Developing Applications of Electrically Conductive Alumina with in Situ Nano-carbon Networks (NCN)

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Electrically conductive alumina (CA) with two forms conductive dense alumina (CDA) and conductive porous alumina (CPA) fabricated by combination of gelcasting and high temperature reductive sintering (HTRS) was claimed to a novel functional material with high-performance. With the aid of HTRS, polymer networks were thoroughly converted to carbon with graphitic structure. Taking the unique structure of CA into consideration, it is no suspicious that CA is available as electro-catalyst and microwave-induced heater. Herein, in this study, several modification methods have been designed in order to get the enhanced performances.

1. INTRODUCTION

Electrically conductive ceramic (CC) has been one of the research points recently determined by its various advantages. These merits involve physic-chemical and thermal stability, high erosion resistivity, low cost etc. [1-5] So far, either conductive matrices or additives have been employed to get CC via different preparing methods. These methods involve hot press [6], spark plasma [7], sol-gel [8] etc. However, it is still difficult to make uniformly dispersed conductive networks in Al_2O_3 matrix [9-20]. Various carbon additives are facilitated to agglomerate in composite, thereby leading to the segregated conductive phase and weak bending strength.

Thus, that is certainly necessary to explore a new process that not only is simple and direct method, but also provides homogeneously dispersed conductive networks. Herein, a new era has been developed since the initial announce of conductive alumina (CA) which was fabricated by combination of gelcasting and high temperature reductive sintering (HTRS) [21-24]. In this material, it was confirmed that the uniformly dispersed carbon with graphitic structure attributes to the good electrical conductivity of CA. With the aid of mechanically forming by hand-mixer at the highest speed, conductive porous alumina (CPA) with high porosity up to 66.23% was also fabricated in our study.
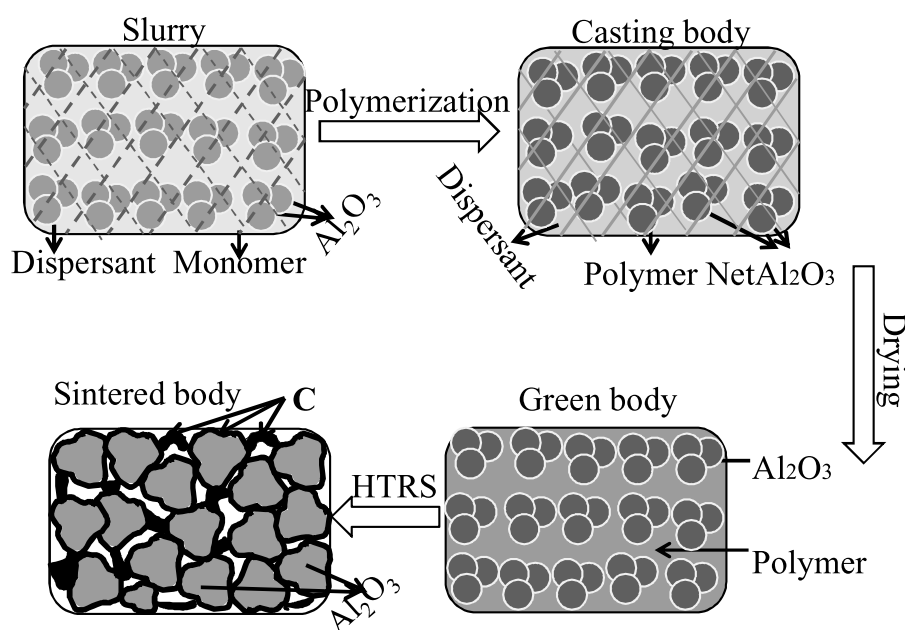

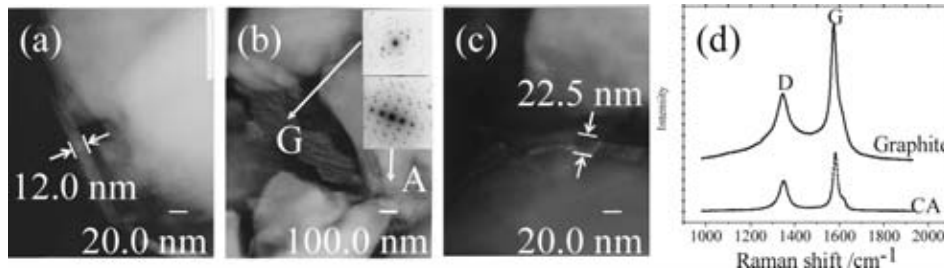**Fig. 1.** Schematic of preparing conductive alumina (CA)[21-24]

Fig. 2. TEM images of CA[21] (a), (b) and (c) and Raman spectroscopy of CA (d)[28]
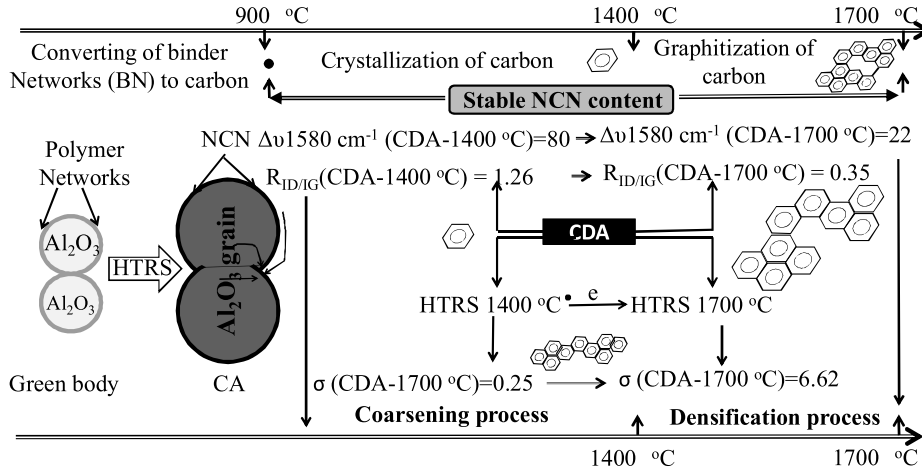

Fig. 3. Schematic illustration between densifying and coarsening procedures micro-structure changes of CA via high temperature reductive sintering (HTRS) resulting graphitization of polymer networks
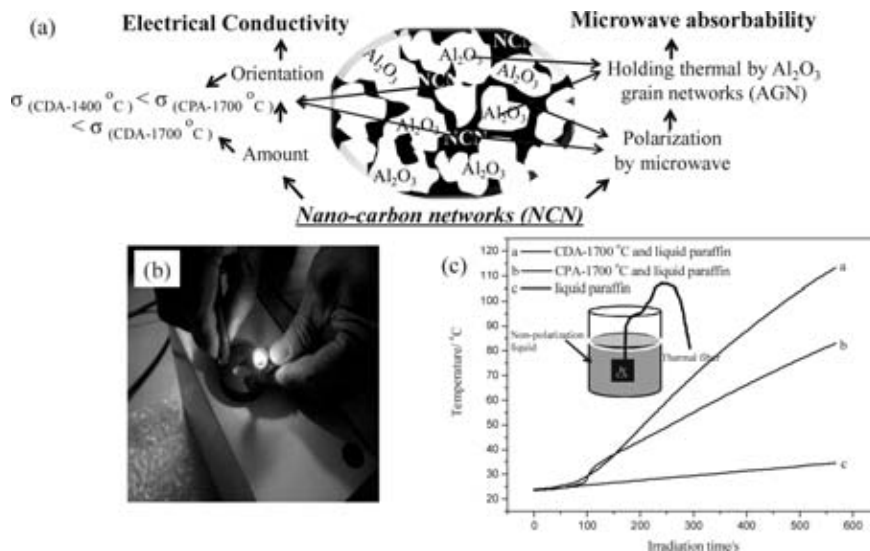

Fig. 4. (a) Schematic diagram of relationship between electrical conductivity and thermal conductivity of CA, (b) Photograph of CA electrical conductivity and (c) Temperature-time curves of CA for liquid paraffin via microwave irradiation

Therefore, there are two forms for CA, namely conductive dense alumina (CDA) and conductive porous alumina (CPA).

Taking the unique structure of CDA and CPA into consideration [21-24], it is reasonable that various potential applications are designed as shown as follows. Because of the good conductivity, structure and property stability, microwave irradiation induced increased temperature of CA was confirmed and various modification ways had been completed. Besides the above suppose, due to the electrical conductivity of CA and high accessible surface area, a novel electro-catalyst employing CPA was also constructed.

2. MICROWAVE-INDUCED HEAT PER-FORMANCE

Conductive alumina (CA) was fabricated by

combination of gel-casting and HTRS in Ar [21-24]. With the aid of HTRS, the polymer networks formed in gel-casting technology were totally converted to nano-carbon networks (NCN), thereby leaving the electrical conductivity of ceramic. The preparing process is proposed in Fig. 1.

Nano-carbon and alumina grains co-exist together as shown in Fig. 2 (a), (b) and (c). More, Raman spectrum also confirms the electronic crystal structure of carbon is graphitic as displayed in Fig. 2 (d) [25-28].

It is noticed that HTRS attributes to the completed conversation of carbon from well gelled polymer networks, thereby forming the nano-graphitic carbon

crosslinks in CA.

Then, it is reasonable to conclude that graphene orientation can be controlled by HTRS.

HTRS effect on graphitic orientation is supposed in Fig. 3. As the increased temperature, polymer is initially converted to amorphous carbon followed by accelerating to graphitic structure. Higher temperature benefits to the improved graphitic orientation, which is verified by the decreased surface defects calculated from Raman spectroscopy analysis ($R_{ID/IG}$ (CDA-1400 °C)=1.26>$R_{ID/IG}$ (CDA-1700 °C)=0.35) [21].

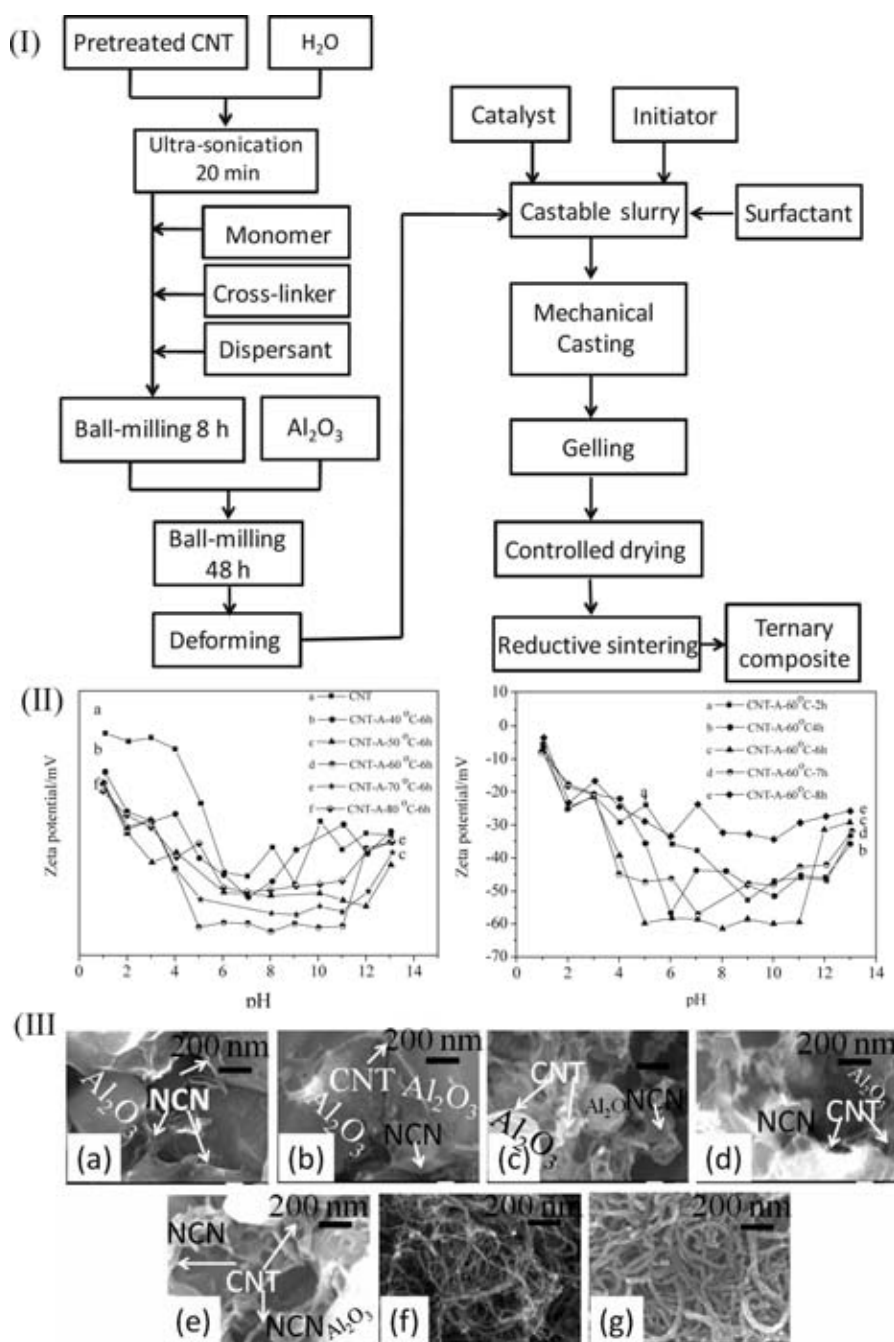Furthermore, besides the good electrical conductivity (Fig. 4 (b)), both CDA and CPA have microwave

Fig. 5. (I) Flow-chat of CNT/CPA[30], (II) Change of CNT by pre-treating[29] and (III) FE-SEM images of CNT/CPA[30]

Fig. 6. Schematic of Pt nanoparticles deposition via different heating methods (EG: Ethylene glycol)

absorbability, which benefits from the graphitic networks in them, which could be confirmed by the increased temperature of detected sample as shown in Fig. 4 (c).

Generally, graphitic structure results in not only conductivity, but also electromagnetic wave absorbability. It is noticed that various properties of CA results from graphitic structure of carbon. Taking the similar graphitic structure of carbon nanotubes (CNT) into consideration, CNT/CPA was developed. The corresponding experimental flow-chat and microstructure of CNT/CPA is shown in Fig. 5 (I) and (III), respectively [29-30].

It is noticed that additive CNT was uniformly dispersed in matrix as shown in Fig. 5 (III), which merits from the surface pre-treatment by concentrated acids [29-30]. CNT co-exist with NCN and alumina forming ternary composite. Comparing with other CNT-based composites prepared by hot press [25], spark plasma [7], sol-gel [26-27, 31] etc., CNT is more uniformly dispersed in ceramic matrix. More, as introduced by Mao et al. [32], microwave absorbability is not only related with electron but also phonon. The increased phonon intensity induced by CNT in composites attributes to this performance. More, Vázquez et al. [20] have reported that CNT with higher impurities owns stronger absorptions than 'perfect' one benefiting from impurities-induced localized superheating and heating performance of CNT is little related with its length.

Generally, the intensified phonon accelerates the increased D intensity leaving the higher heating performances [33].

Furthermore, Wei et al. [34] has claimed that match of absorbers plays an important role for accelerating the electromagnetic wave absorbability and developing various potential applications in many fields. To date, kinds of ferrite/dielectric (Fe_3Al/Al_2O_3, $YBa_2Cu_3O_{7-x}/Al_2O_3$, $FCC-Co/Al_2O_3$, Al_2O_3-coated FeCo, $BA_{0.65}Sr_{0.65}TiO_3$, $(ZnMg) TiO_3$) have been reported [34-39]. It was proven by Suttisawat et al., Pt nanoparticles with uniform distribution was not only catalyst but also good absorbent [40-41]. More, CA also has good heating performance at the irradiation of microwave. Herein, it is possible to design another composite by anchoring Pt nanoparticles via chemical reductive reaction employing CA as substrate. Two heating methods have been conducted. One is conventional oil bath heating, another is microwave-assisted heating. The fundamental experimental mechanism is proposed in Fig. 6.

Benefiting from carbon polarization by microwave radiation, high selective surface modification of porous ceramic with large size was completed.

Structural modification by both employing CNT and surface modification via Pt nanoparticles at the aid of microwave-assisted heating chemical reductive reaction attributed to the enhanced heat performances, which also claimed the potential application of CA as non-
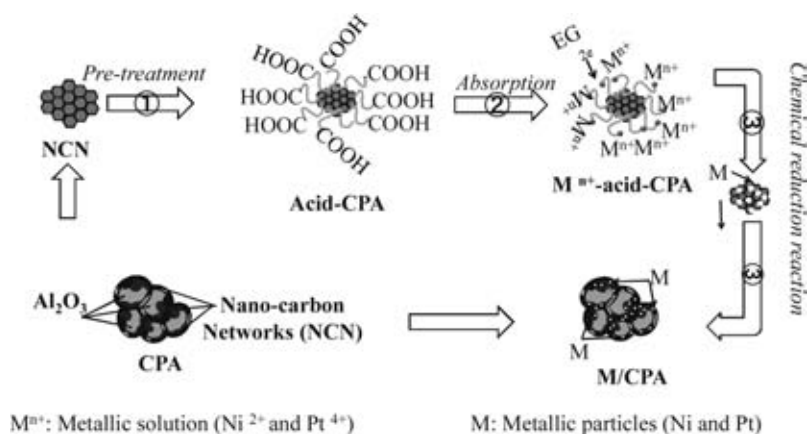
Fig. 7. Schematic representation of preparing M/CPA (Pt/CPA and Ni/CPA) via chemical reductive reaction[46]

touching heater. And the increased heat phenomena results from the intensified phonon signals. This conclusion was valid by Raman spectroscopy.

3. ELECTROCHEMICAL PERFORMANCE EVALUATION

As shown in Fig. 7, the schematic employed in this experiment was proposed. Briefly speaking, three steps were involved for making CPA-based composites M/CPA. (a) Surface pre-treating, by which various surface defects on NCN with graphitic structure are available. These defects include five- or seven-membered rings in the carbon networks instead of normal ring, sp^3-hybridized defects (H or OH) and vacancies in the carbon lattice [27]. Pre-treating of CPA attributes to increased sp^3-hybridized defects (-COOH, -

COH etc.) [42]. (b) Absorption of M^{n+} onto substrate via electrostatic interaction and (c) Chemical reduction of M^{n+} to M particles [46]. More, conventional three-electrode evaluation system was constructed to evaluate the electro-performances of different composites.

Using CPA as reference, it is confirmed that functional particles have been successfully deposited onto the surface of matrix by surface decoration (Fig. 8 (a), (b) and (c)). Comparing with Ni/CPA composite, it is noticed that Pt/CPA has higher selectivity. The electro-performances of as-resulted composites have been evaluated in 1 M NaOH solution at the same experimental condition. The enhanced performance of pre-treated CPA is attributed to grafted functional groups by covalent modification [28]. As-received and pre-treated CPA display electro-catalytic activities
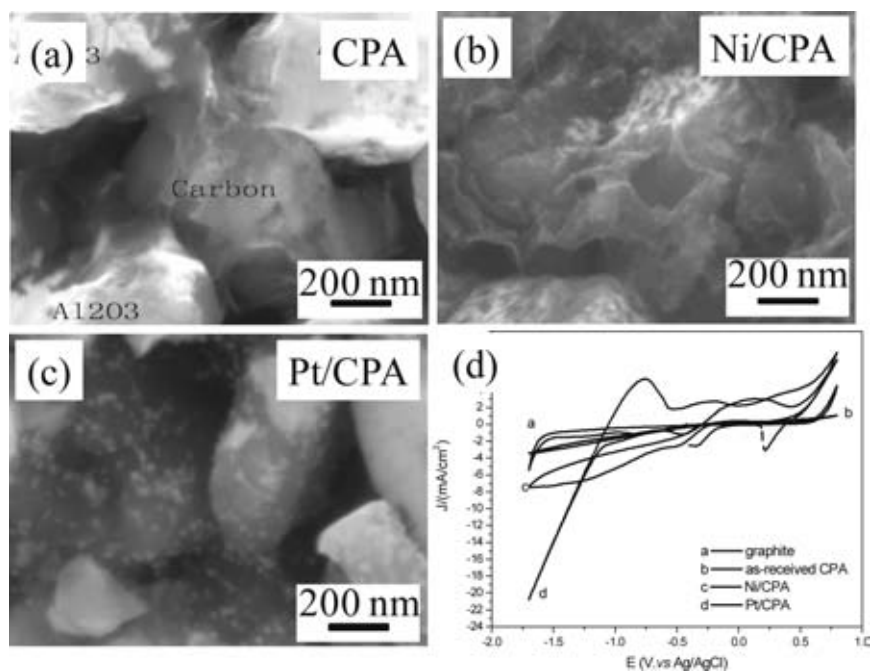

Fig. 8. FE-SEM images of (a) CPA, (b) Ni/CPA and (c) Pt/CPA and (d) Cyclic voltammetric (CV) curves of different electrodes developed in this study[45-46]

toward oxygen reductive reaction (ORR), which can be proven by similar slopes of the reductive current with decreasing potential from -0.3 V to -0.2 V. Moreover, ORR occurred at potentials of -0.1 V~+0.4 V for Pt/CPA (Fig. 8. (d)). It is believed that the ORR activity of the Pt/CPA at more positive potentials is attributed to Pt (5-d orbital vacancies) nanoparticles deposition. And the enhanced performance of Pt/CPA can be verified by the increased current and enlarged time window as shown in Fig. 8 (d). Meng et al. [42] reported the ORR activity of Pt/C at potentials of +0.7 V. Pt/CNT/CHIT was also claimed to be ORR activity electro-catalysts at the same measurement condition and the ORR activity occurred at +0.1 V. Then, by surface modification, it was confirmed in this study that as-fabricated composites have a potential application in fuel cells [43-46]. Based on the features of substrate, different surface modification schematics have been proposed in Fig. 6 and Fig. 7.

4. POTENTIAL APPLICATIONS OF CA WITH MODIFICATIONS

Since good electrical conductivity, micro- structure and enhanced performances of CA via modifications, various attractive wide- spread potential applications ranging from heater [1-5], decomposition [47] and transfer hydrogenation (TH) process [48] etc. are designable. Subsequently, in this section, we will briefly introduce the different application directions of CA as shown in followings.

a. Non-contacting Heater Application

Even though microwave absorbents display intriguing characteristics in many fields [47-49], microwave transparent materials are limited in this field. To date, SiC was reported to good heaters by Kremsner et al. [50] Therefore, due to the graphitic carbon, CA and CA-based composites are available as non-contacting heater for microwave inert medium.

b. Decomposition and hydrogenation application

Pt/substrate composites combining the advantages of matrix and uniformly dispersed Pt nanoparticles permits the possibility for organic decomposition at the aid of different method such as electrochemical evaluation [51], electromagnetic wave radiation [52] or ultra-high-vacuum (UHV) [53] etc. More, according to the varied reaction mechanisms, different reaction routes with high selectivity are accessible. Herein, because of the microwave capacity of CA, TH or decomposition or combination utilizing CA or Pt/CA as heater and

catalyst at the microwave radiation is reasonable.

c. Electro-catalyst application

Commonly, conductor and semi-conductor are regarded as idea electrode materials as introduced in references [44,46,51,54-55]. Therefore, considering the electrical conductivity of CA and related CA composites, they are believed as electrode candidates with high-performance. It is significant to explore a novel electro-catalyst by kinds of surface modification for different practical applications.

5. CONCLUSIONS

In this review, characteristic, property and influence factors of CA with two forms (dense (CDA) and porous (CPA)) have been demonstrated. Meriting from conductivity and property stability of matrix, various widespread potential applications are accessible for us. In order to gain the improved performances of composites, both structural and surface modifications have been conducted. Eventually, as-prepared composites can be designed as non-contacting heater, decomposition, TH and electro-catalyst etc.

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