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Short communication

Tetrazine-functionalized and vertically-aligned mesoporous silica films with electrochemical activity and fluorescence properties

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ABSTRACT

In spite of their attractive physico-chemical properties making them very promising in the field of functional molecular materials, *s*-tetrazine derivatives remain underexploited in practical devices mainly because their immobilization in a stable form maintaining all their features is still challenging. Here, we show that combining a 'click chemistry azide/alkyne' approach with an electrochemically-assisted self-assembly (EASA) method, which is likely to generate azide-functionalized and vertically-aligned mesoporous silica films, and further derivatization of the ordered mesoporous material with propargyl–tetrazine via a soft Huisgen coupling reaction, enable one to reach this goal. The resulting tetrazine-functionalized films formed onto transparent indium–tin oxide (ITO) electrodes exhibit well-defined voltammetric signals, with peak currents proportional to the functionalization level and stable upon multiple potential scanning, as well as effective fluorescence properties as evidenced from fluorescence spectra with maximum emission at 555–560 nm.

1. Introduction

1,2,4,5-Tetrazines have been known for a long time and are of great synthetic interest for the preparation of a wide range of products (natural or synthetic, bioactive compounds or ligands, highly energetic materials, or a huge amount of intermediates useful in organic synthesis) [1–4]. Being the electron-poorest aromatic system of the classical C,H,O,N,S chemistry, the tetrazine exhibits in a single molecule unprecedented photophysical and electrochemical properties, but its physical chemistry has started to be investigated in detail only recently [3]. For instance, 1,2,4,5-tetrazines can be easily and reversibly reduced to their anion radical forms, which are very stable in the absence of acids [3,5]. Due to an $n-\pi^*$ transition located in the visible spectral range, tetrazines are colored (from purple to orange to red, depending on the nature of substituents on the 3,6 positions) [3]; a large number of them are also fluorescent, especially when substituted by heteroatoms [6], and their fluorescence can be modulated according to their redox states [7]. They thus gather attractive features for new applications in various fields, including, e.g., nonlinear optics, addressable sensors or displays, electrofluorochromism or light-emitting diodes, and molecular electronics [3]. Their use in practical devices requires however the development of suitable immobilization procedures; even if some strategies have appeared (e.g., entrapment in a sandwich cell using a polymer electrolyte matrix [7]), it remains challenging to get such reactive moieties covalently attached in an active form to a solid support. In recent years, ordered mesoporous silica thin films with uniform pore diameter (typically tuneable in the 2–10 nm range) have been developed for various electrochemical applications [8]. They can be notably manufactured by electrochemically-assisted self-assembly (EASA), leading to hexagonally-packed mesopore channels oriented normally to the electrode surface, a feature which significantly improves transfer reactions through the film [9,10]. They are functionalizable with organic groups by grafting or self-assembly cocondensation [11,12], but these approaches are restricted to rather simple functions and rather low amounts, so we recently developed a more general method combining EASA and 'click chemistry' likely to overcome this limitation [13]. Here, we show that azide-functionalized and vertically-aligned mesoporous silica films prepared by EASA can be derivatized with propargyl–tetrazine via a soft Huisgen coupling reaction. It is then demonstrated that the resulting tetrazine-functionalized films generated onto ITO electrodes are electroactive and that the immobilized tetrazine moieties keep their fluorescence properties.

2. Material and methods

2.1. Chemicals

Tetraethoxysilane (TEOS, 98%, Alfa Aesar), 3-azidopropyltrimethoxysilane (AzPTMS, as prepared from 3-chloropropyltrimethoxysilane [13]), ethanol (95–96%, Merck), $NaNO_3$ (99%, Fluka),

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HCl (Riedel de Haen, 1 M solution) and cetyltrimethylammonium bromide (CTAB, 99%, Acros) were used for film synthesis. 3-chloro-36-propargyloxy-1,2,4,5-tetrazine (propargyl-TTZ, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.63 (t, J = 2.3Hz, 1H), 5.30 (d, J = 2.8Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 57.8, 75.7, 77.5, 165.2, 166.1 ppm) was obtained through a reaction between propargyl alcohol and dichlorotetrazine as in [14] and used here for the post-derivatization of the azido groups. The electrolyte solutions used for electrochemical experiments were prepared with dimethylformamide (DMF, 99.8%) and 0.1 M tetrabutylammonium–hexafluorophosphate ($TBAPF_6$, ≥99.0%).

2.2. Preparation and functionalization of mesoporous silica thin films

Azide-functionalized and vertically-aligned mesoporous silica thin films were prepared by EASA, from 1:1 v/v ethanol:water (0.1 M $NaNO_3$) sols containing TEOS and AzPTMS as silane precursors (total concentration = 100 or 200 mM; TEOS/AzPTMS ratios from 95/5 to 60/40), and cetyltrimethylammonium bromide (CTAB) as template (C_{CTAB}/C_{silane} ratio adjusted to 0.32) [13]. After hydrolysis for 2 h (pH 3), sol solutions were used to generate the films onto ITO plates (surface resistivity, 8–12 Ω, from Delta Technologies) by applying a

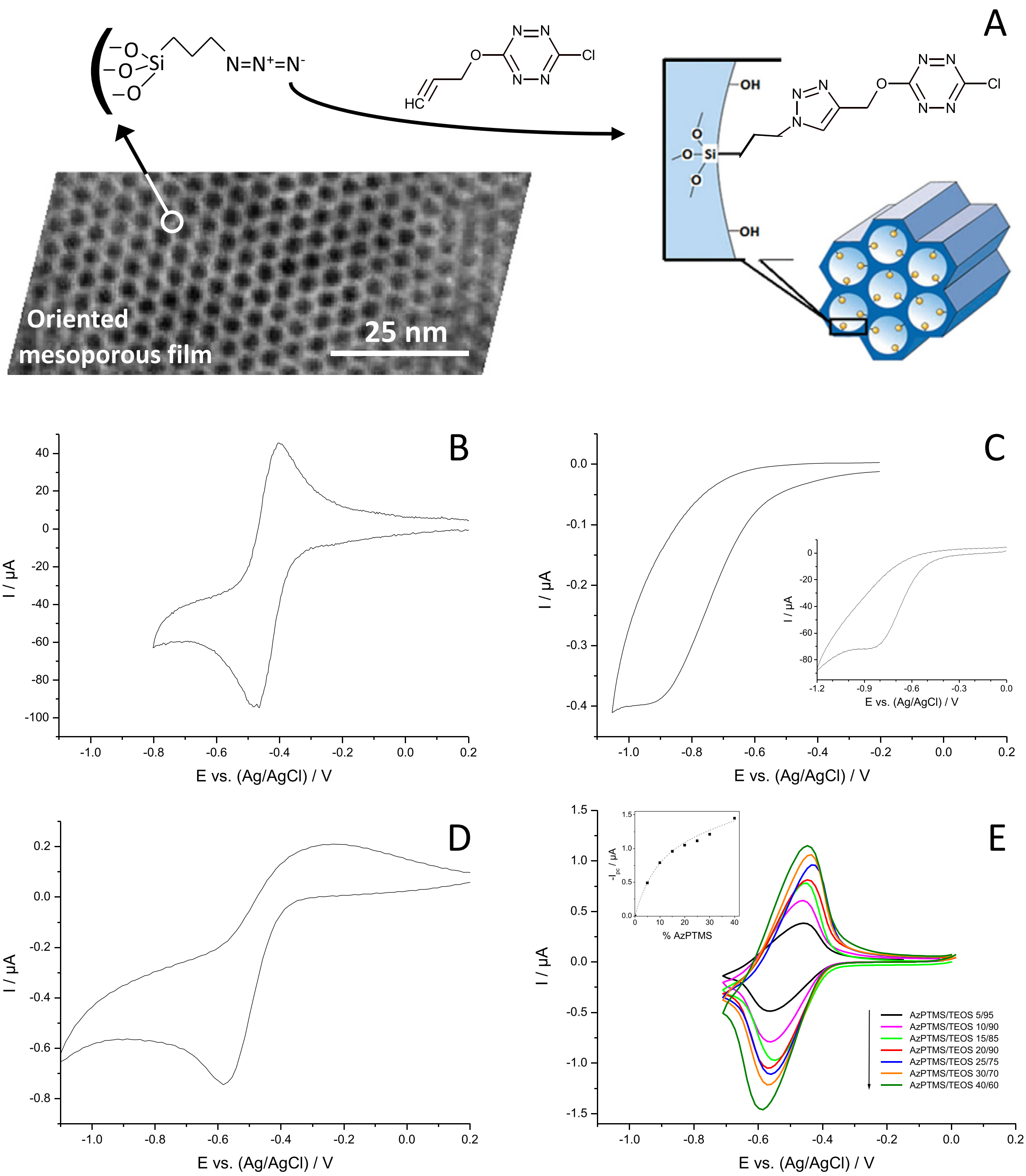

Fig. 1. (A) Schematic representation and TEM views of azide-functionalized and tetrazine-post-functionalized mesoporous silica films generated by EASA. (B-E) Cyclic voltammograms recorded at 100 mV/s in DMF (+0.1 M $TBAPF_6$) using (B) a bare ITO electrode immersed in 1 mM tetrazine, and (C–E) ITO covered with various tetrazine-functionalized mesoporous films derivatized by click coupling in different conditions: (C) H_2O/BuOH + $CuSO_4•5H_2O$/ascorbic acid (insert: tetrazine grafted directly to the silica walls); (D) H_2O/BuOH without catalyst; (E) DMF/EtOH with copper(II) acetate and ascorbic acid (at various functionalization levels, from 5 to 40%).