

MIL-125 (Ti) derived TiO₂ Nanoparticles Confined Carbon Skelton for Supercapacitor Application

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Abstract

“Nanoporous carbon are gaining their interest for the energy storage application due to their high surface area and chemical stability. Here we synthesized TiO₂/C composites through the pyrolysis of MIL-125 (Ti). The obtained sample further characterized with XRD and BET. Further cyclic voltammetry and galvanostatic charge discharge was done to investigate the electrochemical performance or supercapacitor application. It can deliver a high specific capacitance of 311.38 F/g at the current density of 1 A/g.”

1. Introduction

To overcome the losses done by the non-renewable energy sources such as fossil fuels, scientists and the researcher has shown their immense interest toward the renewable sources of energy¹. The ongoing research for the development of efficient energy storage devices mostly includes supercapacitor. Supercapacitor are the device work on the separation of charges present in electrolyte and the involvement of redox reactions on applying a potential. The low-cost material and high cyclic stability of supercapacitor can fulfil the commercialization and market demand. Recently carbon materials are emerging as a supercapacitor electrode material due to their high chemical stability and porosity². However, carbon material only involves the adoption of ions leads to the low energy density. To improve the energy density of the supercapacitor, many researchers are using composites of carbon with redox active species. However, these composites involve the stability issues.

Herein, we report the demonstration of MIL-125 (Ti) derived TiO₂/C composites through the pyrolysis of MIL-125 in an argon flow at the temperature of 600°C. The presence of TiO₂ nanoparticles in the carbon matrix provide the redox activity during charging discharging process which further leads to high energy density. Moreover, nanoporous carbon provide high surface area as well as act as a conductive layer for the fast electron transfer.

2. Experimental Setup

Materials

Benzene-1,4-dicarboxylate (1,4-BDC) and titanium tetra-n-butoxide were purchased from Sigma Aldrich, India. Solvents like dimethylformamide (DMF), and Methanol were purchased from Merck, India. Polyvinylidene fluoride (PVDF) and acetylene black were purchased from Himedia, India.

Synthesis

MIL-125 (Ti) was synthesized through one step hydrothermal reaction. Briefly, 2.4 mL of titanium tetra-n-butoxide and 2 g of 1,4-BDC were mixed into a solution mixture of 36 mL of DMF and 4 mL of methanol. After stirring for 1h the solution was transferred to Teflon lined stainless steel autoclave kept at 150°C for 24h. The obtained yellowish precipitates were centrifuged at 8000 rpm for 10 min with subsequent washing of DI and methanol for 4 times. The obtained MIL-125 (Ti) was dried at 70°C overnight in a vacuum oven.

Further MIL-125 was pyrolyzed at 600°C under the argon flow. The furnace was heated at the rate of 5°C per minute and then hold at 600°C for 4h. Then the furnace cooled at the ramp of 5°C per minute. The obtained black powder stirred in 2M HCL solution to remove the unreacted Ti metal and other impurities. Finally, the solution was filtered with 0.22µm filter paper and then washed with DI until the overall pH becomes 7. The obtained TiO₂/C composites dried at 70°C in a vacuum oven overnight.

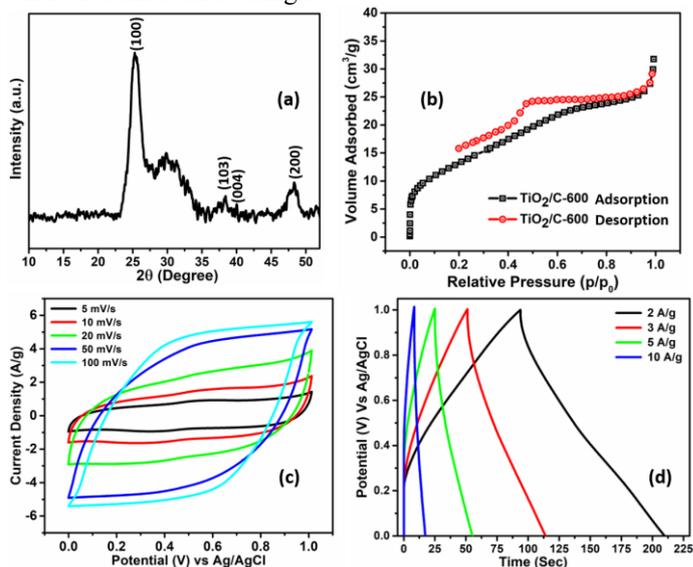


Fig. 1 (a) XRD spectrum of as prepared TiO₂/C composites; (b) N₂ adsorption-desorption isotherm of TiO₂/C composites; (c) Cyclic Voltammetry and (d) Galvanostatic charge-discharge of TiO₂/C

3. Result and Discussion

Structural and surface area analysis

TiO₂/C composites was synthesized from the pyrolysis of MIL-125 (Ti) at 600°C in argon flow. The obtained sample

was characterized with XRD to investigate the final structure and phase. The XRD pattern of the obtained TiO₂/C composites is given in the **Fig 1a**. All the peaks are well matched with the literature. All the XRD peaks are identified as the anatase phase of TiO₂ indexed as (100), (103), (004) and (200)³. The characteristic peak of the carbon at 24° has been merged with the characteristic peak of TiO₂ at 25.2°C. The anatase of the TiO₂ is more conductive than their rutile phase and hence can provide better pathways for electrons. Further surface area of the material is the crucial parameter while dealing with the specific capacitance of the electrode material. The specific surface area of TiO₂/C composites was investigated through the N₂ adsorption-desorption isotherms as shown in **Fig 1b**. TiO₂/C-600 adsorption desorption curve suggests a typical type I sorption behaviour with almost negligible hysteresis loop which demonstrates the presence of micropores with possibly narrower mesoporous structure of the sample⁴. The presence of both micro and meso pores in the sample can effectively provide better storage and transport of electrolyte ions via shorter diffusion paths. The calculated specific surface area of the TiO₂/C was found to be 48.16 m²/g with a pore volume of 0.0468 cm³/g.

Table I Comparison with previous reported carbon and composites

Sample	Current Density	Specific Capacitance (F/g)	References
TE-MOF-5 derived NPC	0.25 A/g	271	5)
MOF-2 derived NPC	1 A/g	170	6)
Zn-BTC derived NPC	1 A/g	134	6)
rGO/TiO ₂ NPs	0.12 A/g	62.8	7)
MIL-125 (Ti) derived TiO ₂ /C	1 A/g	311.38	This work

Electrochemical Studies

The TiO₂/C was further used to investigate the electrochemical performance through cyclic voltammetry (CV) and galvanostatic charge discharge curve in 1 M H₂SO₄. The CV was performed at various scan rates (5-100 mV/s) with in a potential window of 0-1 V as shown in **Fig 1c**. The almost rectangular curve demonstrates the fast ion transport and EDLC behaviour particularly due to the presence of carbon. Additionally, the presence of small redox peaks at lower scan rates demonstrates the redox activity of TiO₂ nanoparticles in the pores of carbon. Thus, the presence of both EDLC and redox behaviour give rise to high energy and power density. Further, for the practical potential of the electrode material, galvanostatic charge discharge was done at various current density as shown in **Fig 1d**. the pattern of the discharge curve was almost linear with small potential drop indicates the low internal resistance. The highest value of specific capacitance was estimated to 311 F/g.

4. Conclusions

The work has demonstrated simple way to synthesize TiO₂/C composites. The as synthesized TiO₂/C composites exhibit the presence of micropores as well as mesopores which is responsible for the better ion diffusion and adsorption. The as synthesized electrode material delivers the specific capacitance of 311.38 F/g at the current density of 1 A/g. the synergy between the carbon and TiO₂ demonstrate their potential as an electrode for the futuristic supercapacitor application.

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