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Review

Pt-Based Multimetal Electrocatalysts and Potential Applications: Recent Advancements in the Synthesis of Nanoparticles by Modified Polyol Methods

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Abstract: In our review, we have presented a summary of the research accomplishments of nanostructured multimetal-based electrocatalysts synthesized by modified polyol methods, especially the special case of Pt-based nanoparticles associated with increasing potential applications for batteries, capacitors, and fuel cells. To address the problems raised in serious environmental pollution, disease, health, and energy shortages, we discuss and present an improved polyol process used to synthesize nanoparticles from Pt metal to Pt-based bimetal, and Pt-based multimetal catalysts in the various forms of alloy and shell core nanostructures by practical experience, experimental skills, and the evidences from the designed polyol processes. In their prospects, there are the micro/nanostructured variants of hybrid Pt/nanomaterials, typically such as Pt/ABO_3-type perovskite, Pt/AB_2O_4-type ferrite, Pt/$CoFe_2O_4$, Pt/oxide, or Pt/ceramic by modified polyol processes for the development of electrocatalysis and energy technology. In the future, we suggest that both the polyol and the sol-gel processes of diversity and originality, and with the use of various kinds of water, alcohols, polyols, other solvents, reducing agents, long-term capping and stabilizing agents, and structure- and property-controlling agents, are very effectively used in the controlled synthesis of micro/nanoparticles and micro/nanomaterials. It is understood that at the levels of controlling and modifying molecules, ions, atoms, and nano/microscales, the polyol or sol-gel processes, and their technologies are effectively combined in bottom-up and top-down approaches, as are the simplest synthetic methods of physics, chemistry, and biology from the most common aqueous solutions as well as possible experimental conditions.

Keywords: Pt nanocatalysts; nanoferrites; nanoperovskites; electrocatalysis; alloy and core-shell nanostructures; modified polyol processes; modified sol-gel processes

1. Introduction

At present, fuel cells (FCs), proton exchange membrane fuel cells (PEMFCs), and direct methanol FCs (DMFCs) using excellent Pt electrocatalysts have played an increasing role for engineering, science, technology, and industry [1,2]. An FC provides electricity via the generation of ion carriers by electrocatalysis at the electrodes as well as a positive or negative ion transport mechanism and direction of motion through electrolyte membranes. In many recent years, modified polyol methods have played an important role in the controlled synthesis of various kinds of crystal nanoparticles used as the nanostructured catalysts applied in energy and environment [3–9]. Firstly, we must clarify the very huge need for the systematic study and synthesis of metal, oxide, and alloy nanomaterials by the polyol process, and their enormous applications [10–15]. Secondly, we must make discussion with a typical Pt nanomaterial. As far as we all know, Pt nanomaterials are used in the catalytic layer components of low-temperature FCs associated with the clean H_2 fuel industry, which are the most successful and typical examples of generating clean electric energy and power [16,17]. In addition, clean water (H_2O) and heat are generated in the output end [16,17]. Thirdly, other metal, bimetal, multimetal, oxide, glass, and ceramic-based nanomaterial systems are the same: they have the different industrial applications in solid FCs, which are also very important in various related industries. An FC is a power generation system used to produce electricity using hydrogen fuel with an electrode membrane assembly, which is considered an ion conductor. The electrocatalyst layer involved in the purely so-called standard Pt nanocatalyst, or the special nanocatalyst layer was equivalent relatively to Pt nanocatalyst standard [10–15]. It is explained that their catalytic and electrocatalytic characterizations originated from high surface-to-volume ratio and quantum size [3]. The various types of Pt-based, Pd-based, Pd-free, Pt-free multimetal nanocatalysts have been being studied as promising candidates to replace the standard Pt catalyst because of its very high cost for low temperature FCs. Here, Pt-group metals (PGM) consist of Ru, Rh, Pd, Os, Ir, and Pt, which means that Pt-M bimetal catalysts for FCs can be synthesized by modified polyol methods. It is known that Pt electrocatalysts are widely used for studying hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and oxygen evolution reaction (OER) processes in cyclic voltammogram (CV) cycles. In the key points, ORR/OER and HER/OER of Pt- and Pd-based alloy and core-shell nanoparticles electrocatalysts are crucial in order to improve catalytic materials for low temperature FCs. The most important advantages of Pt-based core-shell nanoparticles are applied for reducing the high cost of FCs, DMFCs, and PEMFCs using Nafion® membranes or the hydrophobic perfluorocarbon backbone of -$(CF_2)_n$-groups and the chains ($–SO_3H$) [1,2]. In various works, Ni-, Co-, and Fe-based oxide micro/nanosized particles with grain and grain boundaries were prepared because they showed high structural durability and stability [18–23]. In particular significance, they can be used as the oxide supports for noble metal and multimetal nanocatalysts. They are very promising candidates for FCs, DMFCs, PEMFCs, and high-temperature solid oxide FCs (SOFCs) as well as batteries and capacitors [1,2]. However, the inexpensive cost and long lifetime of PEMFCs and DMFCs are very importantly required [10–17]. In researchers' successful processes, they have experimentally proved that the achievements of synthesis of metal, bimetal, and oxide nanoparticles by the modified polyol processes with the use of polyols have been achieved [24–59]. The main role of PVP is to cover all the crystal surfaces of the prepared nanoparticles and protect the nanosystems but PVP is also not necessary to use for this purpose [60,61]. Here, Pt-based catalysts were prepared to enhance availability, stability, and durability of DMFCs and PEMFCs [14]. Clearly, Pt-based core-shell catalysts show the most competitive advantages of reducing the high cost of next FCs with significant enhancement of catalytic activity, sensitivity, and selectivity because of synergistic effects between the thick core (metal) and the thin shell (Pt) [27,29,39]. On the basis of the experimental results of catalytic selectivity, stability and stability, the high weight of Pt loading in the catalytic layers by bimetal and multimetal catalysts will be significantly reduced. In the operation of PEMFCs and DMFCs, the high catalytic active surface area [34], i.e., ECSA = $Q_H/0.21 \times L_{Pt}$ of Pt catalyst corresponding to the high current density, i.e., J(V) must be fully achieved in their FCs applications. In the processes, the researchers show that in-expensive Fe-based oxide nanoparticles and microparticles with the new structures of grain and grain boundary were produced in large amounts in the μm range for the electrodes of batteries in energy conversion. As such, they can be used as good supports for noble metal nanoparticles for

DMFC, PEMFC, and SOFC, respectively [18–21]. Low temperature FC converts chemical energy directly by chemical reaction into electricity, which is different from multi-stage conversion from chemical energy to thermal energy, and then from mechanical energy to electrical energy generated by engines, which pollutes the environment seriously and heavily today [11–17]. Essentially, thermal power plants produce electricity by burning fuels such as gasoline, crude oil, diesel, coal, natural gas, and other fossil fuels to produce thermal energy that is converted into mechanical energy by gas or steam turbines and eventually convert to electrical energy. Consequently, the various kinds of by-products from fuel combustion have caused serious environmental pollution from the exhaust gases of heat engines, and diesel engines as well as possible pollution from nuclear energy. In this review, we focus on how the low utilization of Pt- or Pd-based nanocatalyst on inexpensive Fe-, Ni-, and Co-based bimetal and multimetal micro/nanoparticles, as well as oxides and ceramics micro/nanosized particles, can be achieved in various FCs [10–14]. Therefore, the well controlled composition, size, shape, structure, and morphology of Pt- and Pd-based catalysts with the Pt or Pd or Pt- and Pd-based alloy atom-monolayers shells are necessary, which leads to prepare a combination of Pt-based metal, Pt-based bimetal, and multimetal alloys and oxide catalysts in multifunctional electrocatalysis. Briefly, the polyol process and its successful evidences will provide a new, cheap, effective-cost mixture multimetal electrocatalysts for all the various kinds of FCs, DMFCs, and PEMFCs using Pt-based electrocatalysts in catalytic nanomaterials' needs and challenges, respectively.

2. The Use of Pt Nanocatalyst in Low Temperature FCs

In summary, low temperature FCs using the preferred Pt- or Pt-free based electrocatalysts include the typical types as follows. FCs use polymer electrolyte membranes, which are PEFCs or PEMFCs, phosphoric acid fuel cells (PAFCs), carbonate fuel cells (MCFCs), SOFCs using yttria-stabilized zirconia (YSZ) or ABO_3 (A: La; B: Mn, Fe, Co, and Ni) that can be synthesized by the polyol or sol-gel processes [1,2]. A typical PEMFC has bipolar plates, gas diffusion layers, polymer memberanes as Nafion®, and the two electrodes with anode catalyst layers and cathode catalyst layers. On the other hand, in PEMFCs running on H_2/O_2 fuel, chemical reaction of hydrogen and oxygen occurs and produces electricity directly. This is a new, effective, and interesting way of producing electricity. Their principle and operation are illustrated with promisingly potential applications on land, in air, and at sea according to technological convergence (Figure 1).

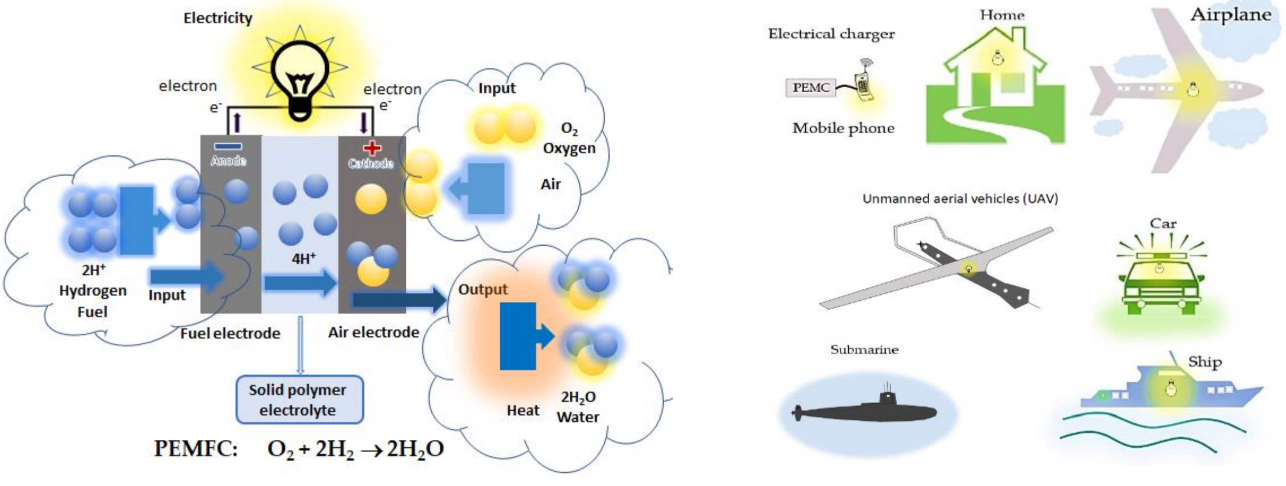


Figure 1. Operation of PEMFCs, and promisingly potential applications for electrical charger in mobile phones, FC cars, FC boats, FC ships, FC airplanes, FC homes and offices, and FC plants in integration with electricity from electric power sources, batteries, and capacitors.

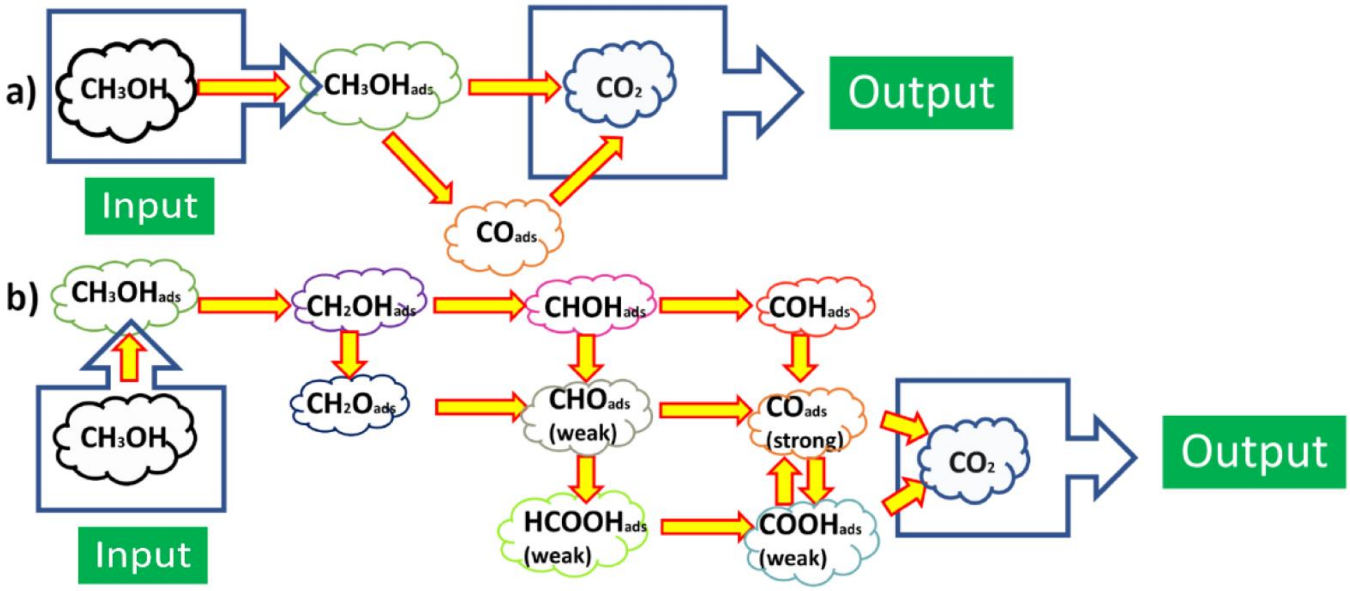
In the operation of PEMFC and DMFC, the catalytic mechanisms of ORR and MOR are the most important keys for their high performance. At the anode catalyst layer,

$2H_2 \rightarrow 4H^+ + 4e^-$, and at the cathode catalyst layer, $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, electricity is generated with clean water and heat via $2H_2 + O_2 \rightarrow 2H_2O$. In its operation, the common appearance of CO-poisoning or catalyst degradation at the catalytic Pt layer reducing PEMFC performance can be reduced by a Pt-based bimetal and multimetal catalyst [10–15]. The operation of PEMFC takes place at low temperature (70~90 °C), and the fuel is hydrogen, with a power generation efficiency of about 30–40% [1]. These PEMFCs can be very suitable for compact power supplies, power chargers used for mobile phones (new generation smart phones), military applications, FC vehicles, and new and future generation FC bicycles and motorcycles [16]. It is known that FC vehicles use 0.4 mg of Pt per square centimetre (mg Pt cm^{-2}), enough for a period of about 6–7 months in their operation or more on the cathode [1]. Clean water and heat are generated as by-products of the process of generating electricity in FC motorcycles, and FC vehicles in the protection of environment and nature. There are various kinds of FCs, classifying into PEMFCs, PAFCs, MCFCs, SOFCs, DMFCs, and AFCs according to their operation principle and ion carriers. The catalytic layers consisting of Pt catalysts are used in both the electrodes listed in Table 1 [1,2,18–21]. The low Pt loading leads to reduce the high cost of the FCs. Therefore, non-noble metal catalysts using the Pt metal group or alternate electrocatalysts free from PMG have been recently developed. In short, the key is the catalytic layers of Pt nanocatalyst for the high-performance operation of FCs using Pt according to working temperatures. The global large-scale commercialization of FCs has high scientific and practical significance, which meets the huge needs of clean energy for our lives. FCs can be potentially used to run various kinds of stationary plants, unmanned aerial vehicles (UAV), large trucks, household power sources, and charge power for portable laptops and mobile phones, which are the typical kinds of PEMFCs [16,17]. Particularly, PEMFCs offer significant energy efficiency and decarbonization benefits to a wide range of industries and technologies—including automotive and heavy transport. This is reason why large companies are investing in mature FC propulsion systems for the aviation market [16,17]. In the future, AFCs may potentially be used for practical applications in submarines and spaceships. By replacing hydrogen with methanol, i.e., CH_3OH, a direct methanol-based liquid FC, i.e., a DMFC, was formed. At present, the hydrogen and methanol production industries are fully developed. In general, the components and operation of a low-temperature FC using hydrogen and liquid fuels, such as alcohol, are based on three main components: the anode, the cathode, and the membrane electrode assembly (MEA) [16]. Table 1 shows the most typical FCs with the use of negative and positive ions for their potential applications in electronics and telecommunications [1,2]. In this context, the Pt catalyst layer is used at both the anode and cathode of a FC. These are the components that use fuel between the two electrodes and the polymer electrolyte membrane or ion conductor. The Pt nanocatalyst layer is the most important kind, and is the most expensive core catalyst layer used on the electrodes. Thus, both researchers and manufacturers want to reduce the cost of the most expensive fuel cell system, i.e., the high cost of Pt catalyst nanomaterial. Therefore, the research and synthesis of Pt-based catalytic nanomaterial systems with low cost and applications for the catalytic layer in electrodes are important for the development of the next FCs. From applications as a source of electricity for smart residential areas, green-energy FCs, and FC trucks to the most compact FC charging applications, FC's operating principle is proven to be relatively simple. It is really simple, but it has great feasibility and commercialization, and has a strong impact and influence on people's lives. The exhaust gas of the FC vehicle is water (H_2O) that is completely harmless to the environment, animals, and people. The basic research on this material system has been fully invested and developed [11–17]. Clearly, batteries, FCs, capacitors, supercapacitors, and their common uses and combination in conventional electricity can evolute energy science and technology in our life. On the other hand, the present technologies to produce oxygen, hydrogen, alcohol, ethanol, and methanol fuels are fully developed. Thus, the current catalytic layers of FCs are described in a combination of electrocatalytic Pt nanomaterials with commercial carbon nanomaterials, acting as an ion conductor, which has a large catalytic area to enhance electrocatalytic efficiency for the Pt-free catalytic material catalysts on their surfaces. The uniform distribution of the Pt nanoparticles on the designed catalytic layer is very essential to obtain the highest catalytic properties. In our current review, Pt-based nanomaterials prepared by improved polyol processes are attractive to prepare electrocatalytic nanomaterials used in FCs using methanol, alcohol, and different liquid fuels. Although the polyol method has been applied recently, Pt and Pt-based electrocatalytic bimetallic nanomaterials, typically such as PtPd, PtCu, PtNi, PtCo, FePt, and binary and ternary Pt-based nanocatalysts fabricated by conventional nanochemistry or the improved polyol methods [11–14], which have produced the electrocatalytic layers that are important for practical application for use in low-temperature FCs, i.e., DMFCs and PEMFCs using methanol or other industrial liquid fuels. The use of a second metal with the precious metal Pt to reduce the cost of FCs in the catalytic layer is a very hard problem predicted by scientists. Instead of using a standard Pt catalyst, it is clear that a Pt_3Ni alloy can be used, wherein the cost will be possibly reduced by about 1/3 to the alloy catalyst layer in the FC system [23]. In the preferred case of using an electrocatalyst as bimetallic shell-core Ni_3Pt nanoparticles, the cost can be significantly reduced around 2/3, which shows the outstanding advantages of core-shell structure with a very thin Pt shell of few atomic monolayers of about 1–3 nm, which is a challenge to science and a new catalyst. The CO-poisoning reducing mechanism on the electrodes containing the nanostructured catalysts has also been introduced by using other metal atoms (second metal atoms) in the preferred Pt-M (M: Ru or Pd) electrocatalysts [13,14], increasing the efficiency and stability of PEMFCs and DMFCs, and reducing the very high cost of the whole system of FCs. Due to crises and disasters from atomic energy sources in nuclear power plants, deadly heavy pollution generated from fuel combustion processes in heat engines, internal combustion engines from petroleum-based energy sources, coal fossils, the generation of greenhouse gases such as CO_2, CH_4, N_2O, O_3, chlorofluorocarbons (CFCs), or refrigerants, we have to develop new energy sources that do not pollute the environment in developed countries, and especially in developing countries [16,17]. To meet the large demand for clean and safe energy, it is very necessary to develop single metal, bimetallic, and multimetal alloy nanomaterial systems based on the various types of single-metal Pt nanoparticles, and combine these with carbon nanomaterials for FC applications. On this topic, the particle size of Pt nanoparticles should be controlled in the range of 10 nm in size for a high quantum effect. Scientists have proposed various methods of chemical synthesis for Pt catalyst materials. The resolution allows using low Pt material as a cost-effective way of creating the electronic catalyst layer in the electrodes of FCs, PEMFCs, and DMFCs, reducing the total cost of the system by about 30–40%, and shows high economic significance [1,2,16,17]. It is found that the practical application of fuel cell use is the practice of providing clean energy as well as taking advantage of clean energy sources from solar cells, biomass energy, ocean energy such as tidal energy, solar energy, ocean wave energy, and wind energy, are very meaningful in terms of clean and green living environment when fossil energy sources are gradually depleted as well as polluting environment. For PEMFCs, their electrodes normally consist of anode and cathode containing an electrocatalytic layer with the required Pt-based nanocatalyst, the principle of operation is mainly based on the electrochemical reactions on the electrode surfaces.

Table 1. FCs, working temperature, and their catalytic mechanisms at two electrodes, both anode and cathode. In addition to the use of Pt catalyst, FCs of high costs must be decreased in the optimization of whole systems and components. Pt-based catalysts or alternative catalysts can be used in both the anode and the cathode of PEMFC, DMFC, and PAFC.

FCs	Input/Output	Anode	Electrolyte	Ion	Cathode
PEMFC WT: 60–120 °C H^+ transport	In: H_2, O_2 (Air) Out: H_2O, heat, extra gases	$H_2 \rightarrow 2H^+ + 2e^-$ Pt catalyst	Membrane $H^+ \rightarrow$ Membrane $\rightarrow$ Cathode	H^+	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$; Pt catalyst; Air as oxidant
DMFC WT: 60–120 °C H^+ transport	In: CH_3OH, O_2 (Air) Out: CO_2, H_2O, heat, extra gases	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ Pt catalyst	Membrane $H^+ \rightarrow$ Membrane $\rightarrow$ Cathode	H^+	$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$; Pt catalyst; Air as oxidant
AFC WT < 100 °C OH^- transport	In: H_2, O_2 (Air) Out: H_2O	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$ Electrode material	KOH Anode $\leftarrow$ KOH $\leftarrow$ OH^-	OH^-	$1/2O_2 + 2H_2O + 2e^- \rightarrow 2OH^-$ Electrode material
PAFC WT: 160–220 °C H^+ transport	In: H_2, O_2 (Air) Out: H_2O, heat, extra gases	$H_2 \rightarrow 2H^+ + 2e^-$ Pt catalyst	H_3PO_4 $H^+ \rightarrow H_3PO_4 \rightarrow$ Cathode	H^+	$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$; Pt catalyst; Air as oxidant
MCFC WT: 600–800 °C ${CO_3}^{2-}$ transport	In: CH_x, CO, H_2 Out: H_2O, heat, extra gases	$H_2 + {CO_3}^{2-} \rightarrow 2H_2O + 2e^-$ Electrode material	Molten carbonate Anode $\leftarrow$ Molten carbonate $\leftarrow$ ${CO_3}^{2-}$	${CO_3}^{2-}$	$1/2O_2 + CO_2 + 2e^- \rightarrow {CO_3}^{2-}$; Electrode material; Air as oxidant
SOFC WT: 800–1000 °C O^{2-} transport	In: CH_x, CO, H_2 Out: H_2O, heat, extra gases	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$ Electrode material	Ceramics Anode $\leftarrow$ Ceramics $\leftarrow O^{2-}$	O^{2-}	$1/2O_2 + 2e^- \rightarrow O^{-2}$ Electrode material; Air as oxidant
DCFC WT: 500–1000 °C O^{2-} transport	In: Carbon, CO Out: CO, CO_2, heat, extra gases	$C + 2{CO_3}^{2-} \rightarrow 3CO_2 + 4e^-$ Electrode material	Ceramics Anode $\leftarrow$ Ceramics $\leftarrow O^{2-}$	O^{2-}	$C + CO_2 \rightarrow 2CO$ Electrode material; Air as oxidant

For the use of hydrogen fuel, ORR at the cathode: $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$, hydrogen oxidation reaction (HOR) at the anode: $H_2 \rightarrow 2H^+ + 2e^-$, and the whole reaction of PEMFC using H_2: $1/2O_2 + H_2 \rightarrow H_2O$ or $O_2 + 2H_2 \rightarrow 2H_2O$. For DMFCs, under the effect of electronic catalytic layer on the basis of Pt electrocatalyst on the electrodes, the principle of its operation is based on the chemical reaction on the electrode surface. In acidic solutions, the catalytic processes and mechanisms occurred at the electrode surface of the Pt-based electrocatalysts exhibiting the seven specific regions of HOR and ORR in CVs in the kinetics of electrochemical reactions [1,2,33,34]: (1) $Pt - H_{ads} \rightarrow Pt + H^+ + e^-$; (2) $Q_{DL}(Charge) \leftrightarrow Q_{DL}(Discharge)$; (3) $Pt + H_2O \rightarrow Pt - OH + H^+ + e^-$; (4) $PtOH + H_2O \rightarrow Pt(OH)_2 + H^+ + e^-$; (5) $Pt - (OH)_2 \rightarrow PtO + H_2O$; (6) $2PtO + 4H^+ + 4e^- \rightarrow Pt - Pt + 2H_2O$; (7) $Pt + H^+ + e^- \rightarrow Pt - H_{ads}$. For methanol fuel, ORR at the cathode as $3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$, methanol oxidation reaction (MOR) at the anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$, and the whole reaction of DMFC as $CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$. [33,34]. In the most effective MOR in acidic solutions, researchers show that electrocatalytic activity of Pt catalysts to methanol oxidation occurs at (111), (110), (100) and (hkl) low-index crystal planes of Pt nanoparticles as follows: (1) $Pt + CH_3OH \rightarrow Pt-(COH)_{ads} + 3H^+ + 3e^-$; (2) $Pt - (COH)_{ads} + H_2O \rightarrow Pt + CO_2 + 3H^+ + 3e^-$. The catalytic mechanisms of both ORR and MOR are also presented in Scheme 1, which only leads to show CH_3OH oxidation into CO_2 experimentally. In recent years, PtRu-based electrocatalytic bimetal nanomaterials have been studied in the effective reduction of CO poisoning by Ru according to bifunctional catalytic mechanism, i.e., $Ru + H_2O \rightarrow Ru - OH + H^+ + e^-$, and $Ru - OH + Pt - CO \rightarrow Pt + Ru + CO_2 + H^+ + e^-$. However, the cost of Pd and Ru is relatively high to PtRu electrocatalyst. We need to select other inexpensive, non-noble, non-rare metals, such as Au, Ag, Cu, Fe, Co, Ni, Sn, Mo, Pb, W, etc., rather than Pt metal group (PMG) bimetal catalysts, such as PtPd, PtRh, PtRu, PtIr, PtOs [11–13]. There have been published works related to the synthesis of single metal Pt and bimetallic Pt-based nanomaterial catalysts so that they are elements of PMG, such as Ru, Rh, Pd, Ir, and Os, but their cost is high There are also Pts with another inexpensive metals, such as Cu, Ni, Co, and Fe, and their Pt-based or Pt-free multi-component, alloy, multimetal electrocatalysts by improved polyol processes with a strong reducing agent ($NaBH_4$ or KBH_4) [13] or other strong reducing solid compounds (CaH_2) or reducing gases (H_2) in heat treatment [59]. In future, the application of the improved polyol method is suitable for all the popular laboratories. This is a chemical process popular in laboratory that can be easily applied to create electrocatalytic Pt-based nanomaterials, which is a very necessary composite material in the electrocatalytic layers of PEMFCs and DMFCs today, with increasingly scientific and practical significance. Therefore, the polyol process is one of the focuses discussed in order to address the synthesis of single metal, bimetal, and multimetal nanoparticles, especially for shell-core bimetallic nanostructures. In the synthesis of metal, oxide, and alloy nanostructures, especially instead of using inexpensive precious metals, bimetallic alloys, multimetal alloys, or multi-component materials for catalyst of FCs, and magnetic nanoparticles for practical applications in medicine and biology, issues of size, shape, structure and composition are of great importance. Therefore, these parameters must be studied and controlled. In order to confirm that Pt-based nanocatalyst materials can be applied to FCs (PEMFCs and DMFCs), such nanomaterials must be intensively studied for the electrochemical properties of the used catalytic materials on the surfaces of the electrodes. The important electrochemical reactions of using oxygen, methanol, ethanol, or other fuels are ORR, MOR, and ethanol oxidation reaction (EOR) [10–14]. It is certain that Pt-based catalysts are used in the anode and cathode of low-temperature fuel cell systems. For catalytic applications, other nanoparticles (Au, Ag, Cu, and their related oxides), iron oxide particles (iron and their compounds), spinel oxide particles, and ABO_3-type perovskite oxide particles could potentially be used in the future [1,2,11–17]. In addition, multi-component, multi-metallic particle catalysts, or functional catalytic oxide particles need to be studied with regard to their practical applications and commercialized products [16]. Scientific research methodology and theoretical and experimental research methods of other nanomaterials are applied as for the special case of Pt nanoparticle materials. The polyol method is a good solution for the comprehensive fabrication of platinum nanoparticles. Over the past ten years, there have been the intensive studies on the successful synthesis of Pt-based catalysts by polyol method by researchers in laboratories which have been presented, reported and published. Therefore, it is believed that the nanomaterials capable of replacing Pt catalysts, such as bimetal catalysts, i.e., PtCu, PtAg, PtAu, PtFe, PtNi, PtCo, and other catalytic alloys that are much cheaper in order to replace expensive Pt that can be used for applications of low-temperature FCs [13]. The two kinds of FePt and CoPt magnetic nanomaterials have been also used in hard disk drives. The deep discussion of research results on the successful synthesis of Pt nanoparticles by nanochemistry has been carried out on published works, typically for modified polyol methods or nanochemistry [3–9]. It is known that Pt nanoparticles have been successfully fabricated by the chemical methods. Given the scientific implications of current research on Pt nanoparticles, precious metals, inexpensive metals, oxide materials, and alloys nanoparticles are very necessary to be mainly focused on their structures and properties. Up to the present time in 2021, Pt nanoparticles, and Pt-based shell-core nanoparticles have been applied in energy technologies, typically such as FC technology, allowing the fabrication of creating mobile phones, transport vehicles, and clean energy sources for households in remote places. Many energy projects have mainly focused on Pt nanomaterials as well as PGM-free catalysts and alternative electrocatalysts [1,2,16,17]. In a number of present studies, it is possible to synthesize Pt nanoparticles in the range of 10 nm, and Pt-based bimetallic nanoparticles in the range of 30 nm or up to hundreds of nm in size. Thus, the successful synthesis of metal, bimetal, and multimetal nanoparticles has very high scientific and practical significance for potential application in new technologies of electronic catalysis, photocatalysis, energy, medicine, and biology [45,46]. At present, a large number of Pt single-metal nanostructures are also researched and developed by chemical methods. Through the polyol process, scientists have successfully fabricated Pt simple-metal nanoparticles for catalysis, but Cu, Au, and Ag nanoparticles are commonly applied in medicine and biology [2–4]. Accordingly, the research results have only focused on Au and Ag nanoparticles by modified polyol methods for medical and biological applications. It is obvious that the more complex Pt-based metal nanostructures, typically such as bimetallic and multi-component nanoparticles with alloy or mixing structures, Pt bimetallic shell-core nanostructures, and multi-component nanostructures by modified polyol methods, have not been researched yet, due to the use of much more complex synthesis technologies [14,15]. The catalytic mechanisms and oxidation of methanol by the crystal planes of Pt nanoparticles were revealed in acid and alkaline electrolyte, changing methanol in to CO_2 [15]. Thus, the successful synthesis of Pt-based core-shell nanoparticles with Pt shells of 1–10 nm in new promising properties will open up new and excellent applications that are not available to single-metal nanostructures. Therefore, the as-prepared Pt nanostructures and Pt-based core-shell nanostructures are of particular interest because of their very high practical importance. The main reason is that metal, bimetal, and alloy nanoparticles are potentially used to provide a large extent, and have a wide range in interdisciplinary sciences, typically such as physics, chemistry, electronics, biomedicine, pharmaceuticals, optics-photonics, and catalysis. Typically, Pt-Pd core-shell nanostructures are also nanomaterials that exhibit their outstanding properties. The synergistic properties can be discovered from the Pt shell catalytic property, from the core property, or generated from the co-electrocatalytic properties of both the core and the shell when the Pt-based core and shell nanoparticles are the different catalytic nanomaterials. By changing the shape, structure, size, and composition of the metal core or shell, the electrocatalytic properties of Pt-Pd core-shell nanostructure system can be well controlled. The atom-monolayers shell is an alloy of Pt with another element that also reduces the high cost of the FC system, typically such as Pt_3Co, Pt_3Ni, Pt_3Fe, and Pt_3Cu [22]. This means that the price of the Pt catalyst material layer has been reduced by one-third compared with only Pt-based nanostructured catalysts. On that basis, the core-shell nanostructures of the different types of Pt atom-monolayers shells can be studied and developed by physical and chemical methods, such as modified polyol methods. For example, expensive metallic nanoparticles (typically such as Au, and critical elements, such as Pt) are used in order to coat with inexpensive nanoparticles (such as Co, Cu, Ni, Fe etc), leading to the amount of Pt being greatly reduced, but the electrocatalytic properties of the Pt-based catalytic nanoparticles are not less, or even much better. To confirm the catalytic activity of Pt catalyst in the CV cycles, the HER involved in the (111), (100), (111) crystal planes, and other crystal planes of the pure Pt catalyst followed the key reactions of Volmer, Tafel, and Heyrovsky that must be clearly measured as follows. It is simply emphasized that the electrocatalytic properties of Pt catalyst in acid solution are $\mathrm{Pt} - \mathrm{H}_{\mathrm{ads}} \rightarrow \mathrm{Pt} + \mathrm{H}^{+} + \mathrm{e}^{-}$ (the region is characterized by double–layer charging and discharging), $\mathrm{Q}_{\mathrm{DL}}(\mathrm{Charge}) \leftrightarrow \mathrm{Q}_{\mathrm{DL}}(\mathrm{Discharge})$, $\mathrm{Pt} + \mathrm{H_2O} \rightarrow \mathrm{Pt} - \mathrm{OH} + \mathrm{H}^{+} + \mathrm{e}^{-}$, $\mathrm{PtOH} + \mathrm{H_2O} \rightarrow \mathrm{Pt(OH)_2} + \mathrm{H}^{+} + \mathrm{e}^{-}$, $\mathrm{Pt} - (\mathrm{OH})_2 \rightarrow \mathrm{PtO} + \mathrm{H_2O}$, $\mathrm{2PtO} + \mathrm{4H}^{+} + \mathrm{4e}^{-} \rightarrow \mathrm{Pt} - \mathrm{Pt} + \mathrm{2H_2O}$, and $\mathrm{Pt} + \mathrm{H}^{+} + \mathrm{e}^{-} \rightarrow \mathrm{Pt} - \mathrm{H}_{\mathrm{ads}}$, respectively [32,33]. During the catalytic mechanisms and processes, it is confirmed that the Pt catalyst has shown the two peaks of catalytic activity of CH_3OH electrooxidation in the CV cycles. Above all, the selectivity, durability, stability, and catalytic activity of multimetal Pt electrocatalysts should need to be certainly verified by a very large number of the CV cycles in order to address the applications of FCs. The high electrochemically active surface area of Pt nanocatalysts, the relationship of high current density vs voltage, the chronoamperometric measurement, or that of current density vs time for a long time must be clearly measured in order to prove in the detail. Similarly, Pt-based multimetal, alloy, and core-shell multimetal nanoparticles need to be intensively confirmed in their high and stable electrocatalytic activity, enough for the applications of FCs.



Scheme 1. Oxidation of methanol in to CO_2. (**a**) Simple mechanism. (**b**) Proposed mechanism.

In this context, it is certain that Pt-based multimetal catalysts are promising candidates for electrodes, which significantly reduces the high cost of Pt standard catalysts. It is important that the standard electrolyte solutions for CV measurements to the survey of catalytic activities of Pt-based catalysts are 0.5 M H_2SO_4 or 0.1 M $HClO_4$, 1.0 M CH_3OH, etc., (Figure 2) [32,33]. Their systematic comparison of catalytic activity of between standard Pt nanocatalysts and Pt-based multimetal nanocatalysts will lead to finding an inexpensive, effective, and highly active catalyst for PEMFC and DMFC [10–14]. A wide variety of Pt core-shell nanoparticles can be synthesized by modified polyol methods from inorganic core nanoparticles with thin Pt shells on their defined nanostructured cores. Depending on the properties of the as-prepared nanoparticles fabricated by different methods, nanoparticles of core-shell nanostructures are definitely classified into several types, including inorganic-inorganic shell-core nanostructures, organic-inorganic shell-core nanostructures, and shell-core nanostructures (organic shell-organic core nanoparticles for the pharmaceutical-medical industry) [10–14]. Moreover, the core-shell (inorganic-inorganic) nanostructure is one of the most important nanostructures because it shows great practical applicability that leads to the synthesis of multimetal core-shell and alloy nanoparticles. This capability allows optimal and thorough exploitation of the superior properties of nanostructures in various applications such as catalysis, biomedicine (MRI imaging agent in cancer therapy), and nanomagnetism (hard drives using Fe-Pt and Co-Pt nanomaterials) [47]. The chemical synthesis of multimetal nanomaterials mainly focuses on new research and fabrication technologies that allow the size and shape of the fabricated nanoparticles to be controlled. Therefore, in addition to performing basic studies, the research results of nanochemistry will be very meaningful in practice through the creation of new generations of catalytic nanoparticles by modified polyol methods with promising applications. In particular, the synthesis of metal or bimetallic nanostructures with sizes in the sized ranges of 10 nm, 100 nm, and 1000 nm is of great significance in the field of catalysis and aims to apply for FCs [13,14]. Specifically, Pt-based bimetallic, Pt-based multi-metallic alloy, or Pt-based core-shell nanostructures are structures of durability and stability with multifunctional new applications. These Pt-based bimetal metal and multi-metal nanoparticle alloy nanostructures and shell core nanostructures in relation to the cheap metal and multimetal cores, the thin Pt or Pd shells are the types currently being researched by the leading research research groups and incorporations. Scientists intensively focus on fabrication research and explore the electrocatalytic properties of new next-generation Pt-based nanomaterials by modified polyol methods. In this respect, recently, a group of authors has researched and devised a new synthesis process, initially successfully fabricating a bimetallic shell core structure [27,29,39]. The thickness of the shell is several nm, consisting of monolayers of Pd or Pt atoms. The main results of our research groups have shown that it is necessary to continue researching and mastering the synthetic technology of nanoparticles with desirable crystal structures systematically, and with high repeatability of new metal nanoparticles, bimetallic alloy particles, and multi-component alloy particles. The designed nanoparticle has a novel structure such as core-shell configuration, or Pt-based alloy configuration with a reduction in the amount of Pt-catalyst loading used on the electrodes [27,29,39]. Then, thee are applications for alloy-structured and core-shell-structured nanoparticles, as well as magnetic alloy and oxide nanoparticles, in catalysis for chemical production, catalysis, FCs, capacitors, and batteries for energy and environment, drug carriers, and markers in biomedicine in the integration of technologies. In the polyol process, the fabrication of metal- and Pt-based metal, bimetallic, multimetal, and multicomponent nanoparticles to bring about applications in catalysis, medicine, and biology [10,46,47], there are four major problems that need to be solved, which are the characteristics of the size, shape, structure, and composition of the nanostructures. Thus, an important focus of the researchers is the need to develop various kinds of nanocatalysts by modified polyol methods with strong catalytic activity and high strength and stability on the basis of Pt. The key of nanoelectronic catalysis technology applied in PEMFC and DMFC is the polyol process to produce catalytic Pt nanoparticles. On the basis of investigating the pure Pt nanoparticles (single metal particle and its application) leading to Pt-based multimetal alloy and core-shell nanoparticles, it has been seen that the great power of the application of the ultra-narrow size Pt nanoparticle less than 10 nm is very large, and has high value in science. Other types of multimetal nanoparticles replacing of Pt nanoparticles can also be synthesized and fabricated by chemical polyol processes, and also have other special applications in many key areas. Multimetal alloy and core-shell nanocatalysts are also studied for similar applications to the various structural kinds of Pt nanomaterials; when using each expensive metal or cheap metal, their application range will expand. The high cost of the Pt catalyst layer on the two electrodes of low temperature FCs will be significantly reduced.

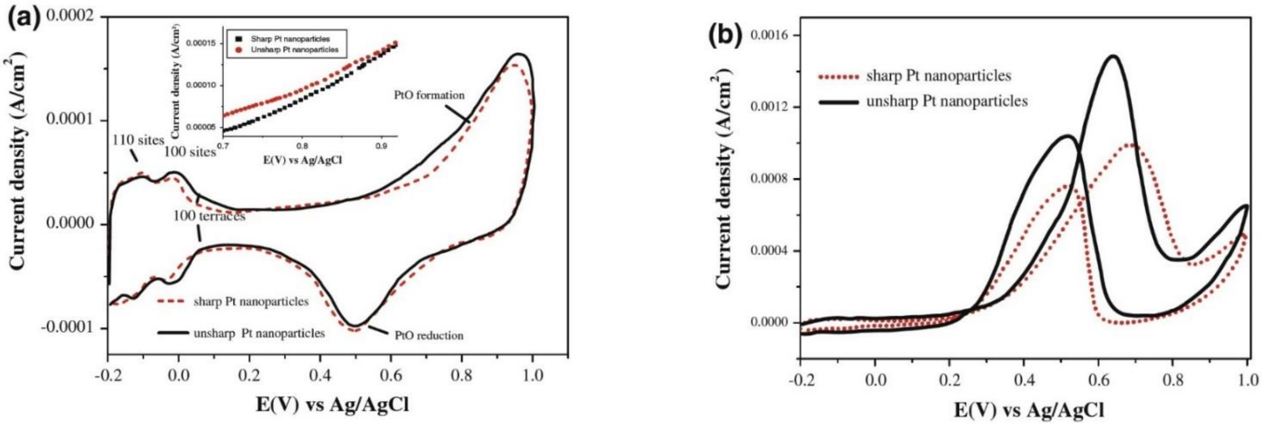


Figure 2. (**a**) Cyclic voltammogram of Pt nanoparticles in electrolyte solution of 0.1 M $HClO_4$ (scan rate: 50 mV/s, N_2 bubbling time: 30 min). (**b**) Cyclic voltammogram of Pt nanoparticles the solution of 0.1 M $HClO_4$ and 1 M CH_3OH (scan rate: 50 mV/s, N_2 bubbling for 30 min prior to catalytic measurement [33]).

3. Synthesis of Pt- or Pd-Based Multimetal Nanoparticles by Modified Polyol Methods

The polyol process begins in the reaction flask, where metal nanoparticles are produced through reduction reaction of metal precursors by water, alcohol or/and polyol, or a mixture of water/alcohol or water/polyol in the protection of polymers or copolymers with the additions of controlling-structure agents according to the stages under mixing and stirring the homogeneous mixture continuously at the various speeds [3,4]. As such, the size, the shape, the morphology, the structure, the composition, and all the related properties of nanoparticles are driven through a modified polyol process [3–10].

To synthesize single-metal nanoparticles effectively for catalysis, it is necessary to use the synthetic reaction equations in solvents such as ethylene glycol (EG) and polyEG (PEG). Simply, the various nanoparticles can be effectively synthesized in the flask in water, alcohol, or EG (or various polyols) with PVP (or protective agents and controlling agents) according to time and temperature. To synthesize Au nanoparticles by modified polyol methods, experimenter needs to control the following reaction carefully in a detailed process (Figure 3a–c). Both EG and PEG solvents are effectively used in all of the synthetic processes because of their availability as clearly shown in our polyol process and experimental design [24–59]. It is a fact that $HO-CH_2-CH_2-OH \rightarrow CH_3-CHO+H_2O$; $6(CH_3-CHO)+2HAuCl_4 \rightarrow 3(CH_3-CO-CO-CH_3)+2Au^{(0)}+8HCl$ (the crystal formation of Au nanoparticles) [42]. Similarly, Ru nanoparticles can be synthesized by modified polyol methods. It is a fact that $HO-CH_2-CH_2-OH \rightarrow CH_3-CHO+H_2O$; $6(CH_3-CHO)+2RuCl_3 \rightarrow 3(CH_3-CO-CO-CH_3)+2Ru^{(0)}+6HCl$ (the crystal formation of Ru nanoparticles). Here, Pt nanoparticles with the most typical crystal structures can be synthesized by modified polyol methods. In many cases, the small content of $AgNO_3$ is added to be a structure-controlling agent to control the size and the shape in the crystal formation of Pt nanostructures at about 160 °C [24–28].

With the mentioned polyol process, researchers can put their ideas into nanoparticles with desirable sizes and shapes in nanochemistry. It is a fact that $HO-CH_2-CH_2-OH \rightarrow CH_3-CHO+H_2O$; $6(CH_3-CHO)+2H_2PtCl_6 \rightarrow 3(CH_3-CO-CO-CH_3)+2Pt^{(0)}+6HCl$ (the crystal formation of Pt nanoparticles) [26]. Similarly, Pd nanoparticles can be synthesized by modified polyol methods. It is a fact that $PdCl_2+CH_3CH_2OH \rightarrow Pd^{(0)}+CH_3-CHO+2HCl$; $H_2PdCl_4+C_2H_5OH \rightarrow Pd+CH_3CHO+4HCl$; $HO-CH_2-CH_2-OH \rightarrow CH_3-CHO+H_2O$; $6(CH_3-CHO)+3Na_2PdCl_4 \rightarrow 3(CH_3-CO-CO-CH_3)+3Pd^{(0)}+6NaCl+6HCl$; $PdCl_2+Na_2CO_3+2H_2O \rightarrow Pd(OH)_2+H_2CO_3+2Na^{+}+2Cl^{-}$; $Pt(OH)_2+H_2 \rightarrow Pd+2H_2O$ (the crystal formation of Pd nanoparticles) [23]. Therefore, the polyol process is a very efficient way to synthesize PGM or PGM-free catalysts. The problem is which researchers can apply it empirically in future research. In a similar way, Rh nanoparticles can be simply synthesized by modified polyol methods. It is a fact that $HO-CH_2-CH_2-OH \rightarrow CH_3-CHO+H_2O$; and $6(CH_3-CHO)+2RhCl_3 \rightarrow 3(CH_3-CO-CO-CH_3)+2Rh^{(0)}+6HCl$; $2RhCl_3+3CH_3OH \rightarrow 2Rh+3HCHO+6HCl$ (the crystal formation of Rh nanoparticles) [28]. In a similar way, Cu nanoparticles can be simply synthesized by modified polyol methods. It is a fact that $HO-CH_2-CH_2-OH \rightarrow CH_3-CHO+H_2O$, and then $4(CH_3-CHO)+2CuCl_2 \rightarrow 2(CH_3-CO-CO-CH_3)+2Cu^{(0)}+4HCl$ (the crystal formation of Cu nanoparticles) [41].

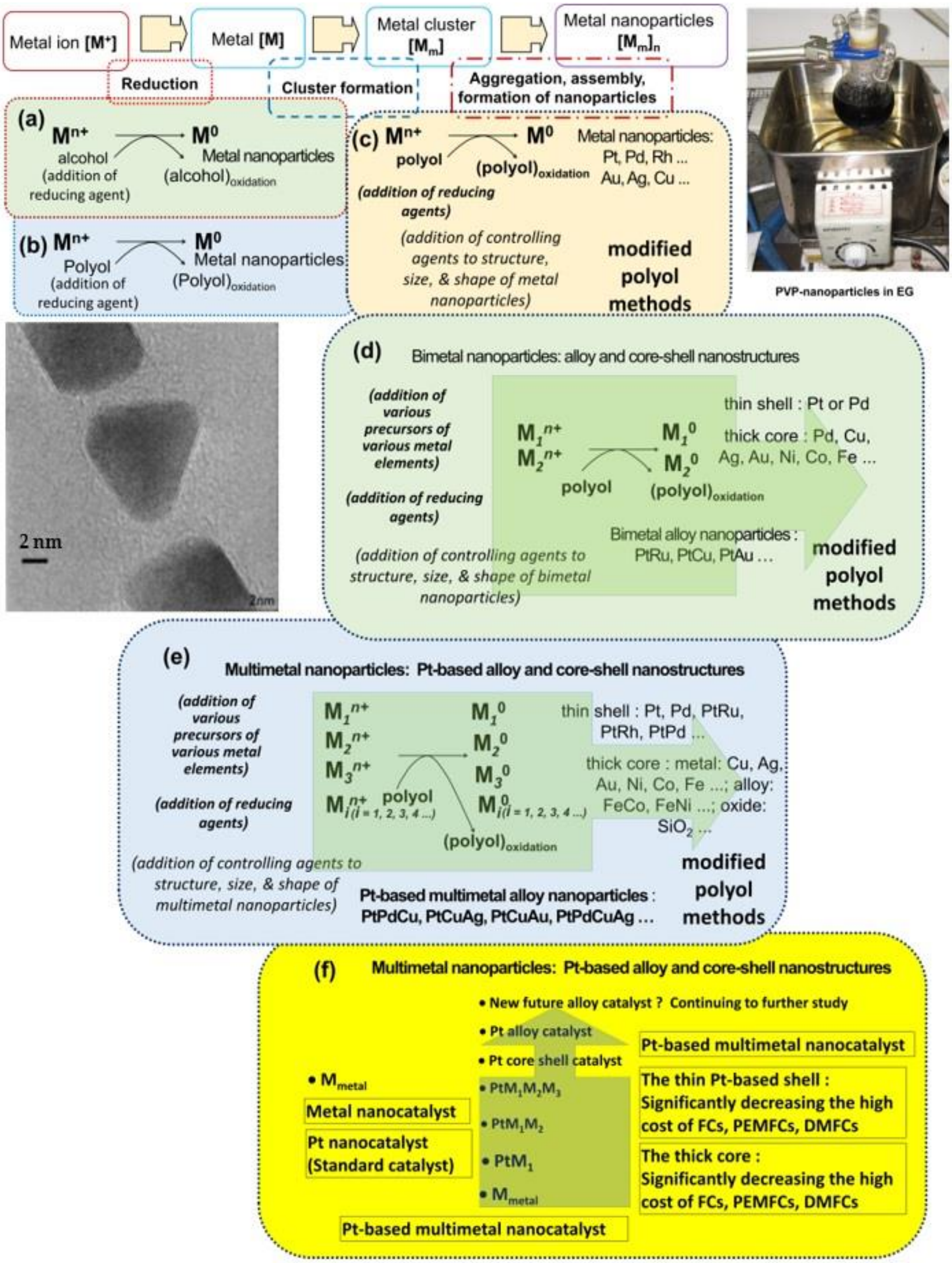


Figure 3. To prepare new multimetal electrocatalysts successfully, we must successfully synthesize single-metal catalysts in a controlled polyol process. The formation and mechanism of crystal structures of metal, bimetal, multimetal alloy and core-shell nanoparticles must be intensively discussed in the detail. The stepwise strategies of modified polyol methods are used in order to fabricate Pt-based multimetal alloy and core-shell nanostructures with the thin Pt shells. (**a**–**f**) Synthesis of metal, bimetal, and multimetal nanoparticles in the special flasks of alcohols, polyols, i.e., EG or PEG by modified polyol methods. High resolution TEM image of Pt nanoparticles from [26].

The successful synthesis of various types of the Pt, Pd, Cu, Ag, Au, and single metal nanoparticles by modified polyol methods has become very important, especially leading to the as-prepared precious Pt nanoparticles, leading to Pt nanocatalysts, which leads to the alloying ability of the above species, and leads to the diversity of their Pt-based nanostructures, leading to the creation of Pt-based multimetal alloy and core-shell catalysts (Figures 3 and 4). Thus, we only need to use the smallest weight of Pt (low Pt loading) for designed core-shell multimetal catalysts for the catalytic layers of low-temperature FCs [14]. It is known that acetaldehyde (CH_3CHO) is the mediated agent for the formation of metal nanoparticles by reduction of the metal precursors. The additions of small contents of the structure-property-controlling agents or the addition of various reducing agents, such as H_2, $NaBH_4$ have led to modified polyol methods for over 30 years (Figures 3 and 4, and Scheme 2) [3–13,24–59]. A highly experienced experimenter can easily and quickly create nanosystems with a uniform distribution of particle size. It is known that the typical simultaneous reduction of two precursors in EG or PEG in existence of protective agent can lead to forming their alloy nanoparticles. The typical successive reduction two metal precursors in EG or PEG can also lead to forming their core-shell nanoparticles with the very thin shell as follows. In fact, it typically shows $6(CH_3 - CHO) + 2H_2PtCl_6 + 6(CH_3 - CHO) + 3Na_2PdCl_4 \rightarrow 3(CH_3 - CO - CO - CH_3) + 2Pt^{(0)} + 6HCl + 3(CH_3 - CO - CO - CH_3) + 3Pd^{(0)} + 6NaCl + 6HCl$ (the crystal formation of Pt-Pd alloy nanoparticles in simultaneous reduction) [21,27,31,39]. To make core-shell nanoparticles for economic purposes, and to reduce the high cost of PEMFC and DMFC, we can make a thin shell of Pd or Pt as follows. First, we can use a typical chemical reaction, such as $6(CH_3 - CHO) + 3Na_2PdCl_4 \rightarrow 3(CH_3 - CO - CO - CH_3) + 3Pd^{(0)} + 6NaCl + 6HCl$ to make the core. Then, we can use a typical chemical reaction: $6(CH_3 - CHO) + 2H_2PtCl_6 \rightarrow 3(CH_3 - CO - CO - CH_3) + 2Pt^{(0)} + 6HCl$ to make the shell. Finally, we synthesized Pt-Pd core-shell nanoparticles with thin Pt shells. The fabrication of homogeneous nanoparticles used as the defined thick cores for the formation of the atomic monolayers shells must be experimentally based on the foundation of chemical synthesis. It is supposed that the large nanoparticles were formed by the assembly of a certain number of smaller nanoparticles. It is clearly evidenced that the assembly of Pt or Pd nanoparticles was clearly presented in the nucleation, growth, and formation of the larger particles, respectively [29,34]. In the reverse order, we can make Pd-Pt core-shell with a thin Pd shell. Therefore, inexpensive or common metals can be potentially used with very thin shells of the Pt group. The Pt-monolayer shells can be made to be a few nanometers thick at the atomic level. The one atomic monolayer is a very big challenge to scientists in nanochemistry or nanophysics. In this complex subject, this is a general principle to synthesize effectively bimetal and multimetal nanoparticles as electrocatalysts that are widely used for catalytic chemical reactions or synthesis of various kinds of new chemical compounds. This leads to the effective synthesis of multimetal electrocatalysts without much difficulty for FCs, PEMFCs, and DMFCs in H_2-based FC technology as well as our urgent energy challenges and demands.

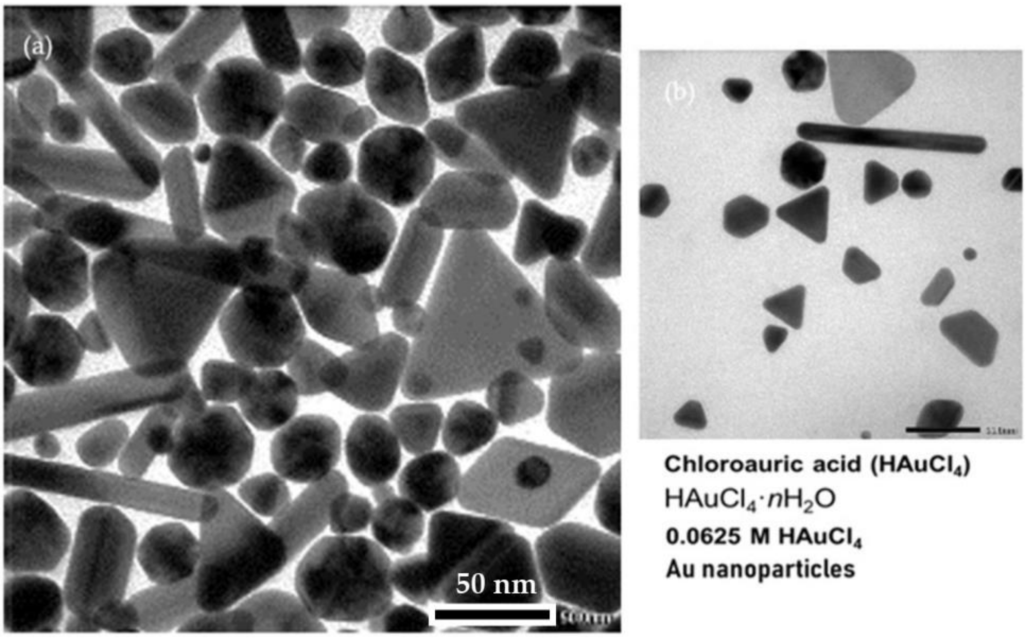
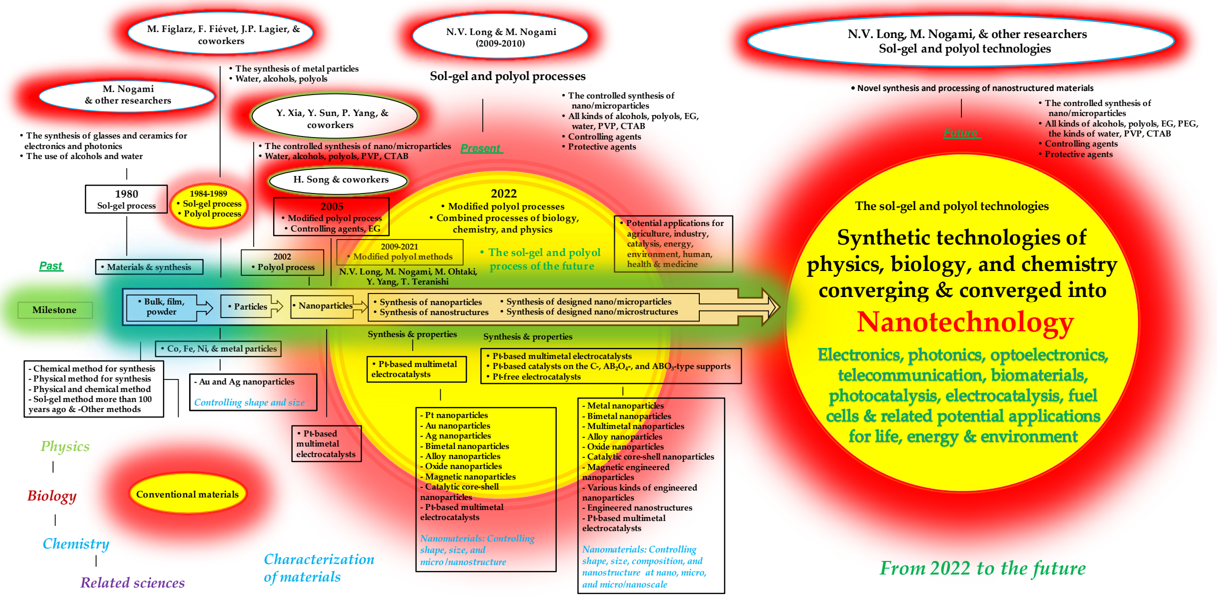


Figure 4. TEM images of Au nanoparticles by modified polyol methods [41]. (**a**) There are the different ranges of the sizes and the shapes of Au nanoparticles synthesized by a simple polyol process. (**b**) The rods, spherical and polyhedral shapes are observed. Scale bars: 50 nm.



Scheme 2. The polyol process over 30 years. See more: Synthesis of Pt-free or Pt-based electrocatalysts in Figure 3. The combined polyol and sol-gel processes are new, improved, modified, highly efficient, and easy to apply.

4. Development of Pt- or Pd-Based Bimetal and Multimetal Catalysts

Recently, researchers have presented key research discoveries of the synthesis of noble metal, bimetal, and alloy particles [11–14], especially for the case of Pt nanoparticles. Through modified chemical polyol methods, shaping expensive (Au, Ag, Pt, Pd, etc.) and cheap (Fe, Co, Ni, Cu, etc.) metal nanoparticles has been simply realized, i.e., nanosystems for electrocatalysis in FCs, and studies of surface plasmon resonance (SPR), surface-enhanced Raman scattering (SER), and tip-enhanced Raman scattering. In order to synthesize Pt nanoparticles effectively, PVP protected polyhedral Pt nanoparticles were synthesized by the reduction of H_2PtCl_6 in EG using $AgNO_3$ as a structure-controlling agent at 160 °C. The uniform size and morphology of the spherical and polyhedral Pt nanoparticles was precisely controlled by the addition of $AgNO_3$ in the ranges of 10 nm, 20 nm, etc., which can be used as the best catalytic layers for fuel cell technology, typically such as PEMFC and DMFC. The crystal surfaces of the Pt nanoparticles are very important to nanocatalysis. Polyhedral Pt nanoparticles typically exhibit mainly low-index crystal facets of (100), (110), and (111), although they do include high-index crystal facets [13,14].

Nevertheless, in the typical TEM method, a certain number of the (hkl) planes of the low-index crystal planes or the certain number of the high-index crystal planes were determined in the selection rule for the various types of fcc crystal structures. In this context, Pt-Pd core-shell nanoparticles were synthesized by a simple synthetic method. The main results demonstrated the homogeneous nucleation and growth of the Pd metal shell in the size range of 10 nm on the definite Pt core in the size range of 20 nm [14]. The synthesized Pt-Pd core-shell nanoparticles in the size range of 30 nm exhibit the sharp and polyhedral shapes and morphologies (Figures 5 and 6). The epitaxial growth of the controlled Pd shells on the Pt cores via a polyol method was observed [27]. The main discoveries led to Frank-van der Merwe and Stranski-Krastanov growth modes coexisting in the nucleation and growth of Pt-Pd core-shell nanoparticles. It was found that the size effect is not as strong as the nanostructuring effect on the catalytic properties of the researched nanoparticles. The catalytic synergistic effect of the Pt-Pd core-shell nanoparticles was evidently found in electrochemical measurements, i.e., the CVs at the prepared electrodes. Therefore, various kinds of Pt-Pd alloy and core-shell nanoparticles with nanostructures have been successfully synthesized by modified polyol methods [29,34,39]. This discovery can be true to most of catalytic core-shell nanoparticles with various core and shell forms (metals, multimetals, oxides, mixtures etc.). In order to reduce the high cost of FCs, PEMFCs, and DMFCs, the thick cores can be oxides, alloys, etc., in the core-shell structures and shapes by the modified polyol processes. This will lead to understand that the very thin noble metal and alloy shells can be produced in the form of monolayers of Pt, PtPd, PtRh, PtRu, and PtRhRu as Pt-group multimetal catalysts, etc., on the defined inexpensive thick metal, alloy, ceramic and oxide cores. The nanosized core nanoparticles need to be synthesized first, and then the thin Pt or Pd shells are synthesized. The thin shells can be prepared in the various forms of the bimetallic thin shells, typically such as the thin shells of PdPt, PtRu, PtRh, PtPd, etc., formed as the atomic monolayers on the previous prepared Pt-based multimetal alloy nanoparticles. In addition, the critical roles of heat treatment to the prepared particle products led to particle deformation, i.e., the levels of the deformation of size, shape, morphology, surface, internal structure, composition, and other crystal parameters during sintering and final densification [48], leading to plastic, elastic, and inelastic deformation on both the crystal surface and inside the particles leading the undiscovered new properties for various practical applications in electrocatalysis. In correct comprehension, the high crystallization or atom-by-atom growth was clearly confirmed in the the great beauty of the arrangement of atoms on the surfaces of nanocrystals as shown in Figure 6.

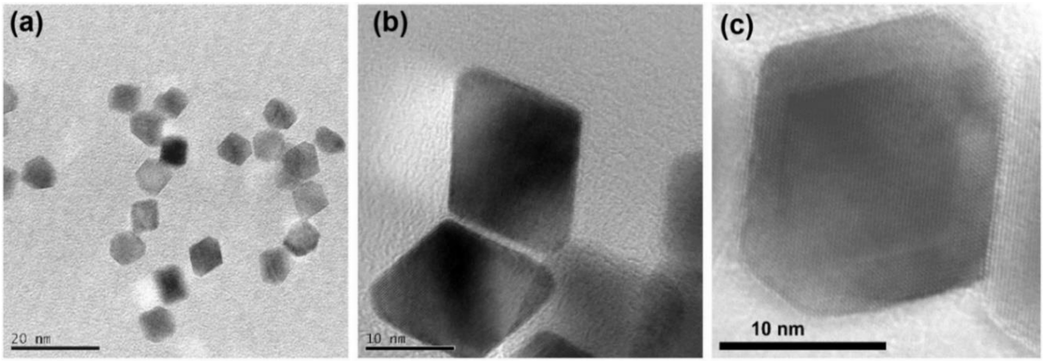


Figure 5. (**a**) Pt nanoparticles by modified polyol method [35], and (**b**) [42]. (**c**) Pt-Pd core-shell

nanoparticles by modified polyol method; their nanostructures with the thin Pd shells with several Pd atomic monolayers [39]. Pt or Pd atomic monolayer is a challenge to science and nanochemistry.

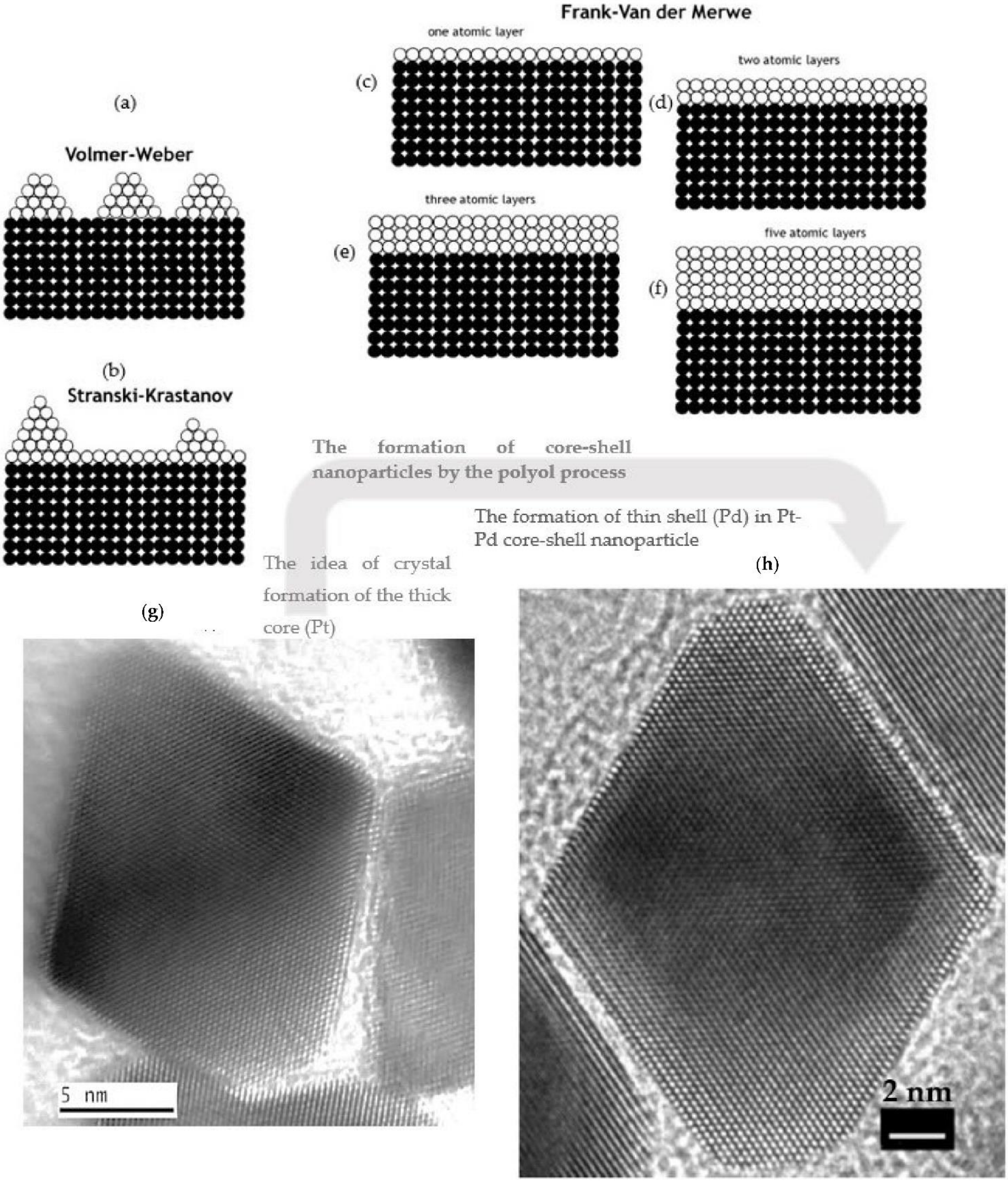


Figure 6. (**a**–**f**) To explain the crystal formation of core-shell structure, the mechanisms, growth, and formation of the thin shell in the shell-core bimetallic nanostructures include Vomer-Weber, Frank-Van der Merwe, and Stranski-Krastanov [27]. (**g**) The crystal core is Pt nanoparticle, exhibiting its crystal surface [38]. (**h**) The thin crystal shell shows several atomic monolayers of 1–3 nm. The Pd-based PGM thin shell with one atomic monolayer is a challenge to surface science, which is the limitation in bottom-up and top-down synthetic processes.

5. Development of Hybrid Pt/AB_2O_4-Type Ferrite, ABO_3-Type Perovskite, Oxide, and Ceramic Catalysts

It is known that the synergic core-shell effects of Pt or Pd based bimetallic catalysts as well as dealloying effects of Pt based core-shell catalysts are important to create new Pt- or Pd-based catalysts for developing sustainable and renewable energy via various FCs [29,34,39]. In main contribution, they have shown the self-attachment, elastic and inelastic self-collision, self-aggregation, and self-assembly phenomena of the nanoparticles according to chemical synthetic processes [35]. The very complex issues of atomic arrangements in order or disorder inside metal, bimetal, and alloy nanoparticle with defects, stacking fault, dislocation, twin planes, etc., at 10 nm by HRTEM/STEM combined methods possibly lead to improve the polyol processes for electrocatalysts, and achieve the robust high performance of Pt-free or Pt-based bimetal and multimetal electrocatalysts in the future [29,33,38]. The durability, stability, and strength of the particles after heat treatment at high temperature significantly enhanced are all the best chemical and physical properties of the as-prepared particles with both micro- and nanostructures. These important improvements and modifications are the gold keys for discovering new functional nanoparticles. Researchers have also presented the key research discoveries of the Fe metal and oxide-based particles, especially for the crystal formation of grain and grain boundary structures (Figure 7) and nano/micro metal, bimetal, multimetal, and oxide structures [49]. In the testing and preparation of thermoelectric materials, the researchers discovered new methods for making various multimetal nano/microsized α-Fe_2O_3 particles with modified polyol methods with $NaBH_4$ and heat treatment at high temperature by chance from research and experimental skills (Figures 8 and 9).

To develop inexpensive catalytic and magnetic particles, typically such as Fe, Ni, Co, and their alloys possibly used at the electrodes of FCs, the researchers have very successfully developed large magnetic PVP-Fe-based particles in the size range of 5 and 10 μm with polyhedral or spherical shapes and morphologies that led to produce various kinds of iron oxide nanostructures with potential applications for the electrodes of batteries in energy conversion, gas sensors, and the environment as well as devices using soft magnetic materials. In simplification approach, Fe oxide and alloy microsystems can be synthesized by chemical methods and heat treatment, which leads to produce various kinds of oxides, alloys, superalloys, micro/nanosized particles, etc., which can use inexpensive core materials. The various kinds of normal and inverse spinel ferrite particles with various grain and grain boundary structures can be facilely created (Figure 8). In the discovery, the special case of the as-prepared spherical $CoFe_2O_4$ oxide microparticles with grain and grain boundary structures was prepared with high-performance synthetic processes in the laboratory. The definition of the best inverse spinel structures AB_2O_4 was proposed by an idea of the best tetrahedral and octahedral locations occupied by A and B ions (i.e., Co and Fe atoms) from experimental according to theory [48–53]. So, we suggest that $CoFe_2O_4$ or $ZnFe_2O_4$ or $ZnCoFe_2O_4$ materials will be easily prepared by this process as well as $ZnCoFe_2O_4$ by sol-gel process [61], Pt/$CoFe_2O_4$-C hollow ball namomaterials [62], NiCoIr oxide and NiCoRu oxide nanomaterials for the promising application in PEMFCs and DMFCs [63]. Recently, $Co_{0.5}Zn_{0.5}Fe_2O_4$ has also become a new superior catalyst for ORR to replace noble metal catalysts of high cost in microbial fuel cell [64].

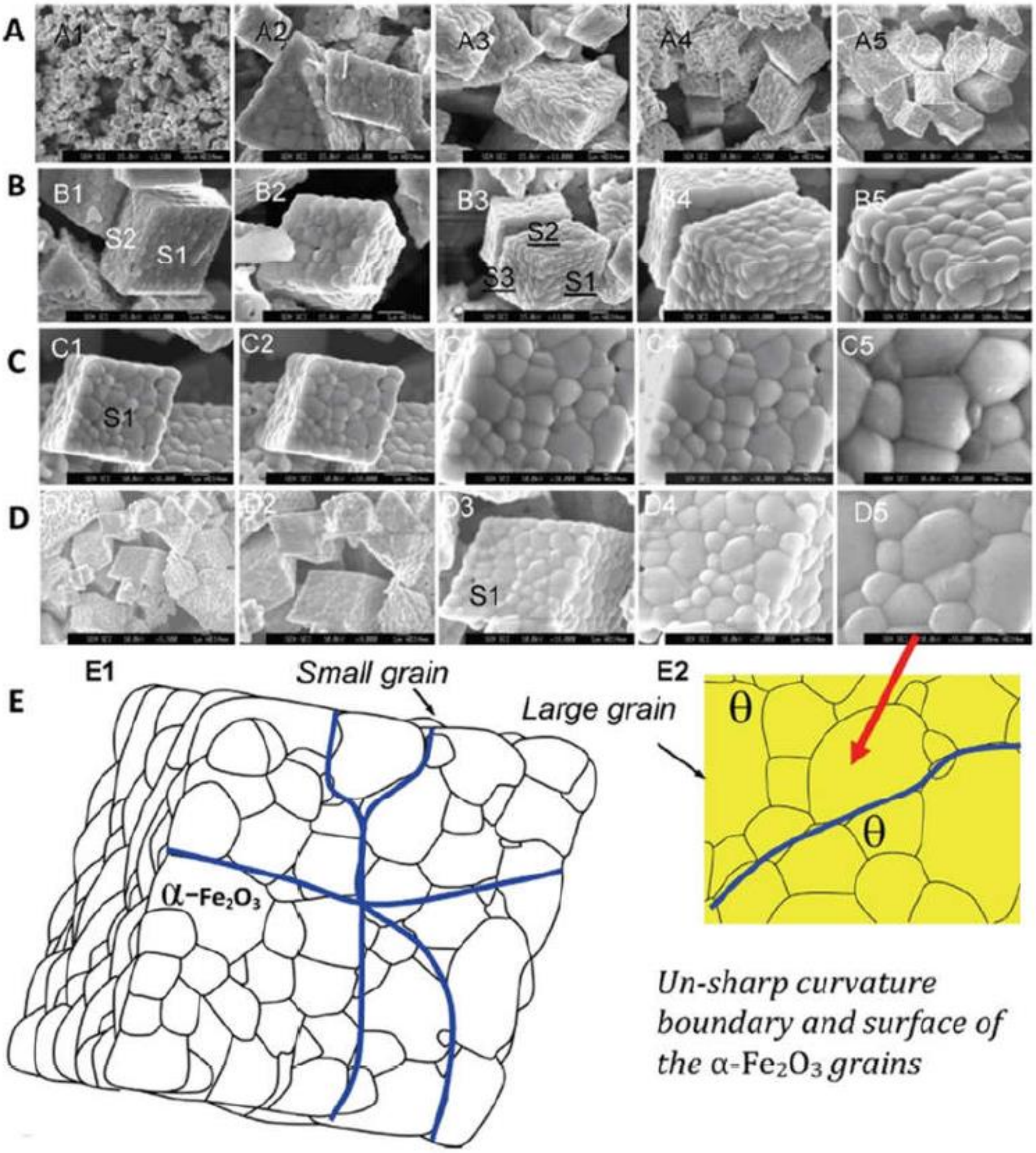


Figure 7. The evidences of α-Fe_2O_3 oxide micro/nanostructures with grain and grain boundary are a challenge to science [49]. (**A**–**E**) The surfaces of α-Fe_2O_3 particles with grain and grain boundary.

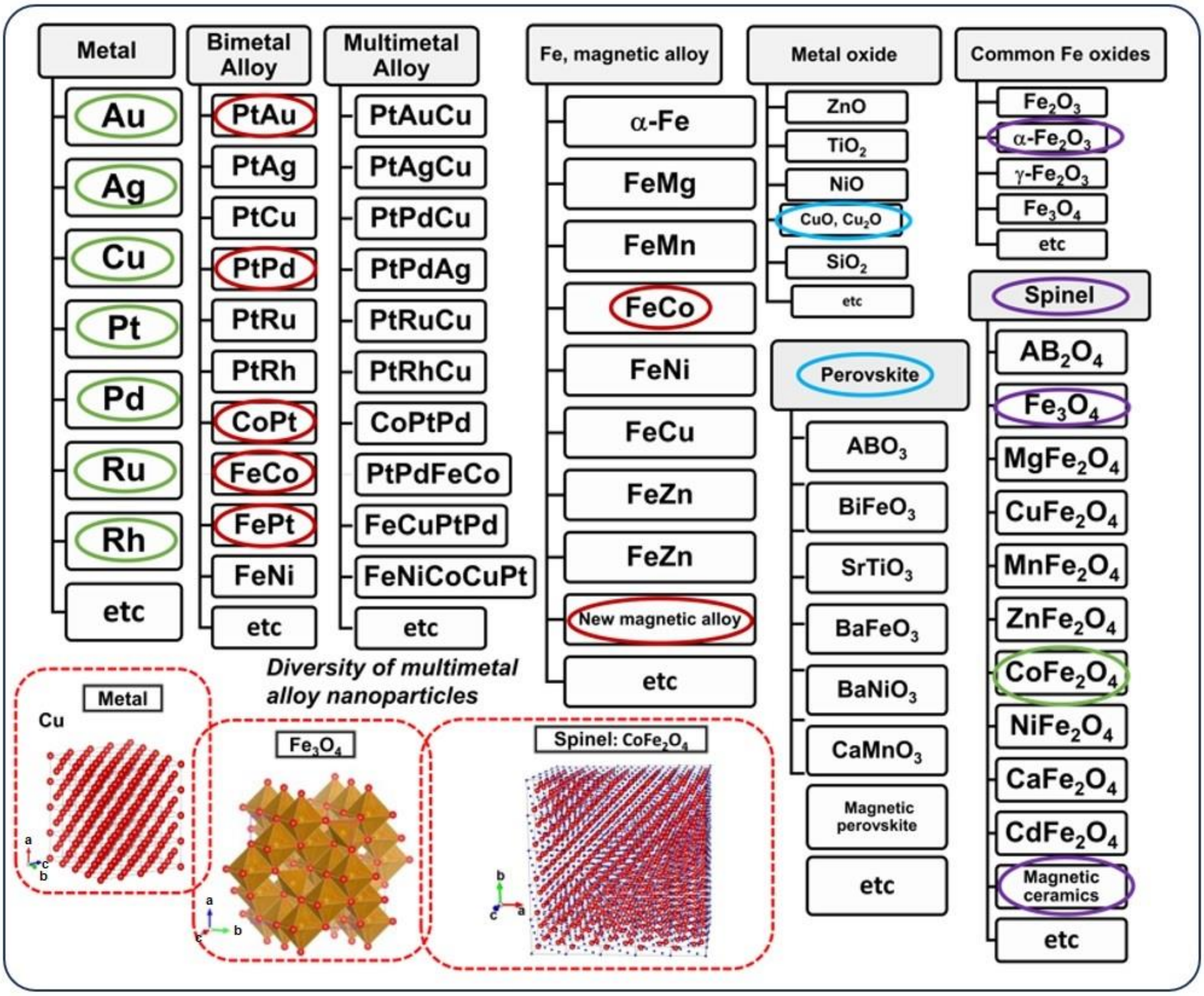


Figure 8. The great possibility in the controlled synthesis of metal, alloy, and AB_2O_4- or ABO_3-type based oxide micro/nanostructures by both modified polyol methods and heat treatment. The polyol process opens a good opportunity of synthesizing multimetal nanoparticles for catalysis. In structural modifications, crystal structure of $CoFe_2O_4$ spinel was clearly discussed in the tetrahedral sites and octahedral sites [52].

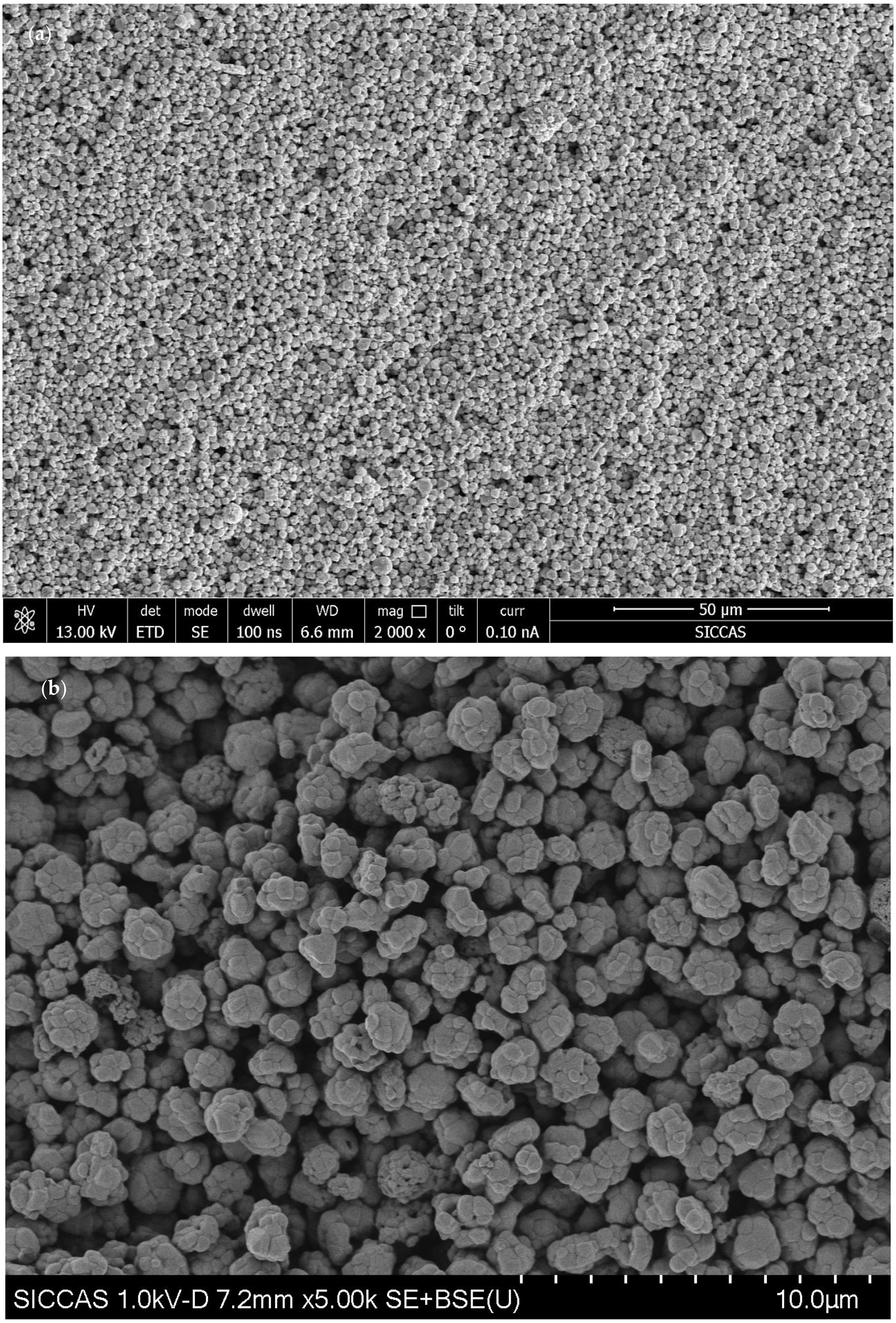


Figure 9. (**a**) The controlled synthesis of AB_2O_4-type $CoFe_2O_4$ micro/nanostructures by modified polyol methods [56]. (**b**) $CoFe_2O_4$ micro/nanostructures with heat treatment at high temperature in a range of 900–1100 °C (SEM data in our new experimental). It is clear that Pt nanoparticles can be potentially integrated in a ferrite matrix of $CoFe_2O_4$ for electrocatalysis.

In the interesting topics, non-noble metal catalysts or alternative catalysts for ORR have been reviewed in PEMFC [65]. For replacing Pt group metal electrocatalysts, PGM-free electrocatalysts were discussed in HOR and ORR mechanisms. There are the various kinds of transition metal-nitrogen-carbon (M-N-C) catalysts, TM oxides, nitrides, carbides, oxynitrides and chalcogenides [66] as well as carbon and graphene metal-free electrocatalysts. The classes of new nano/microstructured AB_2O_4-type ferrites or ABO_3-type perovskites are potentially used SOFC, batteries, capacitor, and supercapacitor. In one research, Pt/$CoFe_2O_4$-C was used as bifunctional or multifunctional electrocatalyst for Zn-air batteries [62]. So, the potential applications of AB_2O_4-type ferrites or ABO_3-type perovskites are the key electrical components and devices in electronics, photonics, optoelectronics, and telecommunications.

In modeling and simulation, the models of grain and grain boundary structures of large oxide, alloy, and mixture particles are very crucial to optimize structures and properties of new magnetic materials according to their complexity of their development and final formation mechanisms. The above nano/microsized oxide systems can be used for the catalytic layers of SOFC technologies in future (Figures 8 and 9). At present, soft and hard magnetic oxides and alloys with grain and grain boundary are challenging to the experimental scientists and researchers. So far, researchers have presented their modified polyol methods can lead to new key research discoveries of soft and hard magnetic alloy particles, i.e., rare earth magnet nanomaterials [50,55,59]. At present, we suggest that two-phase soft and hard magnetic nanomaterials were synthesized with high impact on new magnetic nanomaterials and technologies [48,55]. Researchers have proposed the modified chemical methods with heat treatment for synthetic processes at liquid-phase, solid-phase with a strong reducing like Ca, CaH_2, and interface or internal chemical reactions for making hard magnetic materials with rare earth, such as NdFe, SmFe, SmNdFe, NdFeB, SmNdFeB, and their magnetic alloys, which are different from physical and chemical metallurgy technologies, and other conventional methods and approaches [50,55,59]. The research methods will open new ways of making soft and hard magnetic nanomaterials with grain and grain boundary in both nano and microscale ranges by chemical methods and approaches. The products of the nano and microparticle powders will introduce for practical applications for catalysis. To confirm catalytic activity, electrochemical reactions of the surfaces of the electrodes must be studied in detail. There have been the various works in the details of Pt-based electrocatalysts and alternative catalysts for FCs [66–76]. The critical reviews have demonstrated the electrocatalytic activity of novel kinds of PGM-free electrocatalysts [66–76]. At present, non-Pt metal nanoparticle catalysts have been studied in the catalytic ability of ORR or other catalytic mechanisms in the comparison with Pt catalyst. In addition, alternate electrocatalysts (PGM-free nanoparticle catalysts) or Pt-free metal catalysts have been developed for this purpose. Recently, carbon nanomaterials doped with N, B, P, and S can be promising alternative electrocatalysts for ORR in low temperature FCs. Recently, the catalytic investigations of TMO oxide electrocatalysts (TMO: Transition metal oxide) or TMO multimetal and oxide electrocatalysts doped with C for electrode materials of PEMFCs and DMFCs have been reviewed [66–76]. In addition, oxynitride and nitride electrocatalysts will potentially become the new kinds of promising electrocatalysts.

6. Discussion

Specifically, the following important issues of metal, bimetal, and multimetal nanoparticles by modified polyol methods with great advantages for electrocatalysts are of very interest to research. Firstly, we must understand that particle size of multimetal or core-shell nanoparticles is important to electrocatalysis. In general, the particle size of as-prepared has to be controlled within the nano/microsized ranges, for example, 10 nm, the nm and µm ranges, and so on [12,13].

The researchers demonstrated that metal nanoparticles were successfully synthesized by an improved polyol synthesis process that could precisely control the size. When nanoparticles are used as catalysts for chemical production processes, the smaller the particle size and the more homogeneous the particle system is, the more valuable it is because it allows increasing the catalytic surface area as in the case of Pt or Pd nanoparticles [12,13]. The controlling of Pt nanoparticles with the uniform size particles in the nanosized range of 10 nm is scientists' desirable thing, which is being continuously researched in the field of catalytic applications. In particular, some types of nanoparticles such as Au and Ag nanoparticles or nanoparticles smaller than 50 nm or smaller than 20 nm suitable for promising applications in the fields of medicine and biology or nanomedicine have been strongly developed more than the past 30 years. For example, in very potential application of cancer therapy, single-metal, bi-metal, and multi-metal nanoparticles, magnetic oxide nanoparticles can also be studied and realized by modified polyol methods and nanochemistry. Secondly, we must control the particle shape of multimetal or core-shell nanoparticles. The shape of the Pt-based multimetal nanoparticles is also important in applications, such as polyhedra, sphere, rod, wire, and typical shapes and morphologies [12,13]. In catalysis, it is known that polyhedral shapes in the ranges of 10, 20, and 30 nm in sizes are most of the desired shapes that were made by scholars and researchers. Thirdly, we must control the particle shapes and morphologies of multimetal or core-shell nanoparticles. The morphology of a Pt-based multimetal particle refers to a rough or flat crystal surface with particles of different shapes. The particle is a polyhedron, and particle morphology will have more ordered flat atomic surfaces than other types [12,13]. The crystal surface of a particle containing many atoms exhibits high convexity, which is one of the very interesting research problems of researchers today. Fourthly, we must understand the particle structure of multimetal alloy or core-shell nanoparticles. The Pt-based multimetal core-shell nanoparticle structure is currently a very interesting new topic for scientists [66,67]. Finally, utilizing a few nm-thick Pt- or Pd-based shells (or the Pt- or Pd-based atomic monolayers) and the shell properties a few atomic monolayers thick in the field of catalysis opens up new possibilities [12,13]. For example, the controlled synthesis and use of catalytic materials layers, Pt core and Pd shell core-shell nanostructures, or Pd core and Pt shell core-shell nanostructures have led that the significant enhancement of catalytic properties is much greater than using only Pt nanocatalysts, even the actual size of the bimetallic shell-core nanostructure system is much larger than that of Pt single-metal nanostructures [13]. In addition, the bimetallic shell core structure system is considered to have outstanding advantages more than the single-metal nanoparticle structure system because it is more stable and more stable than the characteristics of the single metal nanoparticle configuration. However, the proliferation of the shell on the cores to form a homogeneous core-shell nanostructure system is a challenge in current nanoscale research. In addition, the superior properties of catalytic core-shell nanostructures are becoming an urgent research topic for many researchers because of their high practical applications, especially in many industries related to material and production cost savings. Through the overall survey of multimetal nanostructured electrocatalyst by nanochemistry, and modified polyol methods, this is the hot trend in the scientific research of leading scientists [3–14]. We have presented the polyol processes for the successful synthesis of bimetal core-shell systems with the Pt or Pd thin shell as shown in Figure 10. It is evident that these core-shell-structured nanoparticles have great significance and potential for applications in the fields of catalysis, electronics and telecommunications, biomedicine and many other important applications. Thus, research on applying the polyol process will have a wide range of micro/nanostructures for practical applications and catalytic technologies in laboratories without the very large need for expensive investments. In addition, we must control the particle composition of multimetal or core-shell nanoparticles. The composition of nanoparticles also has important applications in electronic catalysis, electronics, medicine and biology. The composition can be Pt-based single-metal, bi-metal, multimetal and multi-component electrocatalysts [12,13]. To reduce the cost of FCs systems, the good idea of using multimetal alloys is a very possible and economical resolution in the scientific interest. Here, researchers also need to understand the functionalization of the surfaces of engineered multimetal or core-shell nanoparticles. The functionalization of the nanoparticle surface will lead to biomedical applications, experimental properties will be promisingly applied in medicine [46,53]. In surface science, it is needed to understand the theoretical calculation of multimetal or core-shell nanoparticles. Modeling and simulation of Pt-based or Pd-based nanosystems at the most important 10 nm size, especially for nanoclusters (clusters of atoms) at sizes < 5 nm to predict the new or abnormal properties and technological breakthroughs compared with experiment [77]. It is likely that researchers must understand the other physical and chemical phenomena of multimetal alloy or core-shell nanoparticles for better catalytic stability and durability. The investigation of atomic arrangement on the surface and inside the cleanly prepared nanoparticle to explore fully in a broad sense when evaluating the properties of a particular nanoparticle or a particular particle system. The synthetic studies have been discussed in the main focus on Pt nanomaterials, bimetallic Pt nanoalloys, and multicomponent Pt alloy nanomaterials, respectively [77–80]. The Cu-, CuPt-, Cu-based alloy, and Cu-based nanomaterials were widely discussed as an electrocatalyst in PEMFCs [81]. On the basis of the standard Pt catalyst, the experimental comparisons of electrocatalytic properties of Pt and Pt-based multimetal catalysts are done, which is to find ways to gradually reduce the cost of single-metal Pt-catalyzed standard catalyst. In comparison with the standard Pt electrocatalyst, researchers have also investigated the types of electrocatalytic materials of free-Pt or low-Pt or non-Pt nanoparticles (non-noble metal catalyst) or Pt-free multimetal electrocatalysts on the carbon support layers, which are reviewed in various works [82–88], according to the mechanisms of ORR/HOR for PEMFCs and DMFCs, such as various kinds of commercial carbon or graphene nanomaterials with the layers of atomic monolayers used in the engineered catalytic layer of low temperature FCs. For ORR, Pt, Pt catalytic alloys, Pt-based alloy, and core-shell electrocatalysts need to be developed and investigated to select new multimetal electrocatalysts or alternative electrocatalysts. Similarly, for ORR, the wide various kinds of PGM-free oxides-, chalcogenides-, carbides-, Fe-N-C-based-, metal-free-, single-atom-, and carbon-based electrocatalysts have been developed to replace Pt electrocatalysts at the core catalytic layers of the cathodes and the anodes in the future [1,2,10–23,82–89].

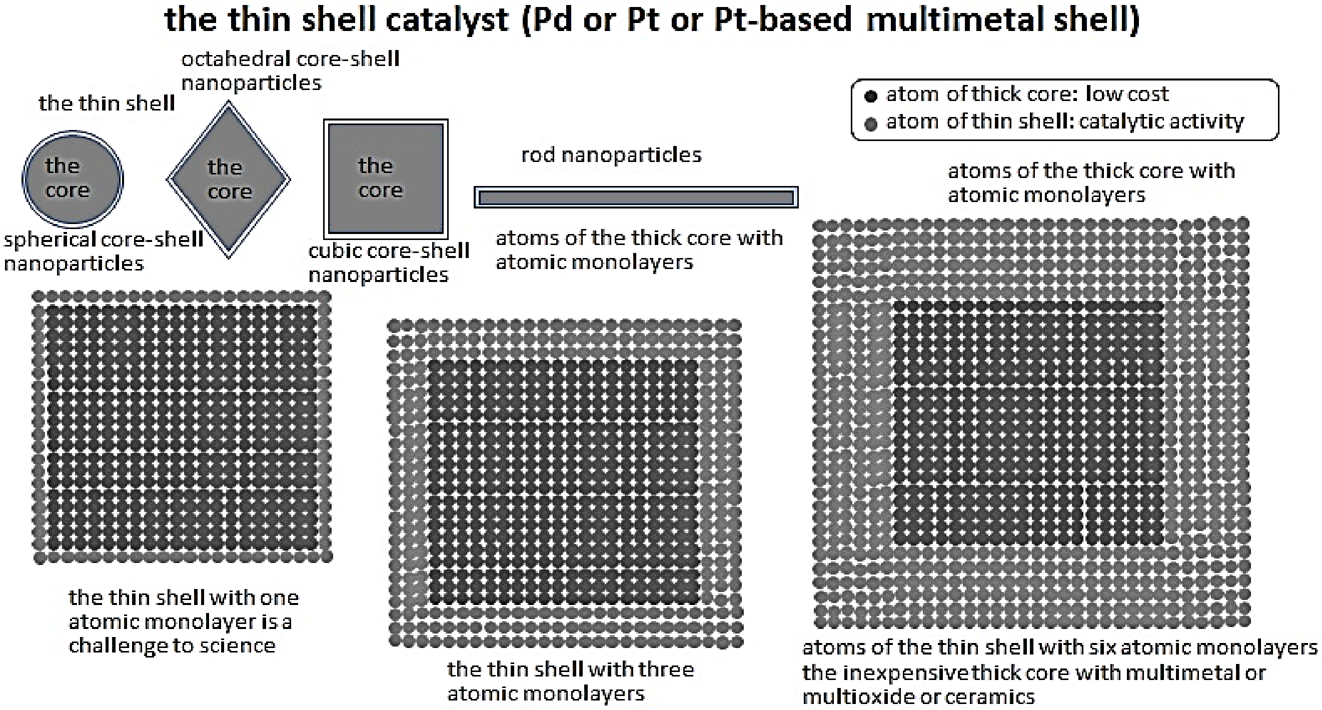


Figure 10. The typical models of the cubic Pt-Pd core-shell nanoparticles with the thin Pd shells with several Pd atomic monolayers on the thick cores. This is also a challenge to science. The thin shells of Pt or Pd on the thick metal, bimetal, multimetal, alloy and oxide cores can be realized by modified polyol methods using agents added during the designed process effectively.

In the component modification of acid or alkaline electrolytes, researchers show that a new kind of membrane using phosphotungstic acid/phosphomolybdic acid/SiO_2 glass was studied for the development of H_2/O_2 FCs [90–92]. In the future, the new kinds of Pt-free multimetal electrocatalysts by modified polyol processes will be predicted as inexpensive alternative electrocatalysts for the development of FCs, PEMFCs, and DMFCs as well as hydrogen and FCs technologies [93]. Their very high costs of Pt catalysts would be greatly decreased in the technological convergence, nanomaterials (metal, alloy, and oxide), and other components derived from the modified polyol processes. The scientific exlanation of nucleation, growth, and formation of as-prepared nanoparticles from the precursors can be intensively understood [93–104]. It is certain that the electronic, magnetic, optical, electrocatalytic, photocatalytic properties of as-prepared micro/nanomaterials by modified polyol processes should be further investigated. We believe the modified polyol process plays a major role in research and application advancement.

7. Conclusions

In our understanding of electrocatalytic ideas, it is increasingly important to understand that Pt is the standard catalyst for the study of its PGM-free electrocatalytic alloys, ceramics, C-based materials, and alternative electrocatalytic compounds [24–59]. These recent trends, Pt-nanoparticle-based electrocatalysts used as the standard catalyst have been successfully prepared by modified polyol methods effectively combined with microwave methods as well as physical and chemical methods in the various experimental approaches from the most typical reactants and reagents, which lead to Pt-based alloy and core-shell nanoparticles multimetal electrocatalysts being synthesized. In the future perspectives, this modified polyol method greatly offers a good way of synthesizing Pt-based multimetal nanocatalysts that will be used in the catalytic layers of FCs, PEMFCs, and DMFCs. In the background, Fe or Pt-based alloy and oxide nanoparticles are effectively synthesized by modified polyol methods. In this way, water, alcohol, and polyol or their mixtures can be potentially used as both solvents and reducing agents in a sol-gel process, i.e., a so-called polyol process. Over 30 years of synthesis of nanoparticles by the polyol process [4,7,8], and modified polyol processes for the controlled synthesis of nanomaterials, it is suggested that the modified polyol processes [13,14,24–59,80] can be very potentially used to synthesize effectively the various forms of the Pt-based metal, bimetal, alloy, and multimetal nanoparticles as well as AB_2O_4-type or ABO_3-type oxide micro/nanomaterials and their products for use in the area of catalysis. In experiments, researchers start from the fact that the polyol process provides unique and indispensable advantages to synthesize various classes of nanoparticles for catalysis compared to other physical and chemical synthetic methods. Over time, more widespread use of core-shell configurations of nanoparticles with the thin shell of Pt atomic monolayers from 1–3 nm formed on the thick core of alloy, ferrite, perovskite, glass, oxide, and ceramic will possibly be realized. In the targeted synthesis, the selection criteria of metal salt precursors were used with dissociation constant and the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) values of polyols derived from molecular orbital theory (MOT) calculation [101]. Major developments are anticipated in the modified polyol methods and ease of use of the polyol processes at various scales, and similar to sol-gel processes that make them ideal routes for controlled synthesis of functional engineered nanoparticles that depend strongly according to the expertise and experimental skills of most the researchers. They are the future technologies for synthesis of nanoparticles and nanomaterials in all the inexpensive laboratories without modern equipment, and without much special difficulty at universities [94–102]. Therefore, the very special concerns are not only focused on the original polyol process but also the modified polyol processes of synthesizing nanoparticles as well. Therefore, the size-shape-composition-structure-property-controlling agents are very important for achieving the noncrystal or crystal formation of nanoparticles and nanomaterials [94–102]. The synthesis of Au, Ag, and Pt nanoparticles were controlled in the designed exprimental conditions with the most typical flask or a popular reaction system [103,104]. Finally, it is certain that nanoparticles and nanomaterials in the various forms of metals, alloys, oxides, ceramics, and their nanostructures in the various forms of alloy structure, core-shell, and multivalent multifunctional features, doped at the single-atom level and possibly fabricated by the modified polyol process, will be new materials with new properties that scientists and researchers will have to study and understand in detail. A person who follows the experimental methods of chemistry, physics, and biology has to carry out experiments every day for his or her lessons from past, present, and the future.

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