**TiO$_2$-coated Ordered Mesoporous Carbon for Phenol Photodegradation**

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Carbon nanotubes, fullerenes and mesoporous carbon structures constitute a new class of carbon nanomaterials with properties that differ significantly from other forms of carbon such as graphite and diamond. The ability to custom synthesize mesoporous carbon with tailored properties has opened up new avenues to design high surface area catalyst supports and materials with high photochemical activity. The photochemical properties of mesoporous carbons facilitate modulation of their charge transfer properties and aid in the design of photocatalysts for phenol degradation. Therefore, we demonstrate an enhanced photocatalytic activity for TiO$_2$ when it is dispersed on ordered mesoporous carbon material.

**Keywords:** mesoporous carbon (MC), photocatalyst deposition, phenol photodegradation

Recently, due to their electronic and mechanical properties, ordered mesoporous carbon materials were used as support materials for the integration of photocatalytic materials to build blocks into novel nanostructure architectures [1,2]. A broad range of applications for these innovative materials with different desirable characteristics, such as energy conversion/fuel storage, catalysis, biotechnology, optoelectronic nanodevices, etc. have been reported [3]. Due to their electronic properties, stability, surface chemistry, and textural properties, nanocarbons are used as supports for photocatalytic materials. A method for enhancing the photocatalytic activity of a photocatalyst is to use an ideal support material, which can increase its effective surface area. When a photocatalyst is supported on ordered mesostructured carbon, an enhanced photocatalytic activity is observed for phenol photodegradation [4]. The improved activity was attributed to the reversible adsorption of phenol on the hydrophobic sites of the carbon support.

With the discovery of photoinduced charge transfer between a photocatalyst as donor and carbon materials as acceptor [2, 3], carbon-based donor–acceptor architectures have been successfully fabricated as photochemical energy conversion systems with the aim of increasing photoresponses of photocatalysts [5].

In this work, we used an ordered mesoporous carbon (labeled in this work as MC) [6] with excellent mechanical stability, high specific surface area, large pore volume and adjustable pore size that showed a faster electron transfer rate and larger current response compared to carbon nanotubes. This behavior is due to the presence of edge-plane-like defect sites, which makes the electron transfer easier [7]. So, the MC is an ideal material for photogenerated electron scavenging due to the multiple graphene layers where electrons can flow through the interface of graphitized carbon when it is in contact with a photocatalyst.

There are some photocatalysts that can be used in the photocatalytic processes, such as TiO$_2$, V$_2$O$_5$, SnO$_2$, WO$_3$, Fe$_3$O$_4$, CeO$_2$, ZnO, and ZnS [8, 9]. Due to its stability, nontoxicity, and broadly defined goal of efficiently detoxifying hazardous organic pollutants, TiO$_2$ has been studied extensively over the last two decades [10]. As well known, phenolic compounds are common persistent organic contaminants, which show low biodegradability, posing serious risks to the environment once discharged into natural waters [11].

Highly dispersed TiO$_2$ anchored on ordered mesoporous carbon by impregnation method showed high photocatalytic activity for the decomposition of phenol compared with that of TiO$_2$ Degusa P25, commercially available. The reason sited for the enhanced activity was the formation of isolated tetrahedral TiO$_2$ species on the carbon surface. Upon excitation of the photocatalyst, photogenerated electrons will be injected into MC, while the resultant photoresponse can be influenced by finetuning the competition between electrons transferred from the excited photocatalyst to the collecting electrode surface and the recombination probability of the electron–hole pairs. The latter is realized by improving electron transport pathways in order to enhance the electron transport. It is believed that the improvement of the interface morphology between the donor and acceptor of such nanoheterojunctions is an important issue in developing novel and versatile optoelectronic devices.

**Experimental part**

The experimental part of this work consists in two steps: the first one is referred to the synthesis of ordered mesoporous carbon and, the second one, to the titanium oxide coating on the synthesized mesoporous carbon.

Mesoporous materials, with a fiber-like structure, were prepared by using mesoporous silica as template and glycerol as carbon source. The silica, SBA-15, was synthesized using a tri-block copolymer (Pluronic P123) [12]. In a typical synthesis, 4 g of Pluronic P123 was dissolved in 30 mL of pure water. When a clear solution was obtained, 120 mL of 2 M HCl was added and the solution was stirred for 2 h. Then, 9 g of silica source (tetaethylortosilicate) were added and the resulting mixture was stirred for 24 h at 40°C, then 48 h at 100°C. After filtration, the recovered solid was washed several times with water, and dried overnight at 100°C, then calcined at 550°C in order to remove the surfactant. Then, the SBA-15 was loaded with glycerol by ‘dry’ impregnation method [6] resulting the silica/carbon composite by pyrolyzing the material at a high temperature under $N_2$ flow. In order to obtain MC material, the silica template was removed by dissolving with HF solution.

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The photocatalytically active material was obtained by inserting the TiO2 precursor within mesoporous carbon fibers by ultrasound assisted impregnation method. Then, the composite was calcined for 4 h at 400°C in order to obtain TiO2 species distributed on the carbon surface.

The photocatalytic activity of MC-TiO2 composite was estimated by measuring the decomposition rate of phenol in 0.2 mM aqueous solution under visible light.

Characterization

Powder X-ray Diffraction patterns (XRD) were collected with a Bruker D8 Advance X-ray instrument, using CuKα radiation (λ=1.54184Å, Ni filter) in a 0:20 configuration. The mean crystallite size of TiO2 particles was determined by line broadening of XRD peak at 2θ = 25.3 using the Debye-Scherrer formula: D=Kλ/β cosθ (K – Scherrer constant, K = 0.9; λ - the x-ray wavelength, λ = 1,5418 Å for Cu; β – the line broadening at half the maximum intensity (FWHM) in radians; θ – the Bragg angle).

Scanning electron Microscopy was performed by means of a SEM VEGA II LSII scanning electronic microscope manufactured by TESCAN for the Czech Republic, coupled with an EDX QUANTAX QX2 detector manufactured by ROENTEC Germany.

N2 adsorption-desorption isotherms at -196°C were performed on a Quantachrome Autosorb NOVA 2200 automated gas adsorption system. The isotherms were measured after outgassing of the samples under vacuum for 6 h at 200°C. The Brunauer–Emmet–Teller (BET) method was used to calculate the specific surface area. The pore diameter was obtained using the Barret–Joyner–Halenda (BJH) method and the total pore volume was determined at P/P0 = 0.95.

The Raman measurements were carried out using a Renishaw InVia micro-Raman spectrometer equipped with a charge coupled device (CCD). The Ar+ laser (514.2 nm) with maximum power of 50 mW was used to excite the samples. Raman spectra were recorded in the 1000-3000 cm⁻¹ region with 30 s integration times using a 50x objective lens. The Raman spectrum of MC was collected (fig. 4). From the Raman spectrum, carbon was burnt out at 500 °C and the XRD pattern of residual TiO2 was obtained (fig. 2). The mean crystallite size of TiO2 particles was calculated using the Debye-Sherrer formula, by line broadening of XRD peak at 2θ =25.3 and it was found to be of about 23 nm in diameter.

Results and discussions

Based on uniform carbon deposition inside silica pores, ordered mesoporous carbon, MC, was formed with a uniform pore system and thick walls. The ordering could be observed from the low angle XRD pattern, that exhibit the (100), (101) and (200) diffraction peaks that are associated with p6mm hexagonal symmetry (fig. 1).

The wide angle XRD pattern of MC sample shows a (002) reflection, that resulting from the stacks of parallel graphene layer planes, and the (101) reflection resulting from the regular structure within the individual layer plane segments. Because of a relatively large amount of mesoporous carbon, the (002) reflection of MC sample overlapped (101) reflection of anatase phase and the intensity of this peak was much higher than that of TiO2 peaks. In order to deconvolute TiO2 reflections from MC

The adsorption/desorption isotherms were used to study the changes of the textural properties of the MC carbon material upon TiO2 loading. Both samples exhibit type IV isotherms according to IUPAC classification, with a hysteresis loop characteristic to ordered mesoporous materials (fig. 3) with a narrow range of uniform cylindrical shaped pores. Since the isotherm shape after TiO2 loading is maintained, it could be concluded that there is no structural collapse induced by the nanoparticles deposition. The BET method allowed textural characteristics calculations for MC and MC-TiO2 samples, as listed in Table 1. A decrease of the BET specific surface area and total pore volume could be observed, which indicates the mesopore blocking by the TiO2 particles. The appearance of the micropores features could also be assigned to the micropore formation between TiO2 nanoparticles and MC walls.

To the best of our knowledge, the graphitic nature of carbon plays the key role for the enhancement of TiO2 photocatalysis. In order to prove that our carbon is suitable to be used for photocatalytic activity enhancement, the Raman spectrum of MC was collected (fig. 4). From the figure are clearly observed the presence of the original D (disordered carbon) and G (sp² carbon) bands associated with graphite [13]. The narrow peak corresponding to an E<sub>2g</sub> mode of graphite is present in the Raman spectrum and is related to the vibration of sp²-bonded carbon atoms in a 2-dimensional hexagonal lattice, such as in a graphite
layer [14]. The existence of a G-band in the Raman spectrum suggests that well defined graphitic domains are indeed developed. The relative intensity ratio of D and G bands (ID/IG) is proportional to the number of defect sites in the graphite layer. Since ID/IG ratio of MC is 0.82, it is concluded that MC contains a high density of edge-plane-like defect sites, which offers favorable surroundings for capturing and transferring the excited electrons, making the electron transfer easier [7].

The thin fiber-like morphology of the mesoporous carbon material was observed as shown in SEM images (fig. 5). The SEM image of the MC-TiO2 composite clearly shows that the TiO2 particles are also uniformly distributed on the external surface of MC support.

The IR spectrum of the MC carbon sample (fig.6) proves that on the carbon surface exists some functional groups which are suitable to fix the titanium dioxide nanoparticles. Because of the graphitic structure, there are also many hydrophobic sites on the carbon surface that are responsible in fixing phenol molecules on the surface and thus increasing the local concentration of the phenol species.

As demonstrated, the synthesized MC carbon sample has two important features: porosity (large surface area and uniform pores) and graphitic structures (conductive \(\pi-\pi\) interactions). The porous structure can adsorb organic molecules and consequently, enriches the local concentration of these types of molecules. The carbon graphitic structure will offer an electron-rich substrate for electron transfer during the surface reactions, which is a great advantage in surface chemistry, especially in photocatalysis.

As well known, the phenolic compounds are commonly persistent organic contaminants in wastewaters from oil refining, pharmaceutical synthesis, electroplating, papermaking, coking and iron-smelting [15], and show a low biodegradability, posing serious risks to the environment once discharged into natural waters. Recently, phenol was proposed as one of four substrates in a multi-photoactivity test [11]. Therefore, we selected phenol as the model contaminant present in wastewaters, in order to test the synthesized MC-TiO2 composite, as well as native MC sample, in phenol photodegradation processes.

From the phenol decomposition study we found that the synthesized MC-TiO2 composite possesses high photocatalytic efficiency under illumination of visible light. The visible-light absorption is resort to the presence of carbon since no other chemical compounds were found except anatase phase (see XRD analysis). The presence of carbon species is coincident with the presence of visible-light absorption and carbon is in the form of C–C bond. It
also suggests that carbon species are associated with catalytic sites on anatase surface, so that carriers generated by photon absorption by the carbon species can transfer quickly onto catalytic sites and perform the subsequent catalytic reactions.

Phenol degradation efficiency results for MC, MC-TiO$_2$ and commercial TiO$_2$ P25 (Degussa) catalysts are shown in figure 7. The most efficient phenol degradation took place in irradiated suspension of MC-TiO$_2$ composite. After 60 min of irradiation, on MC-TiO$_2$ sample, almost 80% of phenol was degraded.

The obtained results confirm that the TiO$_2$ coated mesoporous carbon ensured the reproducible photocatalytic effectiveness based on its special properties. According to a comparison between phenol degradation efficiencies of MC-TiO$_2$ composite, synthesized in this work, and commercial TiO$_2$ P25 (Degussa), we stated that our photocatalyst is more suitable for water purification under visible light. The MC-TiO$_2$ composite exhibits an enhanced photocatalytic activity compared to the commercial TiO$_2$ P25 (Degussa) photocatalyst. Enhanced visible light-activity of TiO$_2$ photocatalyst resulted from the presence of carbon, mainly in the form of C–C species, as well as from the high surface area of the synthesized ordered mesoporous carbon by a template method.

The anatase nanocoated MC showed a high photodegradation rate and its outstanding performance is due to: (1) electron trapping occurs at the interface between the TiO$_2$ anatase nanoparticles and the graphic parts of the MC support and, as consequence, the electron – hole recombination is greatly retarded; (2) between TiO$_2$ anatase nanoparticles and the MC support exist interactions; (3) the interface area was large; and (4) photon absorption was higher in the presence of mesoporous carbon.

The results show that TiO$_2$ coated ordered mesoporous carbon exhibited similar visible light activity with respect to some photocatalysts prepared in other investigations [16, 17] where some elements where intentionally introduced to achieve improved photoactivity. We conclude that our procedure is more acceptable for industrial applications and subsequent reuse.

Conclusions

The synthesized nanocomposite, MC-TiO$_2$, showed a beneficial influence on phenol photodegradation efficiency in visible light. The results proved that the photocatalytic activity of TiO$_2$ nanoparticles increases when the nanoparticles are deposited on the surface of an ordered mesoporous carbon (MC). Due to the high specific surface area (1483 m$^2$/g), the MC sample plays an important role in increasing the surface contact of the organic molecules with TiO$_2$ nanoparticles, this way increasing the specific surface area of the photocatalyst. The hydrophobic sites present on the carbon surface are also favorable in attracting phenol molecules to the photocatalytically active sites. Compared with the best photocatalyst (Degussa Aerioxide® P25) in the market, the deposited TiO$_2$ nanoparticles on the surface of ordered mesoporous carbon exhibit an enhanced photocatalytic activity with a phenol photodegradation efficiency of 80% in 60 min.

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