen's process. J Colloid Interface Sci. 2007;306:41-49. DOI: 10.1016/j.jcis.2006.10.013.
- [74] Ashayer R, Green M, Mannan SH. Synthesis of palladium nanoshell using a layer-bylayer technique. J Nanopart Res. 2010;12:1489-1494. DOI: 10.1007/s11051-009-9721-z.
- [75] Kim J-H, Chung H-W, Lee TR. Preparation and characterization of palladium shells with gold and silica cores. Chem Mater. 2006;18:4115-4120. DOI: 10.1021/cm0528882.
- [76] Guo S, Zhai J, Fang Y, Dong S, Wang E. Nanoelectrocatalyst based on high-density Au/Pt hybrid nanoparticles supported on a silica nanosphere. Chem - Asian J. 2008;3:1156-1162. DOI: 10.1002/asia.200700422.
- [77] Suzuki M, Shinkai M, Kamihira M, Kobayashi T. Preparation and characteristics of magnetite-labeled antibody with the use of poly(ethylene glycol) derivatives. Biotechnol Appl Biochem. 1995;21:335-345.
- [78] Tiefenauer LX, Kuhne G, Andres RY. Antibody-magnetite nanoparticles: in vitro characterization of a potential tumor-specific contrast agent for magnetic resonance imaging. Bioconjug Chem. 1993;4:347-352.
- [79] Wang L, Luo J, Fan Q, Suzuki M, Suzuki IS, Engelhard MH, et al. Monodispersed Core-Shell Fe<sub>3</sub>O<sub>4</sub>@Au Nanoparticles. J Phys Chem B. 2005;109:21593-21601. DOI: 10.1021/jp0543429.
- [80] Sun L, Wang J, Wang Z. Recognition and transmembrane delivery of bioconjugated  $Fe<sub>2</sub>O<sub>3</sub>@Au$  nanoparticles with living cells. Nanoscale. 2010;2:269-276. DOI: 10.1039/ b9nr00152b.
- [81] Stoeber W, Fink A, Bohn E. Controlled growth of monodisperse silica spheres in the micron size range. J Colloid Interface Sci. 1968;26:62-69. DOI: 10.1016/0021-9797(68)90272-5.
- [82] Averitt RD, Oldenburg SJ, Westcott SL, Lee TR, Halas NJ. Optical resonances of gold nanoshells. NASA Conf Publ. 1999;209092:301-306.
- [83] Erickson TA, Tunnell JW, editors. Gold nanoshells in biomedical applications2008: Wiley-VCH Verlag GmbH & Co. KGaA.
- [84] Li J-F, Yang Z-L, Ren B, Liu G-K, Fang P-P, Jiang Y-X, et al. Surface-Enhanced Raman Spectroscopy Using Gold-Core Platinum-Shell Nanoparticle Film Electrodes: Toward a Versatile Vibrational Strategy for Electrochemical Interfaces. Langmuir. 2006;22:10372-10379. DOI: 10.1021/la061366d.
- [85] Hu J-W, Li J-F, Ren B, Wu D-Y, Sun S-G, Tian Z-Q. Palladium-Coated Gold Nanopar‐ ticles with a Controlled Shell Thickness Used as Surface-Enhanced Raman Scattering Substrate. J Phys Chem C. 2007;111:1105-1112. DOI: 10.1021/jp0652906.
- [86] Ghosh Chaudhuri R, Paria S. Core/Shell Nanoparticles: Classes, Properties, Synthesis Mechanisms, Characterization, and Applications. Chem Rev. 2012;112:2373-2433. DOI: 10.1021/cr100449n.
- [87] Izak-Nau E, Kenesei K, Murali K, Voetz M, Eiden S, Puntes VF, et al. Interaction of differently functionalized fluorescent silica nanoparticles with neural stem- and tis‐ sue-type cells. Nanotoxicology. 2014;8:138-148. DOI: 10.3109/17435390.2013.864427.
- [88] Zhang H, Dunphy DR, Jiang X, Meng H, Sun B, Tarn D, et al. Processing pathway dependence of amorphous silica nanoparticle toxicity: Colloidal vs pyrolytic. J Am Chem Soc. 2012;134:15790-15804. DOI: 10.1021/ja304907c.
- [89] Zhang L, Blom DA, Wang H. Au-Cu2O Core-Shell Nanoparticles: A Hybrid Metal-Semiconductor Heteronanostructure with Geometrically Tunable Optical Properties. Chem Mater. 2011;23:4587-4598. DOI: 10.1021/cm202078t.
- [90] Dick K, Dhanasekaran T, Zhang Z, Meisel D. Size-dependent melting of silica-encap‐ sulated gold nanoparticles. J Am Chem Soc. 2002;124:2312-2317. DOI: 10.1021/ ja017281a.
- [91] Radloff C, Halas NJ. Enhanced thermal stability of silica-encapsulated metal nanoshells. Appl Phys Lett. 2001;79:674-676. DOI: 10.1063/1.1389322.
- [92] Ye J, Van de Broek B, De Palma R, Libaers W, Clays K, Van Roy W, et al. Surface morphology changes on silica-coated gold colloids. Colloids Surf, A. 2008;322:225-233. DOI: 10.1016/j.colsurfa.2008.03.033.
- [93] Qi Y, Chen M, Liang S, Yang W, Zhao J. Micro-patterns of  $Au@SiO_2$  core-shell nanoparticles formed by electrostatic interactions. Appl Surf Sci. 2008;254:1684-1690. DOI: 10.1016/j.apsusc.2007.07.136.
- [94] Qi Y, Chen M, Liang S, Zhao J, Yang W. Hydrophobation and self-assembly of coreshell  $Au@SiO_2$  nanoparticles. Colloids Surf, A. 2007;302:383-387. DOI: 10.1016/ j.colsurfa.2007.02.069.
- [95] Liz-Marzan LM, Giersig M, Mulvaney P. Synthesis of Nanosized Gold-Silica Core-Shell Particles. Langmuir. 1996;12:4329-4335. DOI: 10.1021/la9601871.
- [96] Poovarodom S, Bass JD, Hwang S-J, Katz A. Investigation of the Core-Shell Interface in Gold@Silica Nanoparticles: A Silica Imprinting Approach. Langmuir. 2005;21:12348-12356. DOI: 10.1021/la052006d.
- [97] Alejandro-Arellano M, Ung T, Blanco A, Mulvaney P, Liz-Marzan LM. Silica-coated metals and semiconductors. Stabilization and nanostructuring. Pure Appl Chem. 2000;72:257-267. DOI: 10.1351/pac200072010257.
- [98] Li T, Moon J, Morrone AA, Mecholsky JJ, Talham DR, Adair JH. Preparation of Ag/SiO<sub>2</sub> Nanosize Composites by a Reverse Micelle and Sol-Gel Technique. Langmuir. 1999;15:4328-4334. DOI: 10.1021/la970801o.
- [99] Fu W, Yang H, Chang L, Li M, Bala H, Yu Q, et al. Preparation and characteristics of core-shell structure nickel/silica nanoparticles. Colloids Surf, A. 2005;262:71-75. DOI: 10.1016/j.colsurfa.2005.03.028.
- [100] Lee J, Lee Y, Youn JK, Na HB, Yu T, Kim H, et al. Simple synthesis of functionalized superparamagnetic magnetite/silica core/shell nanoparticles and their application as magnetically separable high-performance biocatalysts. Small. 2008;4:143-152. DOI: 10.1002/smll.200700456.
- [101] Aliev FG, Correa-Duarte MA, Mamedov A, Ostrander JW, Giersig M, Liz-Marzan LM, et al. Layer-by-layer assembly of core-shell magnetite nanoparticles. Effect of silica coating on interparticle interactions and magnetic properties. Adv Mater.

1999;11:1006-1010. DOI: 10.1002/(sici)1521-4095(199908)11:12<1006:aid-ad‐ ma1006>3.0.co;2-2.

- [102] Lien Y-H, Wu T-M. Preparation and characterization of thermosensitive polymers grafted onto silica-coated iron oxide nanoparticles. J Colloid Interface Sci. 2008;326:517-521. DOI: 10.1016/j.jcis.2008.06.020.
- [103] He R, You X, Shao J, Gao F, Pan B, Cui D. Core/shell fluorescent magnetic silica-coated composite nanoparticles for bioconjugation. Nanotechnology. 2007;18:315601/315601-315607. DOI: 10.1088/0957-4484/18/31/315601.
- [104] Lu Y, Yin Y, Li Z-Y, Xia Y. Synthesis and Self-Assembly of  $Au@SiO_2$  Core-Shell Colloids. Nano Lett. 2002;2:785-788. DOI: 10.1021/nl025598i.
- [105] Ung T, Liz-Marzan LM, Mulvaney P. Controlled Method for Silica Coating of Silver Colloids. Influence of Coating on the Rate of Chemical Reactions. Langmuir. 1998;14:3740-3748. DOI: 10.1021/la980047m.
- [106] Li C-H, Jamison AC, Rittikulsittichai S, Lee T-C, Lee TR. In Situ Growth of Hollow Gold-Silver Nanoshells within Porous Silica Offers Tunable Plasmonic Extinctions and Enhanced Colloidal Stability. ACS Appl Mater Interfaces. 2014;6:19943-19950. DOI: 10.1021/am505424w.
- [107] Lu X, Liang G, Sun Z, Zhang W. Ferromagnetic Co/SiO<sub>2</sub> core/shell structured nanoparticles prepared by a novel aqueous solution method. Mater Sci Eng, B. 2005;B117:147-152. DOI: 10.1016/j.mseb.2004.11.012.
- [108] Ammar M, Mazaleyrat F, Bonnet JP, Audebert P, Brosseau A, Wang G, et al. Synthesis and characterization of core-shell structure silica-coated  $Fe_{29.5}Ni_{70.5}$  nanoparticles. Nanotechnology. 2007;18:285606/285601-285608. DOI: 10.1088/0957-4484/18/28/285606.
- [109] Fu Y, Shearwood C. Characterization of nanocrystalline TiNi powder. Scr Mater. 2003;50:319-323. DOI: 10.1016/j.scriptamat.2003.10.018.
- [110] Santra S, Tapec R, Theodoropoulou N, Dobson J, Hebard A, Tan W. Synthesis and Characterization of Silica-Coated Iron Oxide Nanoparticles in Microemulsion: The Effect of Nonionic Surfactants. Langmuir. 2001;17:2900-2906. DOI: 10.1021/la0008636.
- [111] Kolhatkar AG, Jamison AC, Litvinov D, Willson RC, Lee TR. Tuning the magnetic properties of nanoparticles. Int J Mol Sci. 2013;14:15977-16009, 15933 pp. DOI: 10.3390/ijms140815977.
- [112] Han W, Yi L, Zhao N, Tang A, Gao M, Tang Z. Synthesis and Shape-Tailoring of Copper Sulfide/Indium Sulfide-Based Nanocrystals. J Am Chem Soc. 2008;130:13152-13161. DOI: 10.1021/ja8046393.
- [113] Radi A, Pradhan D, Sohn Y, Leung KT. Nanoscale Shape and Size Control of Cubic, Cuboctahedral, and Octahedral Cu-Cu<sub>2</sub>O Core-Shell Nanoparticles on Si(100) by

One-Step, Templateless, Capping-Agent-Free Electrodeposition. ACS Nano. 2010;4:1553-1560. DOI: 10.1021/nn100023h.

- [114] Gou L, Murphy CJ. Solution-Phase Synthesis of Cu<sub>2</sub>O Nanocubes. Nano Lett. 2003;3:231-234. DOI: 10.1021/nl0258776.
- [115] Huang C-C, Yang Z, Chang H-T. Synthesis of Dumbbell-Shaped Au-Ag Core-Shell Nanorods by Seed-Mediated Growth under Alkaline Conditions. Langmuir. 2004;20:6089-6092. DOI: 10.1021/la048791w.
- [116] Li F, Yuan Y, Luo J, Qin Q, Wu J, Li Z, et al. Synthesis and characterization of ZnO-Ag core-shell nanocomposites with uniform thin silver layers. Appl Surf Sci. 2010;256:6076-6082. DOI: 10.1016/j.apsusc.2010.03.123.
- [117] Feng L, Wu X, Ren L, Xiang Y, He W, Zhang K, et al. Well-controlled synthesis of Au@Pt nanostructures by gold-nanorod-seeded growth. Chem - Eur J. 2008;14:9764-9771. DOI: 10.1002/chem.200800544.
- [118] Min M, Kim C, Lee H. Electrocatalytic properties of platinum overgrown on various shapes of gold nanocrystals. J Mol Catal A: Chem. 2010;333:6-10. DOI: 10.1016/ j.molcata.2010.09.020.
- [119] Yang J, Lee JY, Too H-P. Core-Shell Ag-Au Nanoparticles from Replacement Reaction in Organic Medium. J Phys Chem B. 2005;109:19208-19212. DOI: 10.1021/ jp052242x.
- [120] Yang L, Guo C, Chen S, Wang F, Wang J, An Z, et al. pH-Sensitive Magnetic Ion Ex‐ changer for Protein Separation. Ind Eng Chem Res. 2009;48:944-950. DOI: 10.1021/ ie800969q.
- [121] Bergbreiter DE, Case BL, Liu Y-S, Caraway JW. Poly(N-isopropylacrylamide) Soluble Polymer Supports in Catalysis and Synthesis. Macromolecules. 1998;31:6053-6062. DOI: 10.1021/ma980836a.
- [122] Jeong B, Bae YH, Lee DS, Kim SW. Biodegradable block copolymers as injectable drug-delivery systems. Nature. 1997;388:860-862. DOI: 10.1038/42218.
- [123] Gupta AK, Gupta M. Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. Biomaterials. 2005;26:3995-4021. DOI: 10.1016/j.biomate‐ rials.2004.10.012.
- [124] Kalambur VS, Han B, Hammer BE, Shield TW, Bischof JC. In vitro characterization of movement, heating and visualization of magnetic nanoparticles for biomedical appli‐ cations. Nanotechnology. 2005;16:1221-1233. DOI: 10.1088/0957-4484/16/8/041.
- [125] Mornet S, Vasseur S, Grasset F, Duguet E. Magnetic nanoparticle design for medical diagnosis and therapy. J Mater Chem. 2004;14:2161-2175. DOI: 10.1039/b402025a.
- [126] Kobayashi T, Kida Y, Tanaka T, Hattori K, Matsui M, Amemiya Y. Interstitial hyper‐ thermia of malignant brain tumors by implant heating system: clinical experience. J Neurooncol. 1991;10:153-163.
- [127] Wang F, Tan WB, Zhang Y, Fan X, Wang M. Luminescent nanomaterials for biological labelling. Nanotechnology. 2006;17:R1-R13. DOI: 10.1088/0957-4484/17/1/r01.
- [128] Holmes KL, Lantz LM. Protein labeling with fluorescent probes. Methods Cell Biol. 2001;63:185-204.
- [129] Lin Y, Weissleder R, Tung C-H. Novel near-infrared cyanine fluorochromes: synthesis, properties, and bioconjugation. Bioconjugate Chem. 2002;13:605-610. DOI: 10.1021/bc0155723.
- [130] Frangioni JV. In vivo near-infrared fluorescence imaging. Curr Opin Chem Biol. 2003;7:626-634. DOI: 10.1016/j.cbpa.2003.08.007.
- [131] Li W, Yang X, Wang K, Tan W, He Y, Guo Q, et al. Real-Time Imaging of Protein In‐ ternalization Using Aptamer Conjugates. Anal Chem. 2008;80:5002-5008. DOI: 10.1021/ac800930q.
- [132] Cheon J, Lee J-H. Synergistically Integrated Nanoparticles as Multimodal Probes for Nanobiotechnology. Acc Chem Res. 2008;41:1630-1640. DOI: 10.1021/ar800045c.
- [133] Kircher MF, Mahmood U, King RS, Weissleder R, Josephson L. A Multimodal Nanoparticle for Preoperative Magnetic Resonance Imaging and Intraoperative Optical Brain Tumor Delineation. Cancer Res. 2003;63:8122-8125.
- [134] Park J-H, von Maltzahn G, Ruoslahti E, Bhatia SN, Sailor MJ. Micellar hybrid nano‐ particles for simultaneous magnetofluorescent imaging and drug delivery. Angew Chem, Int Ed. 2008;47:7284-7288. DOI: 10.1002/anie.200801810.
- [135] Lee JE, Lee N, Kim H, Kim J, Choi SH, Kim JH, et al. Uniform Mesoporous Dye-Dop‐ ed Silica Nanoparticles Decorated with Multiple Magnetite Nanocrystals for Simulta‐ neous Enhanced Magnetic Resonance Imaging, Fluorescence Imaging, and Drug Delivery. J Am Chem Soc. 2010;132:552-557. DOI: 10.1021/ja905793q.
- [136] Ke J-H, Lin J-J, Carey JR, Chen J-S, Chen C-Y, Wang L-F. A specific tumor-targeting magnetofluorescent nanoprobe for dual-modality molecular imaging. Biomaterials. 2010;31:1707-1715. DOI: 10.1016/j.biomaterials.2009.11.026.
- [137] Kim J, Kim HS, Lee N, Kim T, Kim H, Yu T, et al. Multifunctional uniform nanoparti‐ cles composed of a magnetite nanocrystal core and a mesoporous silica shell for magnetic resonance and fluorescence imaging and for drug delivery. Angew Chem, Int Ed. 2008;47:8438-8441. DOI: 10.1002/anie.200802469.
- [138] Liu H-M, Wu S-H, Lu C-W, Yao M, Hsiao J-K, Hung Y, et al. Mesoporous silica nano‐ particles improve magnetic labeling efficiency in human stem cells. Small. 2008;4:619-626. DOI: 10.1002/smll.200700493.
- [139] Lu J, Liong M, Li Z, Zink JI, Tamanoi F. Biocompatibility, Biodistribution, and Drug-Delivery Efficiency of Mesoporous Silica Nanoparticles for Cancer Therapy in Animals. Small. 2010;6:1794-1805. DOI: 10.1002/smll.201000538.
- [140] Hudson SP, Padera RF, Langer R, Kohane DS. The biocompatibility of mesoporous silicates. Biomaterials. 2008;29:4045-4055. DOI: 10.1016/j.biomaterials.2008.07.007.
- [141] Kim BS. Smart Hybrid Core@Shell Nanoparticles: Synthesis, Characterization, and Application. Houston: University of Houston; 2013.
- [142] Kim J-H, Lee TR. Thermo- and pH-Responsive Hydrogel-Coated Gold Nanoparticles. Chem Mater. 2004;16:3647-3651. DOI: 10.1021/cm049764u.
- [143] Kim J-H, Park HH, Chung SY, Lee TR. Hydrogel-coated shell/core nanoparticles for in vivo drug delivery. PMSE Prepr. 2008;99:730-731.
- [144] Kim J-H, Lee TR. Discrete thermally responsive hydrogel-coated gold nanoparticles for use as drug-delivery vehicles. Drug Dev Res. 2006;67:61-69. DOI: 10.1002/ddr. 20068.

