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Electrochemical properties of polyaniline composite electrodes prepared by in-situ polymerization in titanium dioxide dispersed aqueous solution

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ABSTRACT

Polyaniline (PANI)/titanium dioxide (TiO_2) composites were prepared by a chemical oxidation polymerization. The composites were prepared with various amount of TiO_2 to find a relation between electrochemical properties of composites and compositions of TiO_2 and PANI in the composites. PANI/TiO_2 composites which had PANI as a shell and TiO_2 as a core part of the composites were successfully synthesized. Fiber-like PANI was also observed within the composites. The synthesis was explained as two stages of polymerization. First stage is a polymerization reaction occurred by a strong oxidative potential of TiO_2. Second stage is started by adding ammonium peroxydisulfate in reaction solution. Diameters of aggregations of the composites increased with the added amounts of TiO_2. The composite prepared with 10 wt.% of TiO_2 per aniline monomer weight showed the highest capacitance of 784 F g^{-1} among the prepared composites. But the composites prepared with excess amounts of TiO_2 showed lower capacitance than the highest one. The lower capacitances of the composites prepared with excess amounts of TiO_2 was considered as related with the diameters of the aggregations. The composites prepared with excess amounts of TiO_2 had large diameters for the aggregations. The TiO_2 particles in the core of composites that had large diameter are hard to participate in electrochemical reaction due to a long pathway from electrolyte to TiO_2 core and a blocking effect by outer TiO_2 particles.

1. Introduction

Supercapacitors could be used for various applications such as an energy source of electric vehicles, support for fuel cells, portable computers and cellular devices due to their higher power density, larger energy density and longer cycle performance than conventional dielectric capacitors [1,2]. Supercapacitors store electric energy by redox reactions of active materials. Conducting polymer and metal oxide are representative materials for electrode materials of supercapacitors.

Conducting polymers have unusual electronic properties such as high electrical conductivity, low energy optical transitions, low ionization potential and high electron affinity due to their π-electron backbone structure [3]. Among the conducting polymers, polyaniline (PANI) is the most promising one due to its good electrical, electrochemical, and optical properties, low cost of monomer, simple synthesis process and environmental stability [4,5]. Structural degradation caused by volume change during charge–discharge cycles is a limit of PANI applications. On the other hand, titanium dioxide (TiO_2) has received an attention due to its good stability, environmental friendliness, and structural stability during charge–discharge cycles, and long cycle life [6–9]. However, TiO_2 is a dielectric material, and it has lower specific capacity [6,10].

PANI/TiO_2 composites could provide an improved performance and a synergetic effect caused by interactions between them [11]. Many researchers successfully reported moderated electrochemical properties of PANI/TiO_2 composites compared to pristine PANI and TiO_2 particles [12]. PANI is usually known as p-type semiconductor polymer, and TiO_2 is known as n-type semiconductor [13]. PANI and TiO_2 can act as electron donor and acceptor pairs [14]. The amorphous polymer in the composites can act as a buffer layer at the high discharge rate, and this can provide excellent high-rate performance [15]. PANI/TiO_2 composites show large discharge capacity [7], improved electrical conductivity [16], large dielectric constant [12], large photocatalysis properties [17] compared to pristine PANI and TiO_2. PANI/TiO_2 composites could be used as electrode materials of supercapacitors, photocatalysts, and light active materials in solar cells [1,11]. Synthesis of PANI/TiO_2 composites have been reported with various methods such as in situ polymerization, ultrasonic irradiation, and sol–gel method [18]. However,

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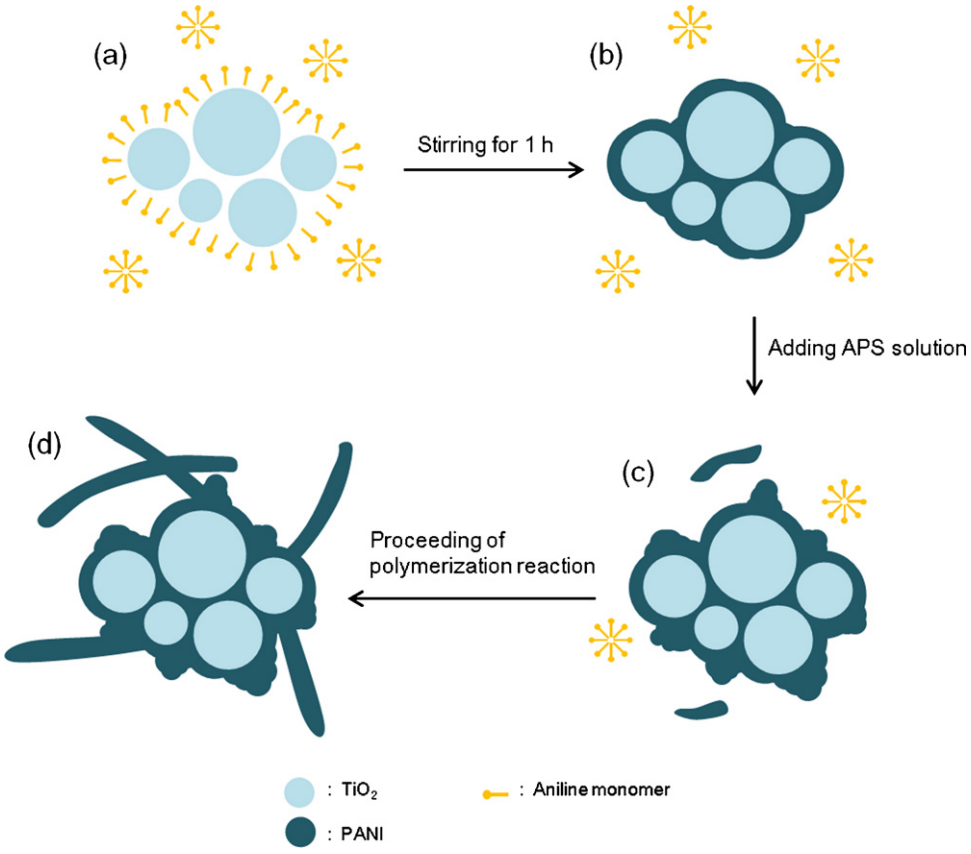

Fig. 1. Scheme of synthesis of PANI/TiO_2 composites.

a relation between the compositions of PANI and TiO_2 in the composites has not been fully investigated, to our best knowledge.

In this study, PANI/TiO_2 composites were prepared with the presence of anatase TiO_2 by a chemical oxidation polymerization of aniline monomer. Diverse amounts of TiO_2 were added to prepare the composites that have various weight percent of TiO_2. The structural and electrochemical properties of the prepared composites were characterized, and the relation between the structural and electrochemical properties was studied. Another objective of this research is to determine an optimum weight percent of TiO_2 in the composite to have the largest capacitance.

2. Experimental

2.1. Chemicals

Aniline (99.5%, monomer), anatase TiO_2 (under 325 mesh), and ammonium peroxydisulfate (APS) were purchased from Sigma–Aldrich, USA. Hydrochloric acid (HCl, 35%) was obtained from Deajung Chemical, Korea. All reagents were used as received without further purification.

2.2. Synthesis of PANI/TiO_2 composites

Various amounts of anatase TiO_2 were added in 150 mL of 1 M HCl solutions, and sonicated for 10 min for homogeneous dispersion. The added amounts of TiO_2 were calculated to be 5, 10, 15, and 20 weight percent (wt.%) per weight of aniline monomer. The HCl solutions containing TiO_2 were cooled, and remained temperature below 5 °C. The solution was stirred for 1 h. 2.5 mL of aniline monomer was added to above solution, and stirred for another 1 h. 50 mL of ASP solution (0.625 g of APS dissolved in 50 mL of distilled water) was added dropwise to the solution. The polymerization reaction was carried out for 24 h with vigorous stirring. Reaction system was kept under 5 °C during the polymerization reaction. Precipitates were filtered and washed with ethanol and distilled water several times. The obtained precipitates were dried in oven at 45 °C for 24 h.

Pristine PANI was synthesized by a chemical polymerization reaction. The synthesis process is similar with the preparation of PANI/TiO_2 except that TiO_2 were not added this time.

2.3. Characterization

Surface morphology of PANI/TiO_2 composites was observed by scanning electron microscopy (SEM, HITACHI S3500N) and transmission electron microscope (TEM, HITACHI MODEL H-7600). Practical weight ratios of TiO_2 in the composites were analyzed with electron probe micro analyzer (EPMA, CAMECA SX-100). An accelerating voltage was 15 keV, and beam current was 20 nA. Beam size was 50 μm, and peak time was 10 s. Structural properties of the composites were observed with X-ray diffractometer (XRD, PHILIPS X'Pert-MPD System) with Cu K_α radiation. Cyclic voltammograms were obtained by using Potentiostat/Galvanostat, IVIUMSTAT at ambient temperature using a 0.5 M H_2SO_4 electrolyte with a three electrode system. Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively. Working electrode was prepared from a slurry containing 5 wt.% of poly(vinylidene fluoride) (PVdF) binder and 85 wt.% of prepared PANI/TiO_2 composites. 10 wt.% of carbon black was added as conductive material. *N*-methylpyrrolidone (NMP) was used as organic solvent, and the slurry was coated onto a glassy carbon and dried.