



Controlled deposition of covalently bonded tantalum oxide on carbon supports by solvent evaporation sol–gel process

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ABSTRACT

A simple strategy for covalently attaching Ta₂O₅ particles onto functionalized graphitic carbon supports has been developed to fabricate hybrid nanocomposites. In this process, tantalum ethoxide was directly reacted with functional groups on the carbon surface to form covalent bonding, which caused the carbonyl stretches of the carbon supports to be blue-shifted to 50–70 cm⁻¹ after Ta₂O₅ particle deposition. Homogeneously deposited Ta₂O₅ particles on the carbon supports have been studied by X-ray diffraction (XRD), FT–IR spectroscopy, scanning electron microscopy (SEM), and transmission electron microscope (TEM).

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1. Introduction

High surface area carbon materials with graphitic nature have attracted intensive research focuses due to their possible applications in the areas of adsorbents, catalyst supports, electrode materials, and energy storage media [1,2]. Main studies have been focused on the control of the nanostructures of porous carbons including, surface area, pore size, and nature of the carbon framework, to meet the particular requirements of specific applications [3,4]. Furthermore, many studies have been focused on depositing metal or metal oxide on the carbon surface [5]. However, chemical inertness and poor solubility of carbon materials essentially make it very difficult to modify surface functionality. Therefore, in order to establish a uniform coverage of metal or metal oxide nanoparticles on the surfaces of the carbon materials, it is necessary to activate the surfaces. Usually, the surfaces of the carbon materials can be functionalized using different acid treatments [6,7] or plasma [8] to create carboxylic, carbonyl, and hydroxyl groups that are able to kind different nanomaterials.

Tantalum oxide (Ta₂O₅) has recently attracted much attention due to its possible enhancement of activity and selectivity in the selective oxidation of hydrocarbons on various oxide catalysts [9]. Ta₂O₅ has been also widely used as a key material of antireflective coating layer, impedance under high temperature, capacitor due to its high reflective index, high chemical stability, and high dielectric constant [10]. Ta-based porous mixed oxides have been recently found to be highly active for water decomposition under UV irradiation [11,12]. Mesoporous Ta₂O₅ has been extensively synthesized by the ligand-assisted templating method for its pho-

tocatalytic application [13]. However, the ordered mesopore network was easily collapsed under low calcination temperature [14].

In this work, we demonstrate a facile one-step method for fabricating Ta₂O₅/carbon hybrid composite materials, where Ta₂O₅ particles are homogeneously distributed on carbon supports, through covalent interaction as shown Scheme 1. The strategy demonstrated that combined sol–gel process with solvent evaporation process is effective for the formation of Ta₂O₅, which was covalently bonded onto carbon surface. Electron microscopes techniques and FT–IR are the key techniques to observe surface morphologies and chemical bonding of Ta₂O₅ particles on the carbon surface.

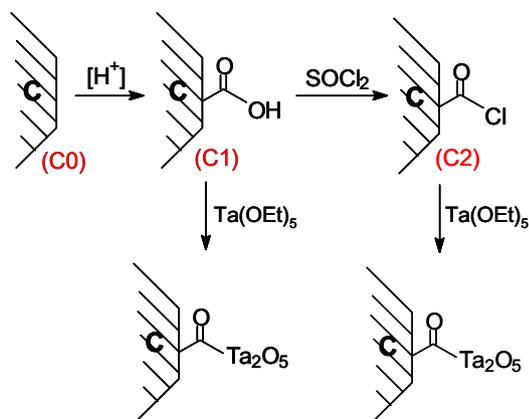
2. Experimental

Tantalum ethoxide [Ta(OEt)₅] and thionyl chloride (SOCl₂) was purchased from Aldrich Chemical Co. and carbon nanoparticle (30 nm) was procured from Asbury Carbons (Grade #: 5345R). The carbon sample (C0) was dispersed in a mixture of concentrated nitric acid and sulfuric acid (5:3 vol. ratio) and refluxed for 1 h. The sample was repeatedly washed with deionized water until the solution reached a pH value of 7. The filtered carbon solid was dried under vacuum for 24 h at 70 °C. Dried carboxylate-functionalized carbon (C1) was suspended in SOCl₂ and stirred for 24 h at 70 °C. The solution was filtered, washed with anhydrous THF, and dried under vacuum at room temperature (C2).

For direct synthesis of Ta₂O₅ on carbon supports, to 2.0 g of either C0 or surface modified carbons (C1 or C2) dispersed in 20 mL of ethanol, different amounts of Ta(OEt)₅ (8, 4, 2, or 1 mL, *d* = 1.57) were added, and stirred overnight at room temperature. EtOH retards rapid hydrolysis and condensation of Ta(OEt)₅ to form Ta₂O₅ on the carbon surface because EtOH stabilizes Ta(OEt)₅.

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Scheme 1. Covalent attachment of Ta_2O_5 on the carbon surface to form $\text{Ta}_2\text{O}_5/\text{C}$ composites.

The remaining ethanol was eliminated at 60°C under vacuum overnight. Each sample was ball-milled for 15 min (Spex Mill).

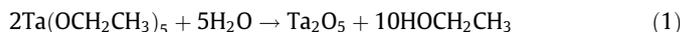
X-ray diffraction (XRD) patterns of each sample were obtained on a Philips X'ert MPD X-ray diffractometer using Cu K (1.54059 \AA) radiation with the X-ray generator operating at 45 kV and 40 mA. For FT-IR analysis of the samples, a very thin transparent KBr pellet containing the dried composites was prepared and the spectra were obtained on a Nicolet 5040 FT-IR spectrometer. A pure KBr pellet was used as a reference background and was subtracted from the FT-IR spectra of the $\text{Ta}_2\text{O}_5/\text{carbon}$ samples. Microstructural analysis was performed using a scanning electron microscope (SEM, JEOL JSM-5900LV) equipped with an Oxford energy dispersive X-ray spectrometry (EDX) system. TEM images were obtained on a JEOL JEM 2010 microscope. For TEM analysis, the composite samples were mixed with ethanol and placed onto a copper grid and subsequently air-dried under ambient conditions.

3. Results and discussion

3.1. Ta_2O_5 formation on functionalized carbon supports

First of all, we have tried the synthesis of nanocrystalline mesoporous Ta_2O_5 through dodecylamine (DDA)-assisted sol-gel process. Crystalline- Ta_2O_5 formation temperature of amorphous Ta_2O_5 is 625°C [12]. However, mesoporous network started to collapse at 400°C and completely collapsed at 500°C due to significant particle growth through agglomeration. Therefore, the pores mainly exist between the particles at high temperature, and low surface areas are available ($40\text{--}80\text{ m}^2/\text{g}$). On the other hand, direct reaction between functionalized carbon and $\text{Ta}(\text{OEt})_5$ followed by controlled hydrolysis leads to a dispersion of Ta_2O_5 nanoparticles

on the carbon surface. Ta_2O_5 was synthesized by slowly reacting $\text{Ta}(\text{OEt})_5$ with functionalized carbon dispersed in EtOH. Through slow evaporation of the solvent, $\text{Ta}(\text{OEt})_5$ hydrolyzes and condenses to form well-dispersed Ta_2O_5 nanoparticles on the carbon support (Eq. 1). The remaining solvent adsorbed on the carbon support was eliminated by vacuum drying.



3.2. XRD and FT-IR spectroscopic measurements

The functionalized carbon materials were characterized by XRD and FT-IR spectroscopy as shown in Fig. 1. The commercial carbon material (Asbury 5348R) showed semi-crystalline structure (carbon onion) and the two broad reflections at $2\theta = 26.56$ and 44.61° , which are attributed to (002) and (101) diffractions. The (004) diffraction peak at 54.74° is very weak. Although the acid treatment considerably reduce the chemical structure due to the introduction of large number of defects, and may even result in the breaking into pieces, this phenomenon can be avoided by shortening the carbon exposure in the acid treatment. The structures of our carbon supports were mainly maintained after acid treatment (1 h) under refluxing. The presence of two absorption bands of the commercial carbon (C0) at 3400 and 1682 cm^{-1} are -OH and carbonyl (C=O) groups. After acid treatment, the carbon sample showed the same absorption peaks. However, after acylation process, the C=O stretching vibration was shifted to 1720 cm^{-1} due to the formation of chlorocarbonyl (COCl) group on the C2 surface (Fig. 1b).

After direct deposition of Ta_2O_5 particles on the functionalized carbon supports upon stirring followed by slow solvent evaporation process, the carbonyl band shifts for the samples with different ratios of $\text{Ta}_2\text{O}_5/\text{C}$ were investigated as shown Fig. 2. Fig. 2a shows the samples with high weight ratios (>1.0) of $\text{Ta}_2\text{O}_5/\text{C}$ and Fig. 2b shows samples with low weight ratios (<1.0) of $\text{Ta}_2\text{O}_5/\text{C}$. The characteristic absorption bands around 680 cm^{-1} are due to stretching vibrations of Ta-O bonds [15]. Ta-O bands can be clearly observed for the samples with high ratios (>1.0) of $\text{Ta}_2\text{O}_5/\text{C}$ (Fig. 2a), but it is very weak for the samples with low ratios (<1.0) of $\text{Ta}_2\text{O}_5/\text{C}$ (Fig. 2b). The carbonyl stretching vibrations of $\text{Ta}_2\text{O}_5/\text{C}$ samples were blue shifted from $1720\text{--}1682\text{ cm}^{-1}$ to $1660\text{--}50\text{ cm}^{-1}$ after the synthetic process (Hooke's law), indicating the formation of covalent bonds between carbon samples and Ta_2O_5 (Table 1) [16].

3.3. Microscopic investigation

Fig. 3 displays SEM images of $\text{Ta}_2\text{O}_5/\text{C}$ samples, which directly shows the morphology and size distribution of Ta_2O_5 particles on

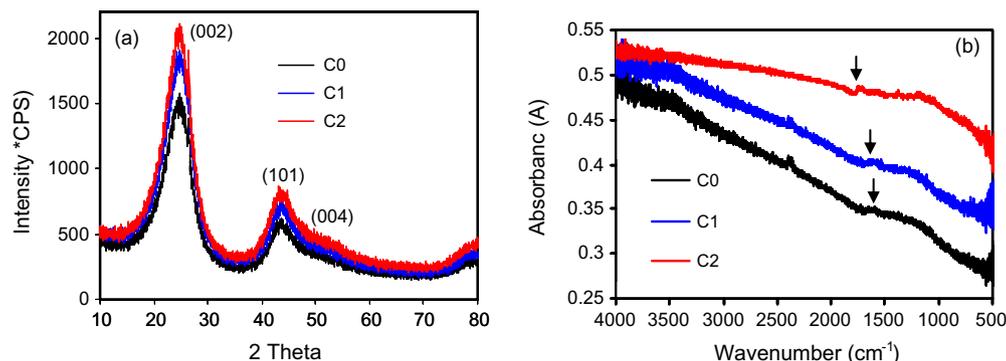


Fig. 1. (a) XRD patterns and (b) FT-IR spectra of commercial (C0) and functionalized carbon supports with COOH (C1) and COCl (C2).

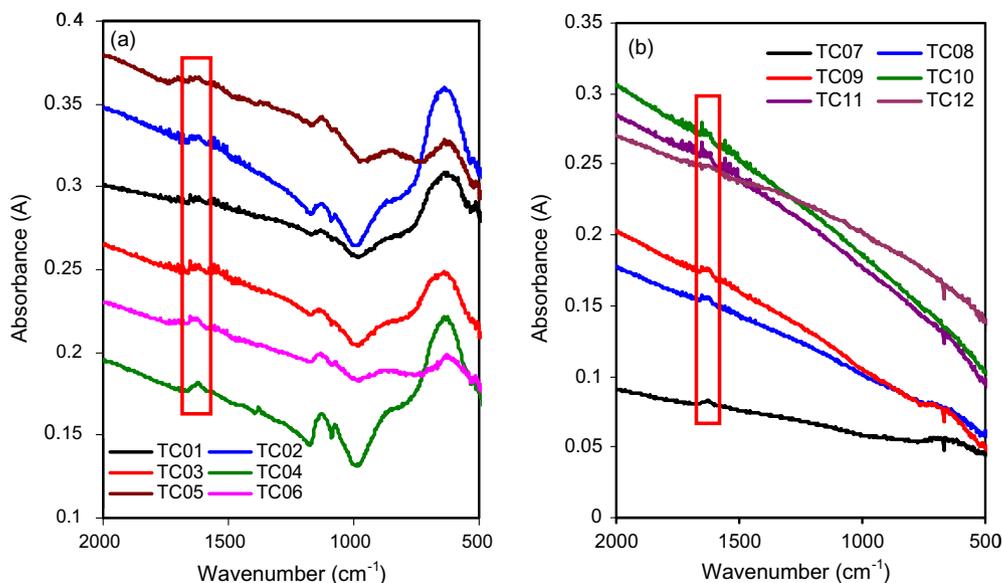


Fig. 2. FT-IR spectra for Ta_2O_5 -carbon samples with high ratios (>1.0) (a) and low ratios (<1.0) (b) of $\text{Ta}_2\text{O}_5/\text{C}$. The red rectangle indicates carbonyl stretching vibration peaks.

Table 1
The C=O vibrational frequencies for $\text{Ta}_2\text{O}_5/\text{C}$ composites.

Sample	Composition	$\text{Ta}_2\text{O}_5/\text{C}$ (wt. ratio)	Carbonyl vibration (cm^{-1})
TC01	$\text{Ta}(\text{OEt})_5 + \text{C0}$	1.71	1655
TC02	$\text{Ta}(\text{OEt})_5 + \text{C0}$	3.42	1655
TC03	$\text{Ta}(\text{OEt})_5 + \text{C1}$	1.71	1650
TC04	$\text{Ta}(\text{OEt})_5 + \text{C1}$	3.42	1655
TC05	$\text{Ta}(\text{OEt})_5 + \text{C2}$	1.71	1653
TC06	$\text{Ta}(\text{OEt})_5 + \text{C2}$	3.42	1653
TC07	$\text{Ta}(\text{OEt})_5 + \text{C0}$	0.85	1653
TC08	$\text{Ta}(\text{OEt})_5 + \text{C0}$	0.43	1655
TC09	$\text{Ta}(\text{OEt})_5 + \text{C1}$	0.85	1651
TC10	$\text{Ta}(\text{OEt})_5 + \text{C1}$	0.43	1662
TC11	$\text{Ta}(\text{OEt})_5 + \text{C2}$	0.85	1655
TC12	$\text{Ta}(\text{OEt})_5 + \text{C2}$	0.43	1660

the functionalized carbon surface. In the first three samples (Fig. 3a–c), Ta_2O_5 particles are seen as dense aggregates. Ta_2O_5 particles are easy to aggregate each other on C0 and C2 surface (Fig. 3a

and c) because the commercial C0 may not be fully activated and the adsorbed trace of SOCl_2 on C2 may interrupt the homogeneous distribution of Ta_2O_5 particles. Fig. 3c–f shows Ta_2O_5 particles with different $\text{Ta}_2\text{O}_5/\text{C}$ ratios on C1 surface, revealing that Ta_2O_5 nanoparticles are quite homogeneously distributed on the surface of C1. The well-distributed Ta_2O_5 particles deposited onto the carbon supports demonstrate that the acid treatment is effective, where Ta_2O_5 particles are homogeneously deposited onto active sites of the carbon surface. Fig. 4 shows high-resolution TEM images of TC10, where Ta_2O_5 particles are homogeneously deposited through the concentric graphitic layers of carbon onion supports without dense aggregates. Ta_2O_5 is not crystalline in this room temperature process. TEM investigation reveals that the direct synthetic process can be very effective to overcome the problem of particle aggregation on the carbon and carbon nanotubes, which is a typical disadvantage in the combination process of particles and carbon supports under heating.

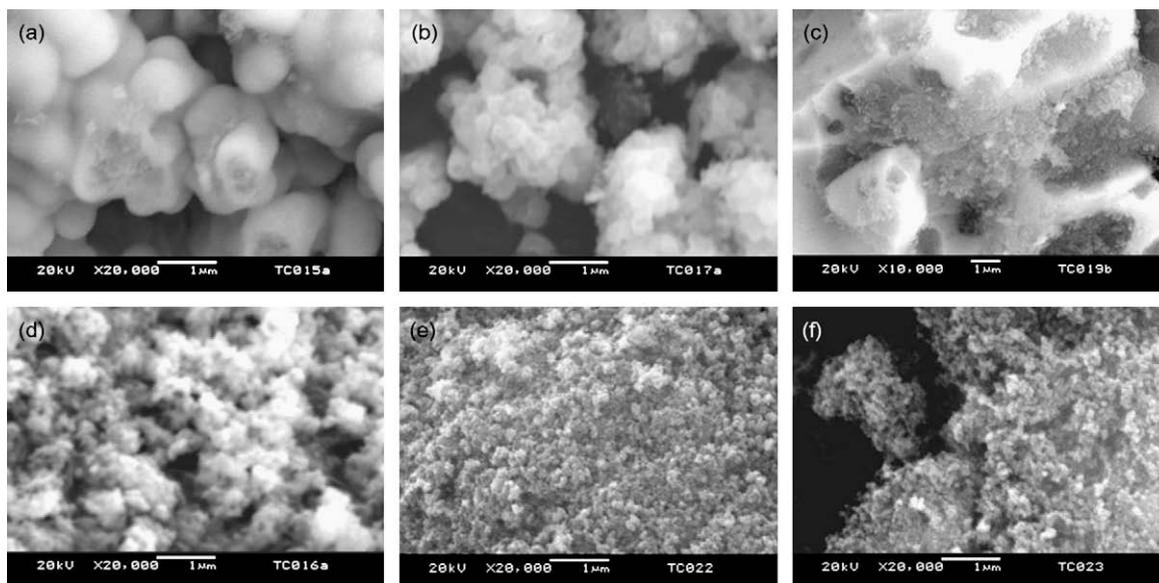


Fig. 3. SEM images of covalently bonded Ta_2O_5 on functionalized carbon surface: (a) TC02, (b) TC04, (c) TC06, (d) TC03, (e) TC09, and (f) TC10.

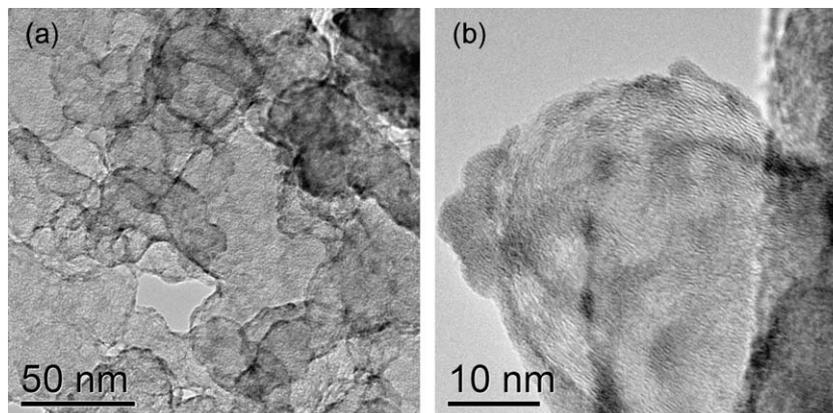


Fig. 4. High-resolution TEM images for TC10.

4. Conclusion

We have developed a facile and effective method for the synthesis of Ta₂O₅/carbon composites by covalent interaction. The covalent attachment of Ta₂O₅ on the carbon supports has been demonstrated by the FT-IR spectroscopy. The homogeneous deposition of Ta₂O₅ particles onto the carboxylate-functionalized carbon supports has been also demonstrated by SEM and TEM investigation. More work under way to extend this method to attach Ta₂O₅ nanoparticles on other crystalline carbon supports. Surface functionalization of carbon supports by other surface functional groups and surface charges, and catalytic applications are also under way. This methodology can open up new possibilities in areas of nanoelectronics, chemical sensing, catalysis, and field-emission displays.

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