Rapid screening of silver nanoparticles for the catalytic degradation of chlorinated pollutants in water

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ABSTRACT

Electrochemical abatement of volatile polychlorinated organic compounds for environmental applications represents a very attractive and feasible alternative for working at mild reaction conditions and reduced costs. We present herein the synthesis of three different sized Ag nanoparticles (NPs) and their electrocatalytic performance in the degradation of a model pollutant (trichloromethane, $CHCl_3$) in aqueous media. Two different methodologies are used: A conventional study based on voltammetry and chronoamperometry and a novel screening approach based on the micropipette delivery/substrate collection (MD/SC) mode of the scanning electrochemical microscopy (SECM). This new approach allows to dose any reactant, in this case $CHCl_3$, even if the latter cannot be electrogenerated. Moreover, we introduce here a novel platform for studying nanomaterials by reducing the current collector background contribution using disposable screen-printed array electrodes. The performance ranking obtained by the SECM for the three different samples of Ag NPs synthesized is validated by its comparison with the results obtained by chronoamperometry, which demonstrates the feasibility and the good sensitivity of SECM in electrocatalysts screening for the $CHCl_3$ reduction reaction. In addition, SECM allows to analyze simultaneously a large number of catalysts in one single experiment under constant experimental conditions. We suggest the proper size range and the presence of abundant superficial defective sites, such as steps or kinks, as the main reasons for Ag NPs C1 exhibiting the best overall catalytic performance in trichloromethane electrochemical reduction.

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1. Introduction

Environmental electrochemistry covers a broad range of applications. In particular, highly efficient and low-cost catalysts for pollutants degradation in wastewater and industrial effluents represent a challenging goal. Electrochemical advanced oxidation processes (EAOPs) [1–8], involving generation of very powerful oxidizing agents, such as, for instance, hydroxyl radical (•OH), have become especially relevant in wastewater treatment, particularly when the organic compounds present in solution are toxic or biorecalcitrant to conventional treatments. More recently, the electrochemical reduction of halogenated pollutants [9], by

removing the halogen groups, has become an economic alternative to the EAOPs where the goal is the total organic mineralization. For this reason, the electrochemical reductive cleavage of carbon–halogen bonds in organic compounds, with the particular focus on volatile organic halides, has been mainly studied and developed in the last decades [10–13] being the subject of numerous studies in aqueous [14–16], non-aqueous [17–19] and mixed solvents [13,20]. The great interest for this process is due to its important role in some environmental applications, such as the abatement of volatile polychlorinated organic compounds, a group of pollutants having hazardous effects on living beings and out of the scope of most EAOPs.

The main core of the development of modern electrochemical systems is largely based on the use of nanostructured materials, since their electrocatalytic properties can be modulated through appropriate design and synthesis [21,22]. Moreover, their application to wide areas of environmental chemistry and energy conversion represents a field in constant growth [23–25]. Thus,

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electrocatalysis at nanoparticles represents one of the most exciting new frontiers in science, since it provides a very flexible and easy scalable methodology for potential industrial applications. In this context, the electrochemical dehalogenation of organic halides using nanostructured materials represents a very attractive and feasible alternative for working at mild reaction conditions and reduced costs [26,27]. As it is well documented in the literature, the process efficiency and the main reaction products depend on the electrode material, exhibiting silver the best electrocatalytic activity among all pure metals [9,10,28,29]. Furthermore, the electrocatalytic reduction of organic halides on silver has been already proved as a surface sensitive reaction, where the surface morphology must be considered as an important parameter for modulating the electrocatalytic effect [30]. Although most of the reported applications are performed on massive Ag electrodes, there are evidences [26,27,31,32] that micro- and nanostructured particles exhibit a better performance than massive silver, allowing a substantial reduction of Ag loading. For all these reasons, it is evident the great interest of studying the electrocatalytic properties of different types of silver nanoparticles (Ag NPs) in the degradation of halogenated pollutants. Moreover, the electrochemical dehalogenation of organic halides is an attractive reaction, not only for the mild reaction conditions, but also for the absence of additional reagents avoiding secondary pollution, which represents an important drawback in other decontamination treatments that may generate dangerous secondary reaction products [33].

The screening of electrocatalysts is a time-consuming task independently on the reaction of interest under scope. In this respect, trichloromethane electrochemical reduction is not different from other processes. Fortunately, new electroanalytical techniques have been recently introduced to improve this screening step. In particular, the scanning electrochemical microscopy (SECM) [34,35] has demonstrated its utility as a rapid and high-throughput technique in screening electrocatalysts [36] for processes such as the oxygen reduction reaction (ORR) [37–42], methanol interference during ORR [43], chlorine evolution [44] and oxygen evolution reactions (OER) [45,46], formic acid oxidation (FAOR) [47,48] and methanol oxidation reactions (MOR) [48]. Among the different modes of SECM, only the micropipette delivery/substrate collection (MD/SC) mode is based on non-electrochemically generated reactants and thus can be applied to study the trichloromethane reduction reaction [48]. The MD/SC mode is conceived for obtaining an electrocatalyst reactivity map by delivering the reactant of interest in the vicinity of an array formed by different electrocatalysts, while the array current is recorded and the micropipette is scanned on the *X–Y*-plane at a constant tip–substrate distance, as is schematically shown in Fig. 1. The rate of the species release is a function of its partition coefficient between two immiscible phases, being this species soluble in both of them, a water-immiscible organic solution within the pipette and an aqueous solution outside the pipette. The specific feature of the MD/SC approach lies on the possibility of dosing, in principle, any reactant, even if the latter cannot be electrogenerated (otherwise, the tip generation/substrate collection (TG/SC) mode represents a better choice). Thus, we herein extend the use of the MD/SC mode of the SECM for screening electrocatalysts for the trichloromethane electrochemical reduction reaction, since so far this mode was only used for studying MOR and FAOR. Note that in Fig. 1, but only for simplifying, we schematize the reaction at the substrate indicating the elimination of one single Cl⁻ per CHCl₃ molecule. But as a matter of fact, we know, from preparative electrolysis experiments reported in the literature using carbon-supported Ag NPs in aqueous solution [27], this reaction leads to a mixture of products, mostly formed by CH₄, which represents the complete dehalogenation (reaction (1)). However, using another electrocatalytic material and/or solvent, the reaction path and thus the product distribution may
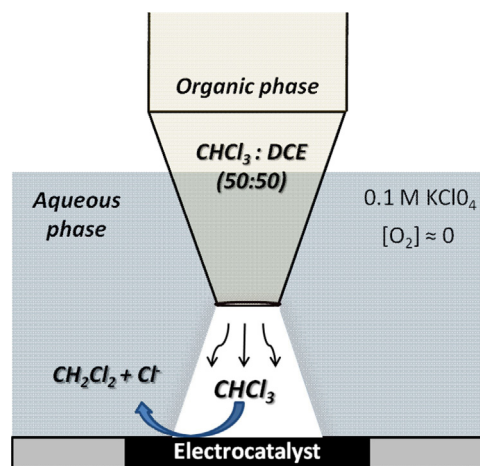

Fig. 1. Schematic representation of the MD/SC mode of the SECM applied to the screening of electrocatalysts for the CHCl₃ reduction reaction in aqueous medium.

strongly vary. We present the SECM as a powerful technique that is able to observe the finest reaction rate differences at several catalysts under the same experimental conditions. To achieve this goal studying the trichloromethane electrochemical reduction, it is necessary to design a novel experimental setup, different from those already proposed previously in the literature. In fact, although the SECM has been already used for studying nano-sized materials as electrocatalysts [38,39], the current collector contribution to the total background current represents an important limitation on these systems, especially when the reaction of interest is close to the potential window limit, which is the case for the trichloromethane electrochemical reduction. For this reason, we introduce here a novel approach to reduce the current collector background contribution by using disposable screen-printed array electrodes [49]:

$$CHCl_3 + 3H^+ + 6e^- \rightarrow CH_4 + 3Cl^- \qquad (1)$$
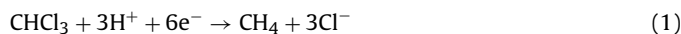
In this work, we present the synthesis of three different sized Ag NPs used as electrode material for the reduction of a model volatile polychlorinated pollutant (trichloromethane, CHCl₃). The considered nanoparticles are prepared by simple colloidal methods, which represent a promising synthetic route for potential industrial scale preparation. The Ag NP activity is studied using two different methodologies: (i) A conventional study based on voltammetry and chronoamperometry, in which different batches of Ag NPs are supported on a glassy carbon (GC) electrode (almost inert material for this type of reaction [50]) and independently tested as catalyst for the reduction of CHCl₃ in aqueous solution. (ii) A novel screening approach based on the MD/SC mode of the SECM that allows for simultaneous analysis of different electrocatalysts under the same experimental conditions and provides rapid information about their activity and their resistance against deactivation. Finally, we also study the effect on the electrocatalysis of increasing the presence of defective sites (steps, kinks and high index planes) at the silver surface by following an electrochemical roughening protocol, using a bulky polycrystalline Ag electrode as a model.

2. Experimental

2.1. Chemicals

All chemicals were ACS reagent grade purchased from Sigma-Aldrich and were used without further purification. Trichloromethane (CHCl₃) anhydrous 99.8%, 1,2-dichloroethane