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ORIGINAL PAPER

Electrocatalytic dechlorination of chloroacetic acids by silver nanoparticles modified glassy carbon electrode

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Abstract A simple potentiostatic method was employed to prepare silver nanoparticles deposited on glassy carbon electrode. The silver nanoparticles exhibit extraordinary electrocatalytic activities toward the reduction process of chloroacetic acids. The electrochemical behavior of trichloroacetic acid, dichloroacetic acid, and monochloroacetic acid has been investigated by cyclic voltammetry at the silver nanoparticles-modified glassy carbon electrode in 0.1 M $LiClO_4$ solution; each compound exhibits a series of reduction peaks which represent sequential dechlorination steps up to acetic acid. The electrocatalytic dechlorination mechanism for chloroacetic acids was also discussed in this work.

Keywords Electrocatalytic reduction · Silver nanoparticles · Chloroacetic acids · Dechlorination

Introduction

Chloroacetic acids (CAAs) are formed upon the reaction of the added chlorine to water with the organic impurities for disinfection purposes [1] and through the use of chlorocarbon and chlorofluorocarbon replacement compounds in various industrial applications [2]. CAAs tend to accumulate in surface waters and pose threats to humans and the ecosystem due to their toxicity and high stability. Many researches have demonstrated that CAAs are also carcinogenic to humans [3]. Contamination of drinking water by these compounds is particularly dangerous in view of their toxicity or even carcinogenic nature and hence efficient remediation technologies are highly desired. Indeed, the development of degradation technologies for water pollutants is an active area of research, and various methods are already known for the abatement of halogenated compounds [4]. Among these, reductive destruction methods are very attractive because reduction of organic halides is feasible under various conditions. However, electrode materials with good catalytic properties for the reduction of carbon–halogen bonds are required to avoid concomitant reduction of water to hydrogen. Recently, much attention has been devoted to silver, due to its powerful catalytic properties, which appears to be applicable to a large variety of organic halides [5].

Metal nanoparticles display interesting optical, electronic, and chemical properties which differ significantly from those of the corresponding bulk metal. In the field of electrocatalysis, metal nanoparticles arouse much attention, owing to their extraordinary catalytic properties over bulk metal electrodes [6]. Metal nanoparticle-modified electrodes are increasingly being used in many electrocatalytic processes, such as the reduction of hydrogen peroxide [7] and oxidation of small organic compounds [8].

This work reports the results of a study on the electrocatalytic properties of supported silver nanoparticles towards the reduction of chloroacetic acids in $LiClO_4$ solution. The electrochemical dechlorination of chlorinated volatile organic compounds (VOCs) such as carbon tetrachloride, chloroform, and trichloroethylene has been widely investigated at various catalytic cathodes [9–11], the dechlorination of chloroacetic acids at some modified electrodes [12–14] was also reported. However, the dechlorination of chloroacetic acids based on silver nanoparticles is still lacking. Metal nanoparticles deposited on solid surfaces can be prepared by a wide variety of methods including, for example, vacuum deposition of metals,

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diffusion controlled aggregation, and chemical and electrochemical deposition [15, 16]. In this work, a simple, fast potentiostatic method was applied to the preparation of silver nanoparticles and their electrocatalytic activities toward the electrochemical reduction of chloroacetic acids were examined. The electrocatalytic dechlorination mechanism for chloroacetic acids was also discussed.

Experimental

Trichloroacetic acid (TCAA), dichloroacetic acid (DCAA), and monochloroacetic acid (MCAA) were purchased from Sinopharm Group Chemical Reagents Co., Ltd, and were used as received. Solutions were prepared using distilled and deionized water.

All electrochemical experiments were carried out on a CHI660A electrochemical workstation (ChenHua Instrument Company of Shanghai, China) in a conventional three electrodes cell. The working electrode was nano-Ag/GC electrode with a diameter of 3 mm, the auxiliary electrode consisted of a platinum foil, and the reference electrode used a Ag/AgCl electrode. The electrodeposition of silver nanoparticles on glassy carbon electrode (GC) was accomplished in 0.1 M KNO_3 solution containing 3 mM $AgNO_3$ by potentiostatic method at the potential of −0.4 V during 100 s. Electrolysis experiments were carried out for 120 min with 10 mM CAAs in 50 ml solution, using a silver nanoparticles-deposited glassy carbon electrode (nano-Ag/GC) as working electrode. The concentrations of chloride in solution were determined by a chloride ion selective electrode. The micrographs of silver nanoparticles on GC were characterized by S-3400N II scanning electron microscopy (SEM) (Hitachi, Japan).

Results and discussion

Characterization of nano-Ag/GC electrode

The potentiostatic deposition of silver nanoparticles on GC was accomplished at the potential of −0.4 V. In this condition, the process is diffusion controlled and, hence, instantaneous nucleation of silver occurs on the GC surface [17]. Figure 1 shows the SEM image of silver nanoparticles deposited on GC. As seen from Fig. 1, silver nanoparticles were distributed over the GC surface, although a few aggregates were observed.

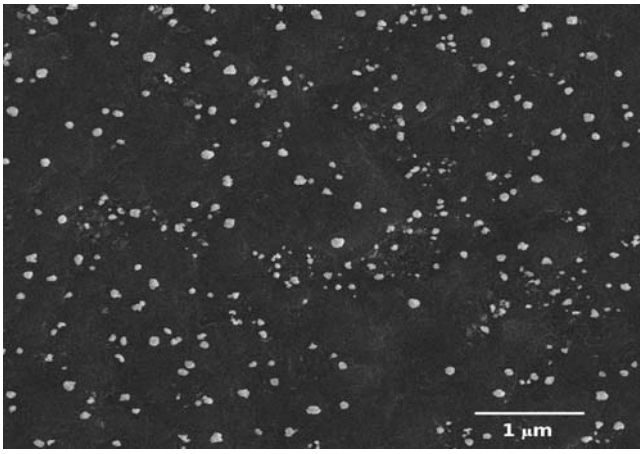

Fig. 1 SEM image of the silver nanoparticles

Cyclic voltammograms (CVs) of chloroacetic acids at nano-Ag/GC

The electrocatalytic activity of silver nanoparticles was tested for the reduction of chloroacetic acids. Figure 2 illustrates cyclic voltammograms of TCAA, DCAA, and MCAA recorded at nano-Ag/GC and TCAA at GC in 0.1 M $LiClO_4$ solution. As shown, no reduction peak was observed in curve d, this indicated that the glassy carbon electrode has no electrocatalytic activities toward TCAA. However, on the nano-Ag/GC, TCAA (curve a) exhibits three irreversible reduction peaks (E_{pc}, −0.33, −0.61, and −1.14 V), whereas DCAA (curve b) and MCAA (curve c) show two (E_{pc}, −0.68 and −1.16 V) and one (E_{pc}, −1.19 V) irreversible reduction peaks, respectively. The peak potentials of the second and third peaks of TCAA coincide with those for the first reduction step of DCAA and MCAA, respectively. Likewise, the second peak of DCAA approximates to the peak of MCAA. As shown in Fig. 2, the last peaks of TCAA, DCAA, and MCAA are located at almost the same potential. These findings clearly indicate that the reduction of TCAA yields DCAA, which in turn is reduced to MCAA at more negative potentials. The last step of this sequential dechlorination process is the reduction of MCAA to acetic acid. The results suggest that silver nanoparticles exhibit extraordinary electrocatalytic activities toward the reduction process of chloroacetic acids.

The CVs of trichloroacetic acid, chosen as a model, on the nano-Ag/GC electrode at different scan rates were investigated. As shown in Fig. 3, it can be seen that the potential and peak current are dependent on the scan rates. The peak-to-peak separation widens with the increased scan rates. In the scan rate range of 10–100 mV/s, the reduction peak currents rise linearly with the increased scan rates with correlation coefficients of 0.994, 0.995, and 0.992, respectively (inset in Fig. 3), suggesting that the sequential dechlorination reaction is a surface-controlled process.

Electrocatalytic dechlorination mechanism

On the basis of the previous report [18], the electrocatalytic hydrogenation mechanism is the main reduction pathway

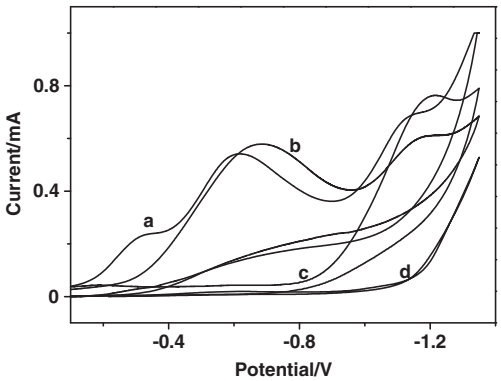

Fig. 2 The cyclic voltammetric behavior of the nano-Ag/GC electrode in 0.1 M $LiClO_4$ solution in the presence of 5 mM TCAA (*curve a*), DCAA (*curve b*) and MCAA (*curve c*), and 5 mM TCAA at GC (*curve d*). Scan rate, 100 mV/s

for the reduction of chloroacetic acid. At certain negative potential, the reduction of water to give chemisorbed hydrogen takes place, and then the chemisorbed hydrogen reacts rapidly with chloroacetic acid to produce the dechlorinated products. The formation of chemisorbed hydrogen probably is the controlled step of the electrode process, the mechanism of the catalytic reduction of chloroacetic acid can be expressed by following equations:

$$2H_2O + 2e^- + Ag \rightarrow 2(H)adsAg + 2OH^- \quad (1)$$

$$Cl_3C_2OOH + Ag \rightarrow (Cl_3C_2OOH)adsAg \quad (2)$$

$$(Cl_3C_2OOH)adsAg + 2(H)adsAg \rightarrow (HCl_2C_2OOH)adsAg + HCl \quad (3)$$

$$(HCl_2C_2OOH)adsAg \rightarrow HCl_2C_2OOH + Ag \quad (4)$$

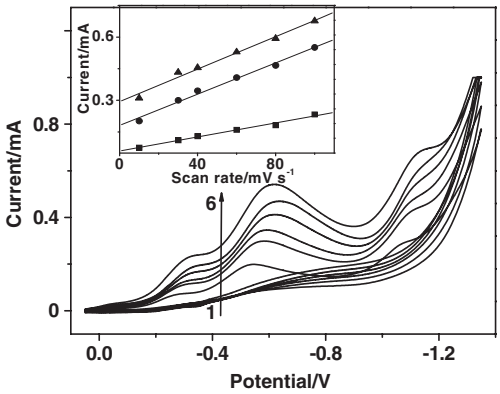

Fig. 3 Cyclic voltammograms of nano-Ag/GC electrode in 5 mM TCAA solution at 10, 30, 40, 60, 80, and 100 mV/s (*1–6*). *Inset* plot of reduction peaks currents versus the scan rates

Such interaction can decrease significantly the great overpotential associated with the dissociative reduction of the C–Cl bond. This is why DCAA and MCAA can be reduced at very low potential values on nano-Ag/GC electrode.

Catalytic dechlorination of chloroacetic acids at nano-Ag/GC electrode

To demonstrate the feasibility of removal of chloride from the chloroacetic acids, preparative electrolysis experiments of chloroacetic acids were carried out. Solutions containing chloroacetic acids were electrolyzed at constant potential (−1.2 V versus Ag/AgCl) on nano-Ag/GC electrode for 120 min. Figure 4 shows the concentration of chloride ion in solution obtained during electrolysis for each chloroacetic acid on nano-Ag/GC electrode. The results indicate that all chloroacetic acids could be dechlorinated at nano-Ag/GC electrode, and the dechlorination activities of chloroacetic acids decreased in the following order: TCAA>DCAA>MCAA.

In order to test the long-term stability of the silver nanoparticles, some electrolysis experiments were repeatedly carried out on the same nano-Ag/GC electrode, without renewal of the Ag deposit. The results were highly reproducible and compared well with those obtained using a freshly prepared electrode. The current decreased less than 9% after about five electrolysis experiments. Therefore, no significant aging effect on the electrocatalytic properties of nano-Ag/GC emerged from our experiments.

Conclusions

In this work, silver nanoparticles deposited on GC can easily be prepared by a simple potentiostatic method. The silver nanoparticles exhibit remarkable electrocatalytic activity for

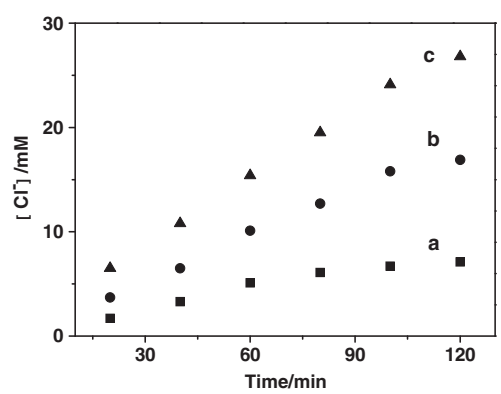

Fig. 4 Concentrations of chloride ion in solution versus electrolysis time. 10 mM CAAs in 50 ml solution at nano-Ag/GC electrode. (**a**) MCAA, (**b**) DCAA, and (**c**) TCAA

the reduction of chloroacetic acids. The dechlorination of TCAA was stepwise, following the pathway of TCAA–DCAA–MCAA–acetic acid, and the dechlorination activities of CAAs decrease in the order of TCAA, DCAA, and MCAA. These facts make the silver nanoparticles useful from the practical standpoint for the treatment of chloroacetic acids in various contaminated water.

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