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Novel, ternary clay/polypyrrole/silver hybrid materials through in situ photopolymerization

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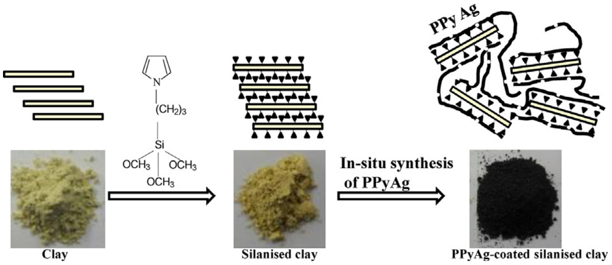
HIGHLIGHTS

- Clay/polypyrrole/silver hybrids via simple photopolymerization process using $AgNO_3$ sensitizer.
- Silanization of the clay imparts polypyrrole/silver-rich surface.
- The ternary silanized clay/polypyrrole/silver hybrids are exfoliated.
- The hybrid structures are effective catalysts for the reduction of methylene blue.

GRAPHICAL ABSTRACT



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ABSTRACT

Clay–polypyrrole–silver hybrid material was synthesized via one pot photopolymerization of pyrrole using silver nitrate as a photosensitizer in the presence of clay (montmorillonite, MMT). We have silanized the clay using a pyrrolyl-functionalized silane to provide anchor sites for the polypyrrole/silver composite coating (PPyAg). The silanized clay was effective in the making of a ternary hybrid material (MMT–Sil–PPyAg) which exhibits a PPyAg-rich surface. The polypyrrole and silver mass loadings were estimated to 19 and 27 wt.%, respectively. Interestingly, silanization by pyrrole functionalized silane permits to fully exfoliate the clay upon the photopolymerization process. In contrast, without silanization, the surface of the ternary hybrid material MMT–PPyAg is rather aluminosilicate-rich despite a black colour of the final product. We demonstrate that the anchored Ag particles are in the metallic state. We evaluated the propensity of the PPyAg-modified silanized clay to catalyse the reduction of methylene blue by $NaBH_4$ and found it levels off to 94% within a few minutes only.

This work conclusively demonstrate that UV-induced polymerization of pyrrole in the presence of a layered silicate is simple and fast; in addition, it permits to design novel hybrid materials with high catalytic performances

1. Introduction

Clay/polymer nanocomposites [1–5] received much attention over the recent years as they are relevant to a broad panel of applications encompassing reinforcing fillers [6], adsorbents [7,8], coatings [5], flame retardants [4]. Among polymers, conjugated

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polypyrrole, polyaniline and PEDOT have been the subject of several studies as they impart conductivity, electrochemical and other interesting properties to the inorganic component clay. Particularly, clay/polypyrrole hybrid materials were prepared by a range of approaches which provide intercalated [9,10] or exfoliated [11] hybrids with controlled surface and interface chemical compositions. It was found that high surface extents of polypyrrole could only be achieved if the clay is first modified by quaternary ammonium salts [12]. These surface modifiers permit to obtain organophillic clay with hydrophobic properties which favor the in situ deposition of polypyrrole and thus the making of hybrid materials with polypyrrole-rich surfaces.

In the majority of cases, polypyrrole is synthesized chemically in the presence of the clay support whether it is used as such or pre-modified [11,12]. However, polypyrrole can also be generated via photopolymerization using silver nitrate [13] and other salts as photosensitizers resulting in the incorporation of Group 1B metal nanoparticles. Indeed, under the UV light, the polymerization proceeds very efficiently with photosensitizers such as $CuSO_4$, $AgNO_3$ and $AuCl_3$; the metal ions oxidize pyrrole which yields polypyrrole while they reduce simultaneously to metallic NPs that remain trapped in forming conductive polymer. TiO_2 nanoparticles can also be used as photosensitizers and the synthesis provides TiO_2/polypyrrole nanoparticles [14]. The photochemical route is simple and versatile as it can also be conducted in the presence of a range of substrates such as polyethylene terephthalate (PET) and glass substrates [15], and cellulose fabrics [16]. Particularly, flexible insulating polymer sheets modified by polypyrrole/Ag NP nanocomposite films can be employed as humidity sensors [17]. Table 1 reports selected examples of ternary hybrid (polypyrrole-nanoparticle)-coated substrate systems, prepared by photopolymerization, and uses thereof.

Table 1 clearly indicates that photo-induced polymerization of pyrrole is a versatile process that permits to generate a broad range of materials.

Despite the progress in the preparation of polypyrrole materials, particularly clay/polypyrrole hybrids, generating such heterostructures via photopolymerization has not been investigated. Indeed, these hybrid materials are produced by chemical oxidative methods. We aim at filling the gap by photopolymerizing pyrrole in situ in the presence of montmorillonite clay using $AgNO_3$ as a photosensitizer therefore leading to PPy–silver composite-modified clay. In order to achieve polypyrrole-rich clay surface, we first silanized the layered aluminosilicate using *N*-(3-trimethoxysilypropyl)pyrrole in order to intercalate organic species for anchoring polypyrrole at the photopolymerization step. Surprisingly, and to the best of our knowledge, there is no paper describing the preparation of silanized clay/polypyrrole hybrids although other silanized supports were modified by polypyrrole [23–25]. Instead of silanization, much work has been achieved to prepare organophilic clay/PPy hybrid materials where the organophilic clay has been obtained using cationic surfactants. Another important aspect of this work is the naturally occurring silver nanoparticles generated from the photosensitizer via this UV-induced polymerization pathway. Polypyrrole and silver nanoparticles are generated simultaneously in the form of a composite coating on dispersed, silanized clay nanosheets. The final heterostructure is expected to have dispersed silver nanoparticles, which is of upmost importance in many applications such as catalysis.

In this very first report on UV-induced clay/polypyrrole/silver hybrids, we employed SEM, XPS, and XRD in order to investigate their surface morphology, chemical composition and crystalline structure. We finished by evaluating the catalytic performances of the hybrid materials in the reduction of methylene blue taken as a reference compound in redox reactions.

2. Experimental

2.1. Materials

Pyrrole (Aldrich) was refrigerated in the dark prior to synthesis. Prior to use, pyrrole (Aldrich) was passed through a basic alumina (Aldrich) to remove the impurities. Silver nitrate (Aldrich) was of analytical grade and used as received. N-(3-Trimethoxysilylpropyl)pyrrole was purchased from Fluorochem (Hadfield, UK) and used as received. The organic solvents used were

Table 1
Summary of the polypyrrole–metal and polypyrrole–semiconductor composite coatings on various kinds of supports.

Support/substrate	Material	Experimental details	Application	Refs.
Cellulose fabrics	PPy–Ag coating	UV induced polymerization with $AgNO_3$ as photosensitizers	NA, potentially useful for antibacterial textiles or catalytic materials	[16]
Bisphenol-A-ethoxylate dimethacrylate (BEMA) polymer chains	PPy–Ag coating	UV-induced polymerization using $AgNO_3$ as oxidant, light intensity ~28 mW/cm^2	Metallopolymer capacitor	[18]
Quartz crystal microbalance	PPy/Ag/TiO_2 nanoparticle composite films	UV-induced polymerization using $AgNO_3$ as oxident, light intensity ~4.5 mW/cm^2, exposure time ~10 min	Humidity sensor	[19]
Al_2O_3 substrate with comb like interdigited gold electrodes	PPy–Ag coating	UV-induced polymerization using $AgNO_3$ as oxidant, exposure time ~5.5 h	Chemiresistive detection of common inhalational anesthetic agent sevoflurane	[20]
Mesoporous TiO_2	PPy coating	UV-induced polymerization using $AgNO_3$ as oxidant,	Photovoltaics	[14a]
Polystyrene, Teflon, mylar substrate	PPy–Ag coating	UV-induced polymerization using $AgNO_3$ as oxidant, pyrrole/$AgNO_3$ = 8:1; pyrrole/surfactant = 15:1; intensity ~1.9 W cm^{-2} with a thermal postcure at 2.3 W cm^{-2})	NA	[21]
Fluorine doped tin oxide glass (FTO)	PPy–TiO_2 nanohybrid films	Photo-polymerization was performed as an anodic oxidation reaction by exciting the TiO_2, under white light from a Xe lamp (320 mW cm^{-2}) or monochromatic light 85 from a Xe lamp through a monochromator	Photochromic applications	[22]
TiO_2 nanoparticle	PPy coating on TiO_2	UV induced photopolymerisation, wavelength ~365 nm, intensity ~13 mW/cm^2, TiO_2 as photoinitiators	NA	[14c]
Glass and poly(ethylene terephthalate) (PET) substrate	PPy–Ag coating	UV-induced polymerization using $AgNO_3$ as oxidant, ratio 1:1 (Py:$AgNO_3$) and excited with a Hg lamp (UV irradiation) for times interval from 30 min to 2 h.	NA	[15]

NA: not available.