

Synthesis of metal and metal oxide nanoparticles, liquid–liquid extraction and application in supercapacitors



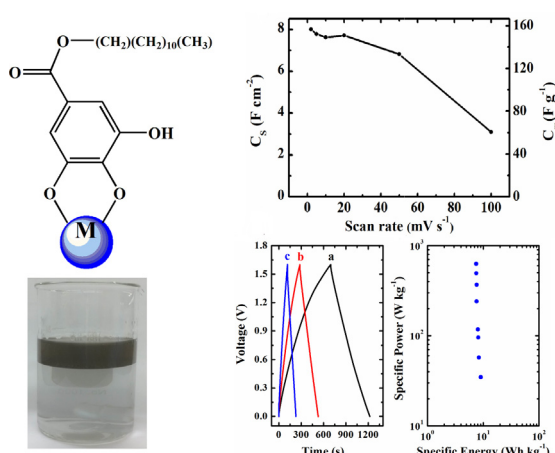
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HIGHLIGHTS

- Ag nanoparticles were prepared using lauryl gallate (LG) for reduction of AgNO_3 .
- MnO_2 nanoparticles were prepared using *n*-butanol as a reducing agent for KMnO_4 .
- Liquid–liquid extraction method has been developed for Ag and MnO_2 nanoparticles.
- LG was used as an extracting agent and a dispersant for Ag, MnO_2 and carbon nanotubes.
- Improved dispersion and mixing allowed for the fabrication of advanced supercapacitors.

GRAPHICAL ABSTRACT



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ABSTRACT

Suspensions of Ag and MnO_2 nanoparticles in *n*-butanol were prepared by synthesis in aqueous solutions and liquid–liquid extraction to the *n*-butanol phase. Lauryl gallate (LG) was used as a reducing agent for the fabrication of Ag nanoparticles from AgNO_3 solutions. MnO_2 nanoparticles were prepared by the reduction of KMnO_4 with *n*-butanol. LG showed strong adsorption on Ag and MnO_2 particles allowing for their liquid–liquid extraction. The adsorption mechanism involved complexation of metal atoms on the particle surface with phenolic OH group of LG. The synthesis and liquid–liquid extraction method offers benefits for nanotechnology, which were demonstrated by the fabrication of advanced supercapacitor electrodes and devices. LG allowed co-dispersion of multiwalled carbon nanotubes (MWCNT) and MnO_2 in the *n*-butanol phase. In this strategy as-synthesized MnO_2 nanoparticles were mixed directly with MWCNT. This avoided the difficulties associated with extracting particles from aqueous suspensions and subsequent particle agglomeration during the drying stage. The MnO_2 -MWCNT nanocomposite electrodes showed an exceptionally high capacitance of 8.0 F cm^{-2} at a scan rate of 2 mV s^{-1} and significant improvement in capacitance retention at high charge–discharge rates. Excellent capacitive performance was achieved at high active mass loading and a large ratio of active material to current collector mass. It was found that such capacitive behavior resulted from improved co-dispersion and mixing of MnO_2 and MWCNT. The composite MnO_2 -MWCNT electrodes were used for the fabrication of asymmetric supercapacitor devices, which showed good electrochemical performance in a voltage window of 1.6 V. The proposed method can be used for other applications of nanoparticles of metals and oxides in nanotechnology.

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1. Introduction

The adsorption of organic molecules on inorganic surfaces is currently under intensive investigation in order to develop advanced capping agents for nanoparticle synthesis [1,2] and efficient surfactants for colloidal technologies [3,4]. Several investigations [5–8] were focused on the applications of organic surfactants for surface modification and separation of inorganic particles by liquid–liquid extraction techniques. In this strategy, hydrophobic particles are transferred to the non-polar phase, whereas hydrophilic particles remain in the polar phase. Various surfactants were investigated, such as sodium dodecylsulfate [5], dodecyl amine acetate [6,8], sodium 1-octanesulfonate [6] among others [7].

The surface modification of inorganic particles with organic molecules requires strong adsorption of the molecules on the particle surface. A new bio-inspired method to develop efficient surface modification agents with strong particle surface adsorption resulted from fundamental investigations of the remarkable ability of mussels to adhere to various surfaces [9,10]. It was found that the adhesion mechanism involved protein macromolecules, containing catecholic amino acid, L-3,4-dihydroxyphenylalanine (DOPA) [9–11].

The adsorption properties of DOPA are related to the catechol ligand, which contains two OH groups bonded to adjacent carbon atoms of the aromatic ring. The adsorption mechanism of DOPA and other catecholates is based on the interaction of the phenolic OH groups with metal atoms on the particle surfaces [9–12]. The pull-off forces of >500 pN were reported for a single DOPA molecule, adsorbed on titanium dioxide [9]. Bidentate chelating bonding and bidentate bridging bonding mechanisms were proposed [13,14]. It was found that the adsorption can involve inner sphere or outer sphere bonding, depending on the nature of the adsorbent material [15,16]. Various molecules from the catechol family, such as dopamine, caffeic acid, 3,4-dihydroxyhydrocinnamic acid, celestine blue, alizarin red, pyrocatechol violet and Tiron have been used as dispersants for the electrophoretic deposition of oxide particles [17]. A large amount of research has focused specifically on Tiron, its adsorption on different inorganic particles [18–23], analysis of colloidal stability and the electrokinetic properties of particles containing adsorbed Tiron [18,19,22–25]. The use of Tiron as an anionic dispersant for TiO₂ particles allowed for the electrophoretic deposition of TiO₂ films [26,27]. Tiron was used as a reducing and capping agent for the fabrication of gold nanoparticles [28], as well as charge transfer mediator and adhesion promoting agent for the anodic electropolymerization of polypyrrole films on non-noble metals [29,30]. The adsorption of catecholates on different materials has also resulted in interesting quantum, magnetic, photovoltaic and optical properties [31–35].

Many investigations were focused on the gallic acid adsorption on various materials, such as Fe₃O₄ [36], MnO₂ [17], TiO₂ [17], kaolin [37], ZrB₂ [38], Au [39]. The chemical structure of gallic acid includes three phenolic OH groups bonded to adjacent carbon atoms of the aromatic ring. However, the adsorption mechanism of gallic acid was found to be similar to that of DOPA and involved bidentate chelating bonding or bidentate bridging bonding. Gallic acid was used as a dispersing and charging agent for electrophoretic deposition of inorganic materials and composites [17]. Moreover, gallic acid was utilized as a reducing and capping agent for the synthesis of Ag nanoparticles for biomedical applications [40]. The use of gallic acid allowed the production of Ag nanoparticles without any waste byproducts [40]. In this strategy, the oxidation of the phenolic groups resulted in the reduction of silver ions. The obtained quinoid product adsorbed onto Ag particles and allowed for their dispersion [40]. The adsorption of gallic acid on inorganic particles was studied in water and organic solvents [17]. Recent investigations [38] showed that gallic acid adsorbed on inorganic particles

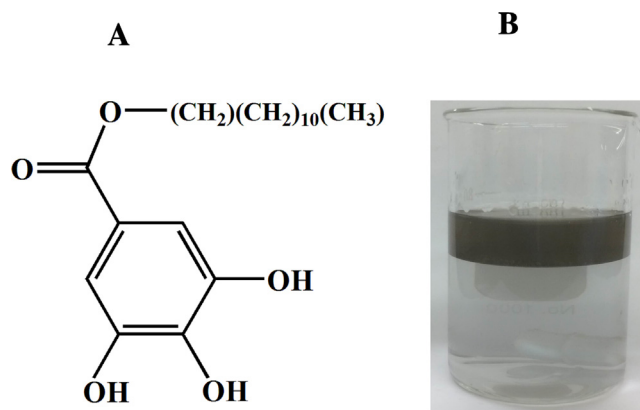


Fig. 1. (A) Chemical structure of LG, (B) extraction of AgNp to the *n*-butanol phase using LG.

in *n*-butanol via the bidentate chelation mechanism and allowed for their dispersion. It is expected that the use of larger molecules with galloyl group would result in improved steric dispersion.

The goal of this investigation was the use of lauryl gallate (LG) for the synthesis and dispersion of inorganic particles and fabrication of advanced composites using a liquid–liquid extraction technique. The structure of LG includes the galloyl group and a long hydrocarbon chain (Fig. 1A). LG is well soluble in *n*-butanol, however it is insoluble in water. The results presented below indicated that LG allowed for the reduction of Ag⁺ ions to form Ag nanoparticles (AgNp) and extraction of AgNp to the *n*-butanol phase. In another strategy, MnO₂ particles were produced by the reduction of KMnO₄ with *n*-butanol and then extracted to the *n*-butanol using LG. We demonstrate processing advantages of this method for the fabrication of MnO₂-multiwalled carbon nanotubes (MWCNT) composite electrodes for supercapacitors. Using LG as a dispersant, MnO₂ and MWCNT were co-dispersed in *n*-butanol. The MnO₂-MWCNT slurry, containing water insoluble polymer binder was used for the fabrication of electrodes of electrochemical supercapacitors. The reduced agglomeration and improved mixing of the individual components of the MnO₂-MWCNT composites resulted in excellent charge storage properties of the supercapacitor electrodes and devices.

2. Experimental procedures

Commercially available KMnO₄, lauryl gallate (LG), polyvinyl butyral (PVB), *n*-butanol, AgNO₃ (Aldrich, USA), multiwalled carbon nanotubes (MWCNT, ID 4 nm, OD 13 nm, length 1–2 μm, Bayer, Germany) and Ni foam (95% porosity, Vale, Canada) were used. A solution of 0.04 g AgNO₃ in 50 mL of water and a solution of 0.3 g LG in 20 mL of *n*-butanol were prepared, then mixed and stirred during 2 h. The reduction of Ag⁺ with LG resulted in the formation of AgNp. The LG molecules adsorbed on the AgNp and extracted them to the *n*-butanol phase (Fig. 1B). The aqueous phase was removed using a separation funnel.

In another procedure, 1 g KMnO₄ was dissolved in 100 mL of water and then 50 mL of *n*-butanol was added. Stirring was performed for 1.5 h. The reduction of Mn⁷⁺ species with *n*-butanol resulted in the formation of MnO₂ particles, which precipitated in the aqueous phase (Fig. 2A). The solution of 0.1 g LG in 25 mL *n*-butanol was added and after stirring for 10 min, the MnO₂ particles were extracted to the *n*-butanol phase (Fig. 2B). The extraction efficiency was close to 90%. The suspension of MWCNT in butanol (Fig. 2C) was added in order to obtain the MnO₂: MWCNT mass ratio of 4:1 (Fig. 2D). The mixture was ultrasonicated using a VWR Model 150T bath ultrasonicator for 30 min. The aqueous phase was

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