Applied Catalysis A: General 447–448 (2012) 89–99

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Photocatalytic synthesis of silver dendrites using electrostatic hybrid films of porphyrin–polyoxometalate

Iftikhar Ahmed[a,h], Xiaoxia Wang[b], Nadia Boualili[a], Hualong Xu[b], Rana Farha[c,d], Michel Goldmann[c,e], Laurent Ruhlmann[a,f,g,*]

[a] Laboratoire de Chimie Physique (UMR CNRS 8000), Bâtiment 349, Université Paris-Sud 11, F-91405 Orsay Cedex, France
[b] Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, People's Republic of China
[c] Institut des NanoSciences de Paris, UMR 7588 au CNRS, Université Paris 6, 4 place de Jussieu, boîte courrier 840, F-75252 Paris Cedex, France
[d] Laboratoire d'Analyse et Contrôle des Systèmes Complexes – LACSC-ECE Paris Ecole d'Ingénieurs, 37 Quai de Grenelle, F-75015 Paris, France
[e] Université Paris Descartes, 45 rue des Saints Pères, F-75006 Paris, France
[f] Laboratoire d'Electrochimie et de Chimie-Physique du Corps Solide (UMR CNRS 7177), Université de Strasbourg, 4 rue Blaise Pascal, 67081 Strasbourg, France
[g] Key Laboratory of Molecular Engineering of Polymers of Ministry of Education, Department of Macromolecular Science, Fudan University, Shanghai 200433, China
[h] SUN Labs, Department of Applied Chemistry, University of Engineering & Technology, Lahore 54000, Pakistan

ARTICLE INFO

Article history:
Received 23 July 2012
Received in revised form 7 September 2012
Accepted 9 September 2012
Available online 8 October 2012

Keywords:
Porphyrin
Polyoxometalate
Photocatalysis
Dendrites
Nanoparticles
Silver
Layers-by-layers

ABSTRACT

Films based on electrostatic interactions between tetracationic porphyrin, 5,10,15,20-(4-trimethylammoniophenyl) porphyrin tetra(*p*-toluenesulfonate), $[H_2TPhN(Me)_3P]^{4+}$ and Dawson type polyoxometalate α_2-$[Fe(P_2W_{17}O_{61})]^{7-}$ (POM) are formed by the so called layer-by-layer self-assembly method. Successive deposition of layers has been monitored by UV–visible absorption spectroscopy. Atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) have been used to explore the morphology and composition, respectively. Electrochemistry and permeability studies have been carried out by cyclic voltammetry.

The photocatalytic properties of these films have been also studied for the reduction of silver ions. Indeed, in these systems, porphyrins can be excited by visible light which play the role of photosensitizers able to give electrons to POM known to be good catalysts. Giant silver dendrites have been obtained.

1. Introduction

Polyoxometalates (POMs) are metal-oxygen polyanionic clusters which absorb in UV range of light. These molecular clusters of early metal elements in their highest oxidation state exhibit variety of applications in catalysis, materials science or medicine [1] because of their rich electronic and optical properties [2–5]. The ability to modify their redox and chemical properties by replacing one or many elements renders them particularly attractive for catalytic applications [6]. For example, we can use these compounds for electrocatalytic reduction of nitrite [7–10].

Polyoxometalates can also play key role in environmentally benign oxidative photodegradation of organics compounds in cleaner water technologies [11]. While photolysis in the presence of a sacrificial electron donor reduces POMs which in turn lead to the reduction of metal cations, it appears finally as a useful alternative for synthesis and recovery of metal nanoparticles [12] wherein POM can both serve as photocatalyst and act as stabilizer [13].

Nevertheless, POMs absorb in UV range of light thus posing threat to environment, which has been averted by their coupling with a suitable chromophore unit that can absorb the visible solar range of light likewise porphyrin [1,14]. Indeed, chromophores like porphyrins are attractive components in materials because of their appealing chemical and photochemical properties: intense visible absorption bands, long-lived excited states, and tunability by chemical derivatization [14–17]. Thus, with appropriate central metal ions, they are well suited as electron donors, and are often used in supramolecular systems [18,19].

* Corresponding author at: Laboratoire d'Electrochimie et de Chimie-Physique du Corps Solide (UMR CNRS 7177), Université de Strasbourg, 4 rue Blaise Pascal, 67081 Strasbourg, France. Tel.: +33 3 68 85 14 15; fax: +33 3 68 85 14 31.
E-mail address: lruhlmann@unistra.fr (L. Ruhlmann).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2012.09.022