

Solder-free electrical Joule welding of macroscopic graphene assemblies

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ABSTRACT

Welding is an important convenient methodology to realize robust coalescence of individual metallic or polymeric objects through local melting of contact boundaries. However, how to firmly conjoin the refractory graphene-based materials via conventional welding remains an open question because of their non-melting nature. In this work, we report an efficient solder-free approach to weld individual macroscopic graphene assemblies via electrical Joule heating. Graphene-based materials with different architectures, including graphene fibers, films, and foams, are covalently welded together with high joint strength. The welding mechanism was studied by *in situ* transmission electron microscope and molecular dynamic simulations. We attributed the unique welding behavior to the defect-facilitated cross-linking between graphene layers at contact interface. The facile electrical Joule welding strategy provides a new reliable connection method for carbon materials, enabling the direct assembling of macroscopic graphene materials to sophisticated three-dimensional configurations.

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1. Introduction

Welding is a reliable connection methodology in modern manufacturing processes, which firmly connects two or more workpieces of the same or dissimilar constitutions to achieve complete interfacial coalescence [1–4]. The most practical welding technique is the fusion welding for metallic and thermoplastic polymeric components, which is achieved by the melting and merging of local contact fronts. As graphene materials become increasingly promising in practical applications, a significant issue is intuitively emerging: how to firmly connect graphene assemblies, just as welding of conventional metallic and polymeric

materials. Generally, macroscopically assembled graphene materials possess combined merits of excellent mechanical and electrical/thermal properties, but these exceptional performances will be degraded severely by the poor interfacial connections among different components in complex architectures [5–9], as in the cases of carbon materials such as fabrics of carbon fibers and carbon nanotube (CNT) fibers [10]. This emerged connection issue needs to be solved but remains greatly challenging. In contrast to metallic and polymeric materials, graphene is non-fusible below its decomposition temperature because of the strong C–C bonding, making conventional welding methods inapplicable. It is highly desirable to explore a novel and efficient connection method for graphene assemblies to fabricate integrations without degrading their overall performances.

Several physical or chemical approaches have been proposed for the welding of carbon materials. The deposition of amorphous carbon layers was used to physically connect crossing multiwalled CNTs, broken CNTs, and macroscopic CNT fibers [11–13]. A covalent welding of crossing single-walled CNTs was observed in the microscopic scale under strong electron beam radiation [14]. Yao

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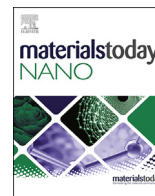
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Gold nanoclusters: synthetic strategies and recent advances in fluorescent sensing

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ABSTRACT

Fluorescent gold nanoclusters (AuNCs) have emerged as ideal sensor probes in different research fields such as environmental, biological and clinical applications. AuNCs have acquired a paramount importance in sensing applications owing to their unique physicochemical and luminescence characteristics including excellent photostability and biocompatibility, high surface to volume ratio, besides size-dependent luminescence, large Stokes shift, and high emission rates. In this review, we will pay special attention on the recent advances in the different synthetic strategies of AuNCs. Different parameters affecting photoluminescence properties of AuNCs and their quantum yield including AuNCs size, core composition, valence state of Au atoms, and ligand effect will be discussed in detail. This review will also provide a comprehensive and recent look on the various AuNCs-based sensing systems developed for the detection of heavy metal ions, inorganic anions, small biomolecules, protein tumor markers, enzymes, and nucleic acids. This review demonstrates the high sensitivity, selectivity, simplicity, and low cost of AuNCs as sensing probes for the various targeted analytes.

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1. Introduction

Over the past decades, gold nanoparticles (AuNPs) have witnessed a paramount importance in various research areas, including chemical sensing, catalysis, biology, medicine, and environmental sciences [1–4]. AuNPs with size larger than 3 nm exhibit unique optical properties and have distinct feature of surface plasmon resonance (SPR), which results from the resonant collective oscillation of electrons in the conduction band with the incident light. While ultrasmall AuNPs (<3 nm), defined as gold nanoclusters (AuNCs), have molecular-like properties owing to the strong quantum confinement effect that causes the continuous energy bands break up into discrete energy levels [5,6]. Therefore, AuNCs possess common features, such as HOMO–LUMO transition, photoluminescence (PL), electrochemiluminescence, lacking SPR peak, electromagnetism, redox behavior, and molecular chirality [7–9].

For AuNPs, several recent studies have extensively discussed their controlled synthesis with different sizes (5–50 nm), shapes (rods, nanocubes, nanoplates, nanoflowers, etc), and compositions (alloys such as Au/AgNPs, Au/Cu, Au/Pd, etc). These varied structural features can effectively affect the physical properties of AuNPs by exposing different facets ({110}, {210}, {111}, etc) and different active sites (corners and edges) [6]. Thereby, AuNPs have large surface to volume ratio and excellent catalytic activities toward many reactions, such as oxidation, hydrogenation, and coupling reactions, resulting in its implication in various applications, such as electrocatalysis, solar cells, and biofuel cells. Further, AuNPs have been widely employed in colorimetry, surface-enhanced infrared absorption spectroscopy, and surface-enhanced Raman scattering owing to the unique SPR feature of AuNPs. Unlike AuNCs, AuNPs are non-luminescent nanomaterials, and they can quench NCs luminescence through Förster/fluorescence resonance energy transfer (FRET) owing to high molar absorptivity constant and overlapping of their photoexcitation with AuNCs emission.

For AuNCs, they have ultrasmall size (0.1 nm–2 nm) consisting of few to several Au atoms; therefore, it is a big challenge to control the core size of AuNCs compared with AuNPs. Different emission

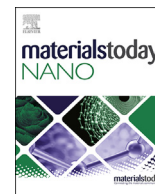
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A brief review on plasma for synthesis and processing of electrode materials

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ABSTRACT

Plasma, as an active, ionized, and electrically neutral gas, consists of electrons, ions, molecules, radicals, photons, and other excited species. Owing to its high activity, plasma can induce rapid and efficient reactions under relatively mild conditions. Hence, plasma has emerged as a powerful tool for material processing in both industrial and laboratory scale. This review provides a timely summary of different plasma techniques and their application in electrode materials. We first provide a brief introduction to the nature of plasma and types of plasma technologies. Then we summarize the recent advance in material synthesis and processing (deposition, conversion reaction, and surface modification) via plasma-assisted techniques with different feedstocks (C, H, N, O, Ar, S, P, etc.). Our focus is to put on electrode materials for energy conversion and storage devices, including batteries, supercapacitors, photocatalyst, and electrocatalysts. The advantages of plasma approaches over conventional technologies are discussed with examples.

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1. Introduction

With increasing concern about environment and energy, a further expanding market for energy conversion and storage devices (ECSDs) has attracted considerable attention, within which electrode materials are the keystone and bottleneck of these devices [1,2]. Herein, the exploitation of new materials and modification of existing materials at the atomic level become two meaningful and feasible strategies to meet the requirement of our society. However, researchers have suffered several challenges in traditional approaches for the fabrication of electrode materials with desirable structures, including sluggish reaction rates, high reaction temperature, and long duration [3]. Hence, the innovation in preparation techniques is urgently required. Recently, plasma-based methods have emerged, which delivers a unique environment, distinguishing from conventional physical and chemical

processes [4]. Such strategy is expected to serve as a promising candidate in the preparation of advanced nanomaterials.

The concept 'plasma', first proposed by Irving Langmuir, is recognized as the fourth state of matters [5]. Unlike other three states (gas, liquid, and solid), plasma is composed of a mixture of electrons, ions, and neutral particles, and most of these species in plasma preserve electronically excited states, exhibiting a highly reactive environment for physical and chemical reactions [6]. Hence, after almost one-century development from 1928, plasma-based techniques have evolved into an indispensable candidate in various applications [7]. Typically, non-thermal plasma has attracted considerable attention in material engineering because of its non-heating effect and relatively high reactivity, especially in the fabrication and modification of nanomaterials [8].

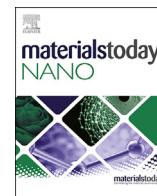
In this review, we briefly introduce the classification of plasma technologies and the principle of typical plasma-based strategies. Then, we will review recent advances of plasma-based techniques in material engineering based on different feedstocks (C, H, N, O, Ar, S, and P). Typically, plasma deposition, conversion, and modification are going to be illustrated with critical examples in recent literature. Representative instances applied in ECSDs will also be inventoried and discussed. Notably, this review mainly focuses on

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Dislocation plasticity reigns in a traditional twinning-induced plasticity steel by *in situ* observation

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ABSTRACT

To twin or not to twin? The critical doubt emerges recently on the dominant role of deformation twinning in contributing to strain hardening and plasticity, which has been long taken for granted specifically in twinning-induced plasticity (TWIP) steels. Here, the dynamic deformation process was *in situ* studied in a typical Fe-30Mn-3Si-3Al (wt. %) TWIP steel by using transmission electron microscopy. It is found that dislocation activities, instead of twinning, reigns over the whole plastic process, including planar slips and especially cross-slips of dislocations, leading to strong interaction of dislocations. An unexpected generation of nanograins is visible because of dislocation activities ahead of the crack tip. Moreover, the dominant dislocation plasticity continues straight down to cryogenic temperatures. The present results evidence the key role of forest dislocation hardening and shed insights into deformation physics in TWIP steels, contrary to our conventional understanding.

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1. Introduction

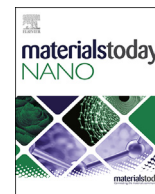
Twinning-induced plasticity (TWIP) steels have been arousing everlasting concerns, in which plasticity majorly comes from deformation twinning (DT), often called the TWIP effect [1–4]. The general understanding lies in that the twin boundaries (TBs) because of progressively twinning act as obstacles to effectively impede the motion of dislocations and reduce the dislocation mean free path gradually, leading to the dynamic Hall–Petch effect [5–8]. As such, the core of TWIP effect lies in extraordinary strain hardening by DT serving as a key mechanism, while the negligible dislocation forest hardening is often hinted. Hence, a good balanced result between tensile strength and especially superior ductility is obtained. In addition, the alloys of more or less TWIP effect always induce high fracture toughness and fatigue resistant properties [9–12].

Yet, the TWIP effect runs into challenges recently in TWIP steels [13]. Tracing to the TWIP effect, DT contributes to plasticity primarily from the following three aspects [13–17]: (1) the formation of deformation twinning accommodates plastic strain; (2) TBs serve as barriers to dislocation motion; and (3) TBs provide

adequate sites for nucleating and accommodating dislocations. In contrast, it is long taken for granted that dislocation behaviors are ignorable, even often observable. This idea gets further intensified especially because of the absence of intragranular cross-slip of dislocations, except for planar slip, in varying TWIP steels with face-centered cubic (fcc) structures of low stacking fault energy (SFE). However, the cross-slip of extended dislocations plays a key effect on work hardening, as the dissolved partials on intersected cross-slip planes may intersect to form Lomer–Cottrell locks, which extraordinarily contributes to work hardening [18]. Actually, DT works through TBs [8,15]. The TBs, if imbedded in grains in advance (e.g. in nanotwinned metals), realize strain hardening by intensifying dislocation-mediated plasticity to produce dislocation generation and strong interplay with TBs. Yet, both the density and spacing of TBs in TWIP steels are usually at least one magnitude lower than that in nanotwinned metals [19,20]. Thereby, the dislocation plasticity may operate freely. Recently, a few results spring up to question whether or not DT indeed plays the dominant role in strain hardening in TWIP steels. For example, it is the forest hardening instead of DT that contributes to up to 90% of flow stress in a Fe-18Mn-0.6C-1.5Al-0.8Si (wt. %) TWIP steel [21]. In a Fe-22Mn-0.6C TWIP steel, DT happens only in part of grains because of orientation anisotropy [14,22]. The quantitative measurement

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Exploration of nanowire- and nanotube-based electrocatalysts for oxygen reduction and oxygen evolution reaction



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ABSTRACT

Electrocatalysts for oxygen reduction and/or evolution are key components for proton-exchange membrane fuel cells (PEMFCs) and water electrolysis. However, the slow kinetics of oxygen reduction and/or evolution reactions largely hampers the efficiencies of PEMFCs and water electrolysis. Highly efficient electrocatalysts for oxygen reduction and evolution reactions must meet three requirements: (i) rapid transport of electrons, ions, and products of the reaction; (ii) sufficient catalysts/reactants contact area; and (iii) good intrinsic activity. Nanostructuring of electrocatalysts provides an effective approach to overcome the slow kinetics because nanostructured electrocatalysts with rational design can not only provide sufficient active sites but also promote intrinsic activity of electrocatalysts as well as possess the ability of rapid transport of electrons, ions, and products of the reaction. Especially, electrocatalysts in the form of one-dimensional nanostructures (1D-Nano) such as nanowires (NWs) and nanotubes (NTs) have shown significant advantages, such as high surface area, rapid electron and mass transfer, low vulnerability to dissolution, Ostwald ripening, and aggregation, for oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). In this review, we summarize different strategies for fabricating 1D nanostructure-based electrocatalysts (1D-NanoECs), which are categorized into template-free and template-assisted strategies, and emphasis has been placed on anodic aluminum oxide template-assisted strategies. Then, recent advances of 1D-NanoECs for ORR and OER applications are summarized. Finally, future challenges and opportunities about 1D-NanoECs are discussed.

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1. Introduction

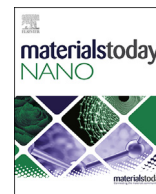
Similar to batteries, fuel cells use the chemical energy of fuels to produce electric energy, but the significant difference is that fuel cells have much faster charging time. For example, vehicles powered by hydrogen fuel cells can be fully refueled within only 3 min, while lithium-ion batteries-based vehicles need at least a few hours. What's more, hydrogen fuel cells have high energy density of 142 MJ/kg, which is more than 200 times that of lithium-ion batteries (0.6 MJ/kg). Especially, fuel cells are also marked by higher efficiencies and no environmental pollution compared with the internal combustion engines [1–3]. Based on these advantages, fuel cells have been widely used in the fields of stationary and portable power devices.

Among various kinds of fuel cells, proton-exchange membrane fuel cells (PEMFCs) have obvious superiorities, including high

simplicity, low working temperature (50–100 °C), high power density, and quick start-up [1,4,5]. In the PEMFC system, H₂ is oxidized at the anode surface to produce electrons and protons that are transferred to the cathode through an external circuit and the proton-exchange membrane, respectively (as shown in Fig. 1). Meanwhile, O₂ is slowly reduced at the cathode surface by reacting with protons and electrons to produce H₂O. Considering the multistep reactions in the PEMFC system, three key issues are still needed to be addressed to further improve its efficiency. (i) The oxygen reduction reaction (ORR) rate is six or more orders of magnitude slower than that of hydrogen oxidation reaction at the anode and thus significantly restricts the rate of the whole PEMFC system [6]. (ii) Most commercial electrocatalysts for ORR are based on Pt with high cost, leading to the increasing price of large-sale PEMFC. (iii) The adequate hydrogen production cannot be satisfied, which is a determinative prerequisite for realizing massive utilization of fuel cells. Therefore, the discovery of high-efficiency and cost-effective electrocatalysts for ORR is critical to improving the overall PEMFC performance. Regarding the inadequate hydrogen

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Polymers of intrinsic microporosity for energy-intensive membrane-based gas separations



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ABSTRACT

This review provides a new perspective on the role of the state-of-the-art polymers of intrinsic microporosity (PIMs) in key energy-intensive membrane-based gas separations including O₂/N₂, H₂/N₂, H₂/CH₄, CO₂/CH₄, H₂S/CH₄, C₂H₄/C₂H₆, and C₃H₆/C₃H₈ applications. A general overview on the gas separation properties of novel PIM materials developed in the past 15 years is presented with updated performance maps on the latest pure-gas 2015 O₂/N₂, H₂/N₂, and H₂/CH₄ permeability/selectivity upper bounds. Specifically, functionalized ladder PIMs and polyimides of intrinsic microporosity (PIM-PIs) are discussed targeting at high-performance, plasticization-resistant membranes for demanding acid gas (CO₂ and H₂S) removal from CH₄ in natural gas and olefin/paraffin separations. Experimental CO₂/CH₄ performance data of nearly 70 polymeric membrane materials available in the literature were gathered and plotted for the first time on the Robeson plot, from which a mixed-gas 2018 CO₂/CH₄ upper bound was proposed to provide guidance for future membrane materials development. A number of PIMs have demonstrated outstanding performances in O₂/N₂, H₂/N₂, and H₂/CH₄ separations, and several functionalized PIMs have shown great promises in CO₂/CH₄ separation under realistic mixed-gas conditions. The potential of PIMs materials and their derivatives for H₂S/CH₄, C₂H₄/C₂H₆, and C₃H₆/C₃H₈ separations are underexplored, and significant efforts are needed to develop stable and high-performance materials under mixed-gas conditions. Ultimately, fabricating PIMs materials into defect-free, inexpensive, thin-film composite or integrally-skinned asymmetric membranes is paramount to their successful large-scale commercialization.

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1. Introduction

Industrial separation processes account for a significant fraction of the global energy consumption. Large energy consumption drives the demand to improve the process energy efficiency and explore alternative technologies to perform less energy-intensive separations. Compared to the conventional thermally driven distillation and absorption/adsorption unit operations, membrane-based gas separation processes have several potential advantages: (i) small footprint, (ii) modular design, (iii) simple continuous operation, and (iv) lower cost. Hence, it is a viable alternative to

conventional separation processes and is a rapidly grown field in both industry and academia [1–10].

Several key milestones occurred during the historical development of gas separation membrane technology based on earlier breakthroughs in water desalination membranes as highlighted in Fig. 1a. The invention of high-flux, integrally skinned, asymmetric cellulose acetate reverse osmosis (RO) membranes composed of a porous support and an ultrathin selective layer with good salt rejection by Loeb and Sourirajan in 1963 [11] made membrane desalination by RO technically feasible. RO technology was subsequently further revolutionized by the development of polyamide thin-film composite (TFC) membranes made through interfacial polymerization by Cadotte, which currently accounts for more than 90% of global RO membranes sales [12,13].

Compared to water desalination, development of membranes for gas separations is much more challenging due to the very small sub-Ångstrom-level differences in size between gas molecules. For example, in air separation, O₂ and N₂ exhibit a size difference of

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