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Functional Micro/Nanostructures: Simple Synthesis and Application in Sensors, Fuel Cells, and Gene Delivery

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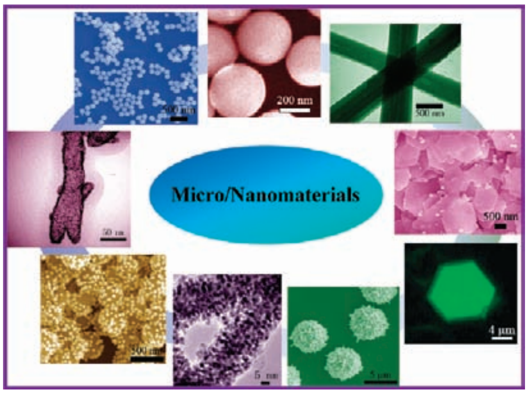

In order to develop new, high technology devices for a variety of applications, researchers would like to better control the structure and function of micro/nanomaterials through an understanding of the role of size, shape, architecture, composition, hybridization, molecular engineering, assembly, and microstructure. However, researchers continue to face great challenges in the construction of well-defined micro/nanomaterials with diverse morphologies. At the same time, the research interface where micro/nanomaterials meet electrochemistry, analytical chemistry, biomedicine, and other fields provides rich opportunities to reveal new chemical, physical, and biological properties of micro/nanomaterials and to uncover many new functions and applications of these materials.

In this Account, we describe our recent progress in the construction of novel inorganic and polymer nanostructures formed through different simple strategies. Our synthetic strategies include wet-chemical and electrochemical methods for the controlled production of inorganic and polymer nanomaterials with well-defined morphologies. These methods are both facile and reliable, allowing us to produce high-quality micro/nanostructures, such as nanoplates, micro/nanoflowers, monodisperse micro/nanoparticles, nanowires, nanobelts, and polyhedron and even diverse hybrid structures. We implemented a series of approaches to address the challenges in the preparation of new functional micro/nanomaterials for a variety of important applications

This Account also highlights new or enhanced applications of certain micro/nanomaterials in sensing applications. We singled out analytical techniques that take advantage of particular properties of micro/nanomaterials. Then by rationally tailoring experimental parameters, we readily and selectively obtained different types of micro/nanomaterials with novel morphologies with high performance in applications such as electrochemical sensors, electrochemiluminescent sensors, gene delivery agents, and fuel cell catalysts. We expect that micro/nanomaterials with unique structural characteristics, properties, and functions will attract increasing research interest and will lead to new opportunities in various fields of research.

Introduction

Nanoscience and nanotechnology have been recognized as two of the most modish research topics in the past decades. And micro/nanomaterials (MNMs) are undoubtedly the key core and act as the promoter for the deeper development of many new fields related to "NANO". MNMs exhibit many particular properties (e.g., quantum size effect, small size effect, surface effect and tunneling effect, etc.) and have many widespread applications in electrochemistry, electrocatalysis, optics, electronics, analytical devices, energy devices, and so forth.[1] There is currently an intensive effort to develop new methods for producing novel MNMs with different morphologies or compositions or hybrids, which are of great importance in achieving high-performance applications. This new technology area has stimulated researchers to focus mainly on identifying new

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properties and understanding the structure–property (or functions or applications) relationships that relate specifically to certain modish nanostructures and nanomaterials-based assembling architectures. Generally, the size, shape, architecture, composition, hybrid, molecular engineering, assembly, and microstructure of MNMs are the key parameters in revealing their new or enhanced functions and determining their different application potentials. For instance: (a) *Size Effect.* Quantum dots (QDs, e.g., CdTe) exhibit tunable size-dependent emission from green to red emission due to quantum confinement.[2] (b) *Shape Effect.* Gold nanorods (NRs) and gold nanocages have strong near-infrared surface plasmon resonance (SPR) absorption, whereas Au nanoparticles (NPs) only have size-dependent visible SPR absorption.[3] (c) *Architecture Effect.* A single architecture conferring multiple functions in nanoscale in the form of core–shell or heterodimer nanostructures is a promising candidate for dual (or multiple)-functional molecular imaging (i.e., combining magnetic resonance imaging, fluorescent, biphotonic, NIR, and surface enhanced Raman scattering (SERS) imaging).[4] (d) *Composition Effect.* Alloying of two semiconductors at the nanometer scale can produce new materials that display properties distinct not only from the properties of their bulk counterparts but also from those of their parent semiconductors.[5] (e) *Hybrid Effect.* Carbon nanofiber/Pd NPs hybrids have higher electrochemical performance for sensing small molecules than that of individual materials.[6] (f) *Molecular Engineering Effect.* Attaching antibodies, proteins, and dyes to the superparamagetic NPs will effectively extend their application scope.[4] (g) *Assembly Effect.* Ag nanowire (NWs) parallel array produced by Langmuir–Blodgett technique has higher SERS activity than random Ag NW substrate.[7] (h) *Microstructure Effect.* Pt tetrahexahedral nanocrystals with high-index facets have been proven to exhibit higher electrocatalytic activities toward small molecule oxidation and oxygen reduction reactions (ORR) than the commercial catalysts.[8] (i) *Multiple Effect.* The ORR activity on alloyed bimetallic Pt_3Ni nanoctahedra is significantly higher than that on spherical NPs.[9] Actually, one can effectively tune the properties of MNMs or even obtain new properties and functions by controlling any one or two even more of these parameters, but the flexibility and scope of change are highly sensitive to some specific parameters. Needless to say, it is always desirable to reveal (i) the relationships of structure–function, (ii) new size, composition, and shape-based properties, and (iii) the possibility of compelling reasons for functionality and applications. However, still, the design and synthesis of certain functional MNMs with well-defined morphology, and new functions and applications are a significant and ongoing challenge within nanoscience and nanotechnology.

This Account focuses on our up-to-date research on simple synthesis and some salient applications of certain MNMs. The central theme is to highlight the important role of functional MNMs in the fields of sensors, fuel cells, and gene delivery. First, new achievements in developing different simple approaches for the synthesis of diverse MNMs with a rich variety of shapes are summarized. Then, the Account introduces some exciting push in the use of MNMs for some important applications including electrochemical sensors, electrochemiluminescence (ECL) sensors, fluorescent sensors, colorimetric sensors, fuel cells, and gene delivery. Finally, we conclude with a look at the future challenges and prospects in the synthesis and application aspects of MNMs.

Controlled Synthesis of Certain Micro/Nanomaterials

The controllable synthesis of MNMs with an emphasis on producing materials with uniform size and shape is a prerequisite for the advancement of nanoscience and nanotechnology because the properties and functions of MNMs can be finely tuned to enhance their versatility by controlling the different parameters. Since the first reports on monodisperse high-quality FePt NPs,[10] Ag nanocubes,[11] and CdSe nanocrystals,[12] tremendous research efforts have been directed toward the fabrication of MNMs with specific size and shape through a variety of methods, mainly bottom-up chemical approaches. Different from previous contributions, in our investigation, diverse wet-chemical and electrochemical approaches with the priority of simpleness and rapidness to prepare high-quality MNMs with diverse morphologies were mainly developed. A general scheme on demonstrating how we use simple wet-chemical and electrochemical methods to make MNMs is shown in Scheme 1. Through effectively controlling the interior and exterior factors, we can prepare different types of MNMs in a controllable manner. As for gold nanomaterials, through the design of different ligands such as biomolecules, polymers, dendrimers, and so forth, as protecting agents, the isolated gold NPs with controlled size could be easily synthesized at low temperature, which have a good solubility in water.[13−15] Particularly, we developed a facile one-step one-phase synthetic route to achieve size-controlled (from 150 nm to 1 μm) monodisperse gold micro/nanoparticles by using *o*-diaminobenzene as a reducing agent and poly(*N*-vinyl-2-pyrrolidone) (PVP) as protecting agent (Figure 1A),

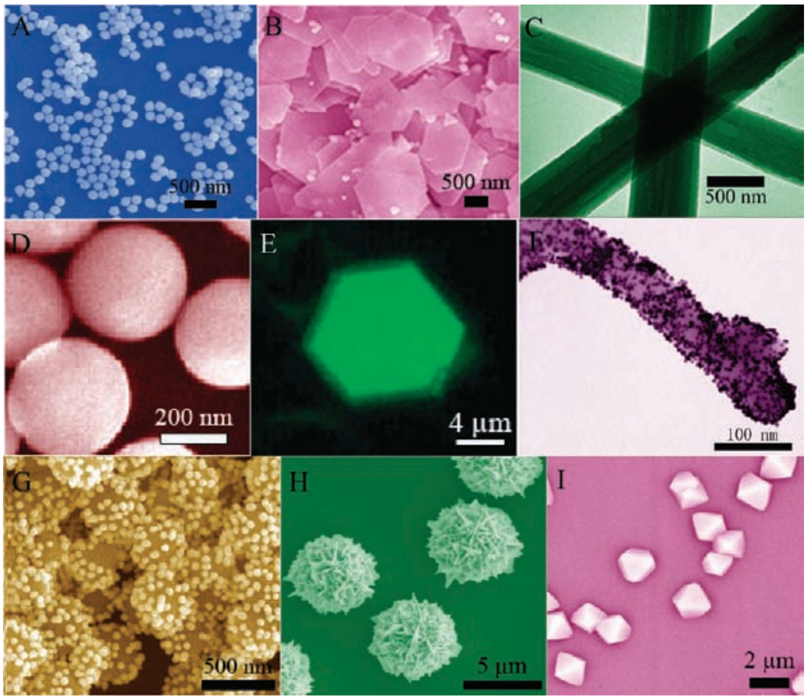
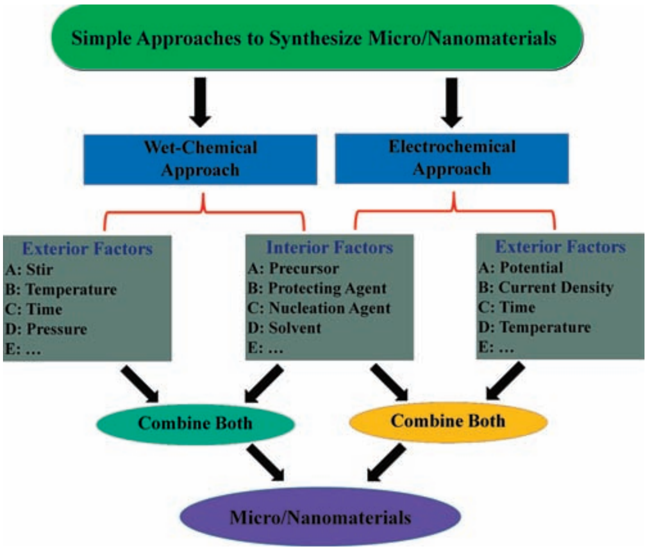


FIGURE 1. Electron microscopy images of our new micro/nanostructures: (A) monodisperse gold NPs,[15] (B) gold nanoplates,[16] (C) poly-*o*-phenylenediamine nanobelts,[18] (D) organic–inorganic hybrid colloid spheres,[19] (E) 3D microhexagonal columns of CdTe-cystine nanocomposites,[21] (F) CNTs/TiO_2/Au hybrid nanostructure,[23] (G) magnetic NPs/Au@Pt NPs hybrid architecture,[24] (H) flowerlike gold microstructure,[27] and (I) Cu_2O octahedra.[29]

SCHEME 1. Schemetic Procedure for Simple Synthesis of MNMs



which is an important extension for the size range of gold NPs usually synthesized through citrate reduction method.[15] In addition to spherical gold NPs, anisotropic gold nanomaterials are of great interest because they can exhibit more novel physical and chemical properties than spherical gold NPs. We presented our findings that micrometer-sized hexagonal single-crystalline Au nanoplates could be synthesized on a large scale by a mild wet-chemical route, carried out by the chemical reduction of $HAuCl_4$ with *o*-phenylenediamine in aqueous media at ambient condition (Figure 1B). The as-prepared Au nanoplates exhibited two surface plasmon absorption bands at about 680 and 925 nm.[16]

Colloid chemical approaches have been employed by us to synthesize other types of high-quality MNMs including conducting polymer nanobelts (Figure 1C),[17,18] organic–inorganic hybrid coordination colloid spheres (Figure 1D),[19,20] CdTe QDs,[2] luminescent one-dimensional (1D) NWs or 3D microhexagonal columns of CdTe QDs-cystine nanocomposites (Figure 1E),[21] silica hollow spheres,[22] carbon nanotube (CNT)/TiO_2/Au hybrid nanostructure (Figure 1F),[23] magnetic NPs/Au@Pt NPs hybrid architectures (Figure 1G),[24] and graphene/Au hybrid nanostructure.[25] For instance, uniform poly-(*o*-phenylenediamine) (PPD) nanobelts has been prepared through directly mixing an *o*-phenylenediamine-$HAuCl_4$ aqueous solution at room temperature without using any template or surfactant.[17] However, the resulting precipitates containing Au NPs are not "pure", and particularly the use of expensive reagent ($HAuCl_4$) makes the industrialization of these nanobelts unpractical. Later, we interestingly found that the gram-scale synthesis of width-controlled, high-quality ultralong PPD nanobelts could be rapidly conducted via directly mixing $FeCl_3$ and *o*-phenylenediamine solution at room temperature, which provided a novel route for industrially producing 1D conducting polymer nanostructures (Figure 1C).[18] In the case of coordination colloid spheres, we presented the first preparation of submicrometer-scale, monodisperse, spherical colloids of coordination polymers, which could be carried out through rapidly mixing H_2PtCl_6 and *p*-phenylenediamine aqueous solutions at room temperature.[19] Electron microscopy results reveal that these particles with smooth surfaces are monodisperse colloids with the diameter of 420 nm (Figure 1D). Furthermore, submicrometer-scale spherical colloidal particles of adenine–gold(III) hybrid materials were also facilely prepared through supramolecular self-assembly adenine and $HAuCl_4$ at room temperature.[20] As for semiconductor MNMs, one interesting example is that we demonstrated a facile heating protocol to prepare luminescent 1D nanofibers or 3D microhexagonal columns of CdTe-cystine nanocomposites through slow or rapid oxidation of L-cysteine by oxygen in air or H_2O_2 in the presence of CdTe QDs (Figure 1E).[21] In addition, we also developed wet-chemical approaches combined with self-assembly technique for constructing a series of CNTs/metal hybrid nanostructures using homogeneous TiO_2 as a linker (Figure 1F),[23] magnetic NPs/metal hybrid architectures using 3-aminopropyltrimethoxysilane as a linker (Figure 1G),[24] and graphene/Au NPs hybrids using polymer as a linker.[25] In the above assembly strategy, bifunctional molecules are usually required to provide one end group to connect support materials. And their other end group was employed to assemble the desired MNMs onto desirable support materials. Electrochemical routes for high-quality MNMs are also of great interest due to their simpleness, rapidness, and ease of tuning of different electrochemical parameters.[8] Sun and co-workers first employed a square-wave potential electrochemical method for treatment of Pt[8] and Pd[26] nanospheres on electrode to synthesize unconventional tetrahexahedron Pt and Pd nanospheres with high-index surfaces. Our group developed a simpler electrochemical route to synthesis of diameter-controlled flowerlike gold microstructures with "clean" surfaces (Figure 1H),[27] Pd nanourchins,[28] and Cu_2O octahedral microcrystals[29] (Figure 1I) just via simply changing the potentials of electrodeposition to reduce corresponding MNMs precursors, which paves new avenues for directly synthesizing high-quality MNMs on conducting substrates.

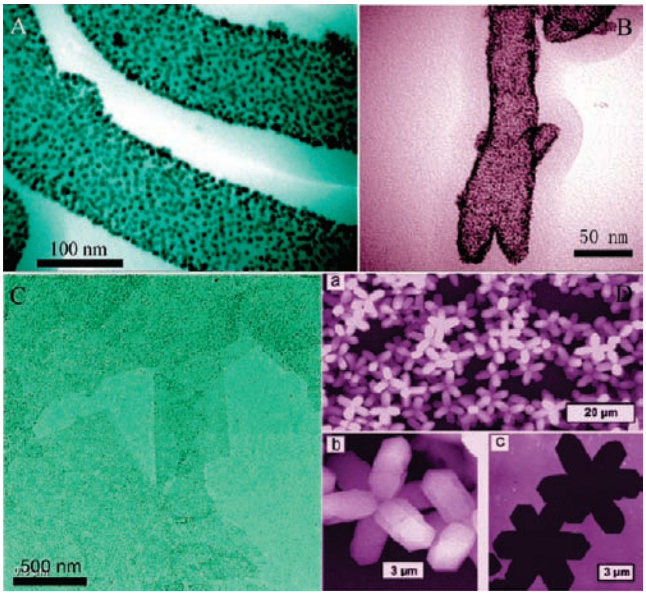


FIGURE 2. New electrocatalytic sensing materials: (A) CNTs/SiO_2/Au/Pt hybrid nanocables,[30] (B) polyaniline/Pt–Pd hybrid nanofibers,[31] (C) graphene/Pt NPs hybrids,[32] and (D) $Ru(bpy)_3^{2+}$-$PtCl_6^{2-}$ supramolecular assembly microstructures.[39]

Micro/Nanomaterials for Sensing Applications

Electrochemical Sensors. Nanoelectroanalytical chemistry, a rising interdisciplinary field, has become one of the most exciting topics. MNMs, as the key component, are most widely used in electroanalytical investigations and play an important role in constructing high-performance electrochemical sensing platforms to detect target molecules through different analytical principles. Therefore, searching new electrode materials for further improvement of sensitivity of electrochemical detection remains highly desirable and has been a great challenge. The clever combination of different nanoscaled inorganic nanomaterials or functional molecules, leading to development of an enhanced or multifunctional nanoassembly system, may open a new avenue for utilizing hybrid nanomaterials as enhanced elements for constructing electrochemical sensors with high performance.[6] For instance, our group developed some wet-chemical approaches to synthesize a series of hybrid functional nanomaterials for constructing an enhanced electrochemical sensing platform for amperometric detection of different molecules. Prominent examples include CNT/silica coaxial nanocable supported Au/Pt hybrid NPs (Figure 2A),[30] polyaniline nanofiber/high-density Pt NP hybrids (Figure 2B),[31] graphene/Pt or Au NP hybrids (Figure 2C),[25,32] and cyclodextrin–graphene hybrid nanosheets.[33] All the above contributions reveal that the

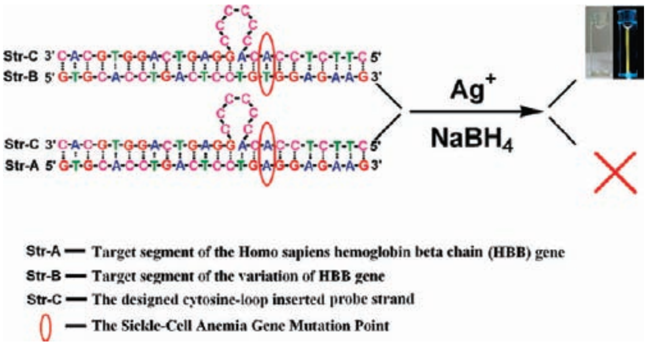


FIGURE 3. Use of two different DNA duplexes with inserted cytosine loops working as synthetic scaffolds to generate fluorescent silver NCs for the identification of the sickle cell anemia gene mutation.[42]

as-obtained mutilcomponent hybrids have a higher larger electrochemically active surface areas for the adsorption of target molecules and thus lead to a more rapid and sensitive current response than individual nanomaterials.

To develop regenerable $Ru(bpy)_3^{2+}$- based high-sensitivity ECL sensors and detection devices and to simplify the detection system, considerable attention has been paid to the immobilization of a great number of $Ru(bpy)_3^{2+}$ molecules on solid electrode surface.[34] MNMs provide good opportunities for effectively enriching $Ru(bpy)_3^{2+}$ molecules in the form of diverse morphologies due to their high surface area and good conductivity. We found that a series of nanomaterials such as gold NPs,[35] Pt NPs,[36] CNTs,[37] and silica NPs[38] could effectively adsorb many $Ru(bpy)_3^{2+}$ molecules based on the electrostatic interactions between negatively charged MNMs and $Ru(bpy)_3^{2+}$ and in the meantime accelerate the electron transfer between $Ru(bpy)_3^{2+}$ and the electrode. The obtained nanomaterials-based ECL sensors exhibited high ECL performance for sensing small molecules. A solution-based self-assembly process was also developed for the preparation of novel, robust $Ru(bpy)_3^{2+}-PtCl_6^{2-}$ supramolecular microstructures, carried out by directly mixing H_2PtCl_6 and $Ru(bpy)_3Cl_2$ aqueous solutions at room temperature (Figure 2D).[39] Such microstructures placed on an indium tin oxide (ITO) exhibited excellent ECL behaviors and therefore hold great promise as new luminescent materials for solid-state ECL detection in capillary electrophoresis (CE) or CE microchips.

Fluorescent Sensors. The nanomaterials-based fluorescent sensors are particularly attractive because of their some obvious advantages such as high sensitivity, easy operation, and multiplicity of measurable parameters. Generally speaking, three main schemes have been developed for devising new fluorescent sensors as follows. (1) Fluorescent nanomaterials such as QDs and metal nanoclusters (NCs) in particular, as a new class of fluorescence reporters, have been explored for detecting different targets mainly through fluorescence quenching or recovery mechanism induced by the target. Chang et al. synthesized a series of water-soluble, highly fluorescent alkanethiol-Au NCs, which were capable of sensing Hg^{2+} ion with high sensitivity.[40] Our typical fluorescent sensors include the detection of Hg^{2+} and biothiols in biological fluids using oligonucleotide-stabilized Ag NCs as probes,[41] identifying single-nucleotide mutations (SNMs) through the use of hybridized DNA duplexes protected Ag NCs (Figure 3),[42] sensitive and selective sensor for biothiols based on the recovered fluorescence of the CdTe QDs-Hg(II) system, and utilizing a CdTe QDs-enzyme hybrid system for the fluorescent determination of both phenolic compounds and H_2O_2.[44] (2) The second frequently adopted scheme was the utilization of the ultrahigh quenching ability of nanomaterials to the fluorescence of nearby fluorophores. For instance, our group designed a sensitive and selective fluorescent sensor for the detection of Hg^{2+} or adenosine triphosphate (ATP), which was based on the noncovalent assembly of single-walled CNTs (SWNTs) and dye-labeled T-rich single-stranded DNA or dye-labeled ATP aptamer.[45,46] Figure 4 shows the concept and process for fluorescent Hg^{2+} detection. In the absence of Hg^{2+}, the ssDNA wrapped around SWNTs and thus formed the stable ssDNA/SWNTs complexes, which quenched the dye's fluorescence. Upon addition of Hg^{2+}, the ssDNA formed a double helical structure with Hg^{2+} via T-Hg^{2+}-T base pairs, which detached from the nanotube surface, resulting in an increase of fluorescenct emission. Furthermore, Au NPs have also been used as quench agents to develop new fluorescent methods for sensitive detection of biological thiols in human plasma[47] and cyanide[48] based on a "turn-on" model that the fluorescent signal of the dye would enhance dramatically due to desorption of dye from the surfaces of Au NPs when adding the targets (e.g., thiol molecules). (3) The third

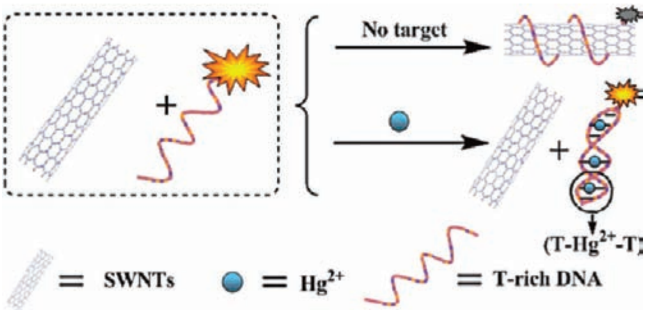


FIGURE 4. Schematic description of fluorescent sensing of Hg^{2+} based on the SWNTs and T-rich DNA.[45]

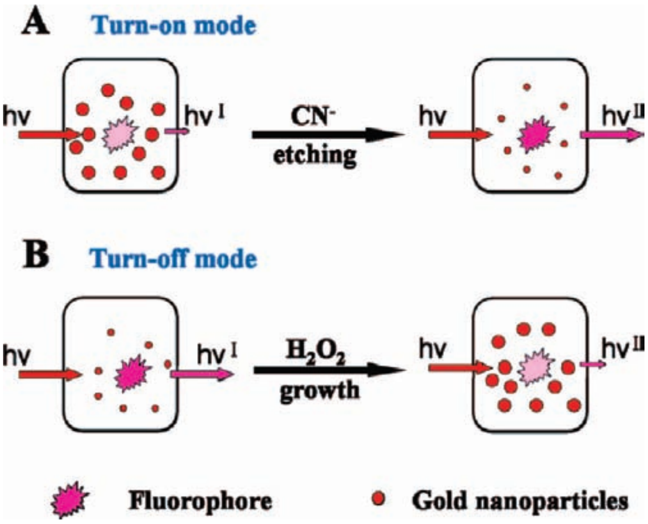


FIGURE 5. Schematic illustration of fluorescence assays based on the inner filter effect of Au NPs. (A) Turn-on assay for cyanide and (B) turn-off assay for H_2O_2.[49]

scheme was based on the inner filter effect (IFE) of metal NPs, which did not require a direct link of fluorophore onto the surface of metal NPs. In this strategy, metal NPs worked as an absorber to modulate the emission of the fluorophore. In this aspect, two proof-of-concept processes for the detection of CN^- and H_2O_2 in a turn-on model upon the etching of Au NPs by CN^- or turn-off model upon the catalytic growth of Au NPs by H_2O_2 (Figure 5) were successfully demonstrated.[49] The present IFE-based fluorescent sensors showed high performance for the detection of CN^- and H_2O_2 (e.g., detect H_2O_2 ranging from 1.5×10^{-7} to 2.2×10^{-5} M with a detection limit of 8.5×10^{-8} M). Later, the present system was extended to Ag NPs, and further a turn-on fluorescent assay for CN^- based on the strong absorption of Ag NPs to both excitation and emission light of an anion fluorescent polymer was developed.[50] In general, the biggest advantage of the present IFE-based strategy is to allow the fluorescent assays with high sensitivity in a more simple, time-saving, and economical approach without any modification step of the fluorophore.

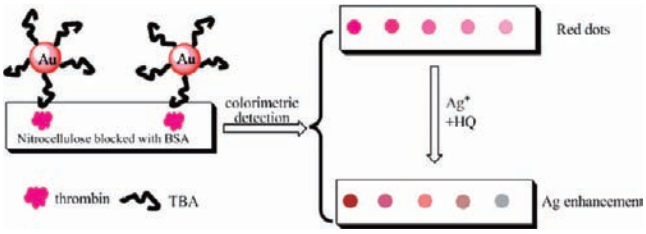


FIGURE 6. Description of colorimetric detection of protein by aptamer−Au-NP conjugates based on a dot-blot assay.[53]

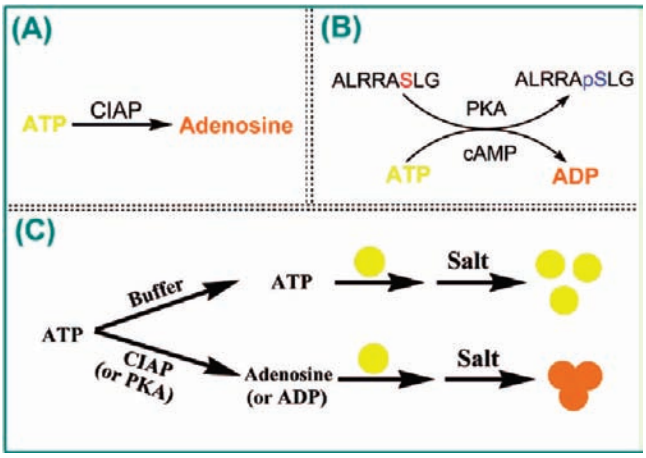


FIGURE 7. Enzymatic reactions with calf intestine alkaline phosphatase (A) and protein kinase A (B); Ag-NP-based enzyme colorimetric assay (C).[54]

Colorimetric Sensors. Colorimetric sensors have received great consideration due to their simplicity, high sensitivity, low cost and easy read out with the naked eye or quantitatively performed with UV/vis spectrometry. Gold and silver NPs are emerging as important colorimetric reporters due to their size-dependent SPR property (e.g., the dispersed gold NPs solution is red, whereas the aggregated gold NPs solution is purple and even blue). Our group described simple and sensitive aptamer-based colorimetric sensing of α-thrombin using unmodified gold NP as probes. In the sensing strategy, when thrombin interacted with its aptamer, the aptamer was much more inclined to fold into a structure of G-quadruplex/duplex, enabling Au NP aggregation.[51] Moreover, we further extended this strategy to detect coralyne with a detection limit of 91 nM.[52] Despite such progress, however, one big disadvantage of the above Au-NP-based colorimetric sensors in solution was the interference from the color of background, leading to the decrease in assay sensitivity. In order to solve this issue, our group explored a simple, rapid and ultrasensitive colorimetric detection of protein based on aptamer−Au-NP conjugates using a dot-blot assay, taking α-thrombin as a model protein. After silver enhancement, the obtained aptasensor had very high sensitivity with a detection limit of 14 fM (Figure 6).[53] In addition, silver NPs are also good candidates for colorimetric sensors because the extinction coefficient of Ag NPs is higher than that of Au NPs under the same condition. Our group developed a sensitive, selective, simple, and label-free colorimetric assay using unmodified a DNA−Ag-NP probe to detect enzymatic reactions.[54] By virtue of our method, dephosphorylation and phosphorylation could be readily monitored by the color change of Ag NPs with a detection limit of 1 unit/mL for calf intestine

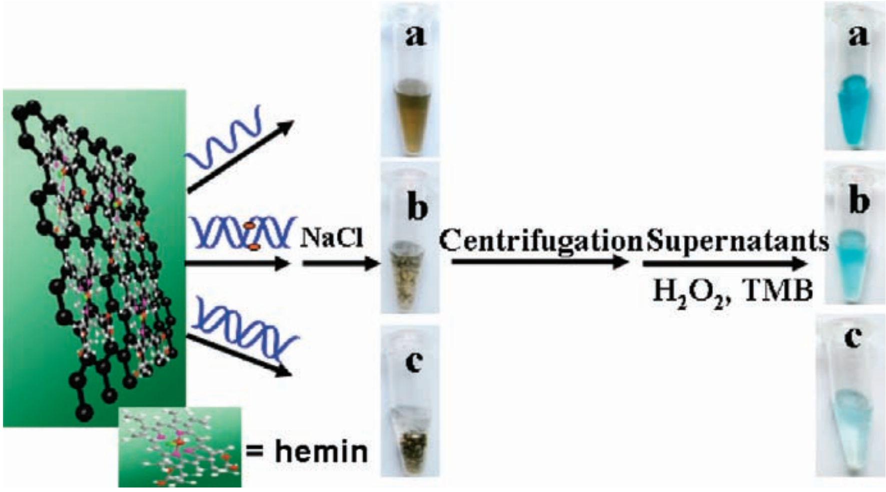


FIGURE 8. Protocol for SNM detection. (a) ssDNA (T1) (no precipitation, dark blue), (b) single mismatched duplex DNA (small amount of precipitation, blue), and (c) complementary duplex DNA (much precipitation, light blue).[56]

alkaline phosphatase (CIAP) and 0.022 unit/mL for protein kinase A (PKA) (Figure 7). Fe_3O_4 NPs[55] and graphene–hemin hybrid nanosheets (GHHNs),[56] new peroxidase mimetics, could be used to catalyze the oxidation of a peroxidase substrate such as 3,3,5,5-tetramethylbenzidine (TMB) by H_2O_2 to the oxidized colored product. Taking this novel property, the colorimetric assay for the detection of H_2O_2 using Fe_3O_4 NPs[55] and SNM using GHHN was developed.[56] A typical example is a label-free colorimetric detection method for DNA sequence specificity on the basis of GHHN as a peroxidase that was developed,[56] which is displayed in Figure 8. It is seen that GHHN solution with dsDNA was easily precipitated by adding electrolyte, whereas GHHN with ssDNA could inhibit precipitation in the presence of TMB and H_2O_2. Different GHHN supernatants have different catalytic abilities for producing the color reaction that can be easily judged by the naked eye.

Micro/Nanomaterials for Fuel Cell Application

Platinum-group metal nanoelectrocatalysts are widely applied in fuel cells, petroleum catalytic reform, automotive catalytic converters, and so forth. However, the price of platinum-group metal is quite high due to their rare reserve on the earth. At present, the key scientific and technological issues of platinum catalysts are how to improve their activity, stability, and utilization efficiency. Surrounded by the key points, several groups have devoted great efforts to synthesizing a series of high-quality supported and unsupported Pt-based electrocatlysts. (a) *Supported Nanoelectrocatalysts.* In order to reduce the electron transfer resistance, we described a convenient approach for the synthesis of CNTs/imidazolium-salt-based ionic liquids (IS-ILs)/Pt NPs hybrids using IS-ILs as linkers. The as-prepared three-component CNTs/IS-ILs/Pt NPs hybrids exhibited very high electrocatalytic activity toward methanol oxidation reaction (MOR) (Figure 9A).[57] More recently, a wet-chemical approach for the synthesis of high-quality 3D Pt-on-Pd bimetallic nanodendrites supported on graphene nanosheets (TP-BNGN) was also demonstrated. The as-prepared TP-BNGN exhibited much higher electrocatalytic activity and stability toward MOR than the commercial E-TEK Pt/C catalyst

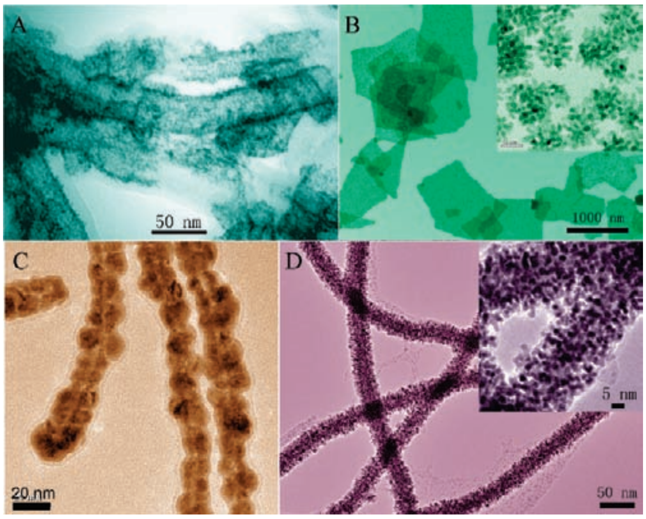


FIGURE 9. Electron microscopy images of new nanoelectrocatalysts for fuel cell. (A) CNTs/ionic liquid/Pt NPs hybrids[57] (B) graphene/Pt-on-Pd bimetallic nanodendrites,[58] (C) Pt/Pd core/shell nanotubes with petal-like surface[62] and (D) Pt-on-Pd bimetallic NWs with nanoporous surface.[63]

(Figure 9B).[58] Yang el al.[59] found that a noncovalent assembly strategy could be used to prepare CNTs/Pt nanocube hybrids, which exhibited high catalytic activity toward ORR. (b) *Unsupported Nanoelectrocatalysts*. Xia et al.[60] demonstrated the first example of the synthesis of Pd–Pt bimetallic nanodendrites with high electroactivity for ORR. However, the durability of their catalyst for ORR is not good for the long-term operation. One-dimensional Pt- or Pd-based nanomaterials could be less vulnerable to dissolution, Ostwald ripening, and aggregation, and eliminate the carbon corrosion problem during fuel cell operation relative to carbon supported catalysts.[61] Inspired by this viewpoint, we demonstrated a wet-chemical strategy for synthesizing small-diameter Pt–Pd bimetallic nanotubes with petal-like surfaces using ultrathin Te NWs as a sacrificial template, which could significantly enhance the activity and durability for ethanol electrooxidation in alkaline conditions relative to commercial Pd/C catalysts (Figure 9C).[62] Moreover, a wet-chemical strategy was further used to synthesize ultralong Pt-on-Pd bimetallic dendritic NWs with nanoporous surfaces, which were used as advanced nanoeletrocatalysts for enhancing MOR (Figure 9D).[63]

Micro/Nanomaterials for Gene Delivery Application

Nanomaterials-based nonviral delivery carriers have attracted great interest because they have good potential for providing great safety during gene or drug therapy. The ability to incorporate drugs or genes into new nanomaterials opens a new era in pharmacotherapy for delivering drugs or genes selectively to tissues or cells for specific biomedical applications.[10] We found that dimethyldioctadecylammonium bromide (DODAB) protected Au NPs not only exhibited better biocompatibility compared with individual DODAB but also could deliver DNA to the HEK 293 cells more efficiently.[64] Particularly, our experimental results showed that the transfection efficiency of DODAB–Au-NPs was 5 times higher than that of DODAB. Later, our investigation showed that nocodazole (NCZ) could be used as a transfection enhancer for DODAB bilayer coated gold NPs to produce about 3-fold transfection efficiency increase on cultured HEK 293T cells measured by flow cytometry than that without any NCZ.[65] Other functional nanomaterials could also been used as delivery carriers for DNA or drug. For instance, cysteamine protected CdTe QDs could conjugate with DNA through complementary electrostatic interaction to form the QD–DNA complexes, which were disrupted by glutathione at intracellular concentrations.[66] We found that the plasmid DNA released from the QD–DNA complexes could retain high transcriptional activity and express the reporter protein after being transfected into HEK 293 cells (Figure 10).

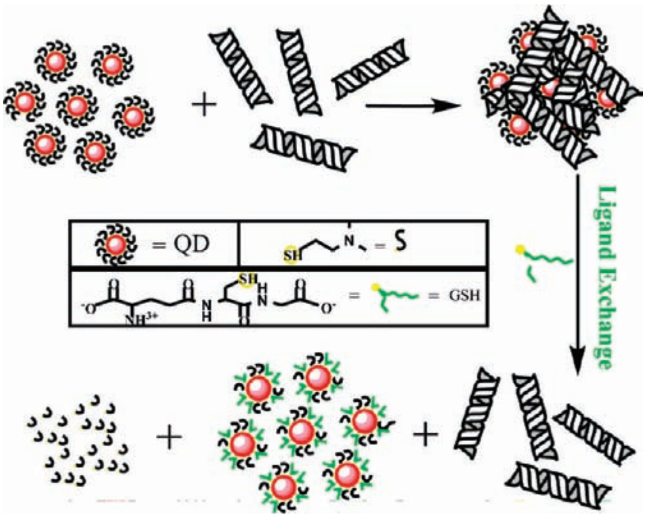


FIGURE 10. Schematic illustration of QD–DNA complex structure and the process of glutathione-mediated DNA release from the complexes.[66]

Conclusion and Outlook

In this Account, we have summarized our recent achievements on controllable synthesis, analytical sensing, and fuel cell and gene delivery applications of certain MNMs. Many new exciting research contributions are highlighted in order to emphasize the importance of MNMs, which include simple strategies for the synthesis of MNMs with controllable size, shape, composition, hybrid, and architecture, designing new nanocatalysts for constructing high-performance electrochemical sensors and application in the field of fuel cells, new analytical sensing strategies based on MNMs for the detection of different targets, and synthesizing new nanobiomaterials for increasing the transfection efficiency of gene. Despite all the above success, there are, however, several important challenges that remain for efficiently directing the development of functional MNMs. One of the most important challenges is lack of a series of high-throughput production methods for synthesizing high-quality MNMs with controllable size, composition, shape, hybrid, and architecture at low cost. Particularly, it is extremely difficult to directly fabricate highly ordered 1D, 2D, or 3D nanomaterials aligned in a desirable manner, which is very important for applications in electronic and photonic devices. That means that the precise control of size, shape, and morphologies and understanding self-assembly processes of MNMs should be further developed in order to obtain their new or enhanced properties and applications. The requirement of highly active catalysts for fuel cell and electrochemical sensing applications has spurred tremendous interests in transferring from single-component catalysts into mutilmetallic or multicomponent new nanostructures with controlled size, shape, microstructure, and architecture. In particular, for practical applications of shape-controlled mutilmetallic nanocrystals, further reduction in size with retention of their shape will be very necessary and is a great challenge. As for the MNM-based sensing applications, new analytical principles are still highly desirable. In this case, the self-powered and intelligent logic aptasensor[67,68] developed by us may provide new opportunities for extending nanomaterials-based analytical techniques.

BIOGRAPHICAL INFORMATION

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FOOTNOTES

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