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A new one step scalable green synthesis for optimize Ag/Graphene hybrid supercapacitor performance.

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Highlights

- rGO/Ag nanocomposites have been prepared by a 'green' one-step synthesis.
- The rGO/Ag NPs nanocomposite was used as electrode materials for supercapacitors.
- Nanocomposite exhibited long stability and capacitance of 1850 F/g.
- The performance can be attributed to the resulting in a highly conductive network generated.

1. Introduction

Graphene-based materials in different configuration have been subject of intense investigation and have proven excellent candidates as electrode material for supercapacitors [1]. Recently, researchers have been focused their attention on the exploitation of the reduced graphene oxide electrochemical properties [2]. Although reduced graphene oxide is light-weight, highly flexible and electrically conductive, the restacking between individual graphene sheets, dramatically lowers the large initial surface area leading to limited specific capacitance values. Metal oxides and conductive polymers have been used as spacers to avoid graphene restacking and improve performances. Although metals are provided with high electrical conductive and able to give pseudocapacitance, they are rarely studied in combination with graphene [3]. In this work, we demonstrated an efficient, "green" and one step "top-down" solution route for the preparation of silver nanoparticles decorated graphene (rGO_Ag) nanocomposite exhibiting extraordinary specific capacitance and high cycling stability in acidic media. The excellent performances of our electrode, also if compared with previously reported results [4], can be ascribed to a combination of factor, including: (i) the high exfoliation of graphene due to the simultaneous reduction of GO and precipitation of densely packed Ag nanoparticles during the one-step synthesis procedure; (ii) the synergy arising from the redox activity or Faradaic process of the Ag NPs and the coupling with graphene; (iii) the long time activity of the graphene stabilizing Ag NPs electrode in H_2SO_4 electrolyte, that compared with other electrolytes can potentially give better performance.

2. Methods

The one-step procedure provides a simultaneous reduction of silver nitrate and graphene oxide, with the GO functionalities favoring the metal coating. This is a very easy and fast procedure in which three different water solution batches: of GO, of reducing agent (D-glucose) and of silver precursor and ammonia are mixed together and kept for 2 hours at 98 °C. The silver nanoparticles precipitation is favored by the presence of ammonia molecules. Indeed, silver nitrate dissolves in water solution and form Tollens' reagent with ammonia; the Tollens' reagent is very reactive and in the presence of a mild reducing agent led to the precipitation of metallic silver.

3. Results and discussion

The images revealed the formation of nanoparticles with highly uniform size (mean diameter 10 nm standard deviation ±1.6 nm), although sonicated remain anchored to the graphene surface. The NPs of Ag are also spherical and cover uniformly the rGO surface. Electrochemical measurements were performed to investigate the electrochemical properties of Ag decorated graphene. Cyclic voltammetry (CV) and galvanostatic charge–discharge curves were obtained in 1M H2SO4 electrolyte. To explore the pseudocapacitive behavior of the Ag nanoparticles, CVs were acquired in the potential windows [0÷1] V. In this range the pseudocapacitive peaks of silver, according to the Pourbaix diagram of the noble metal can be

seen. The well-defined redox process is related to anodic oxidation (from Ag to Ag^+, peak potential maximum at ~0.5 V) and the cathodic reduction (Ag^+ back to Ag, peak potential maximum at ~0.3 V). The capacitances measured in this voltage windows, that are due to the complete development of faradaic processes, reach values of 1850 F/g at 2 mV/s. The discharge curves, at a constant current density of 0.5 A/g, allow to evaluate the specific capacitance at constant current density by using the equation, $C = (I*\Delta t)/(\Delta V*m)$, where C is the specific capacitance, m is the mass of working electrode, I is the current, ΔV is the applied voltage and Δt is the discharge time. The specific capacitance of the rGO_Ag was estimated to be 665 F/g.

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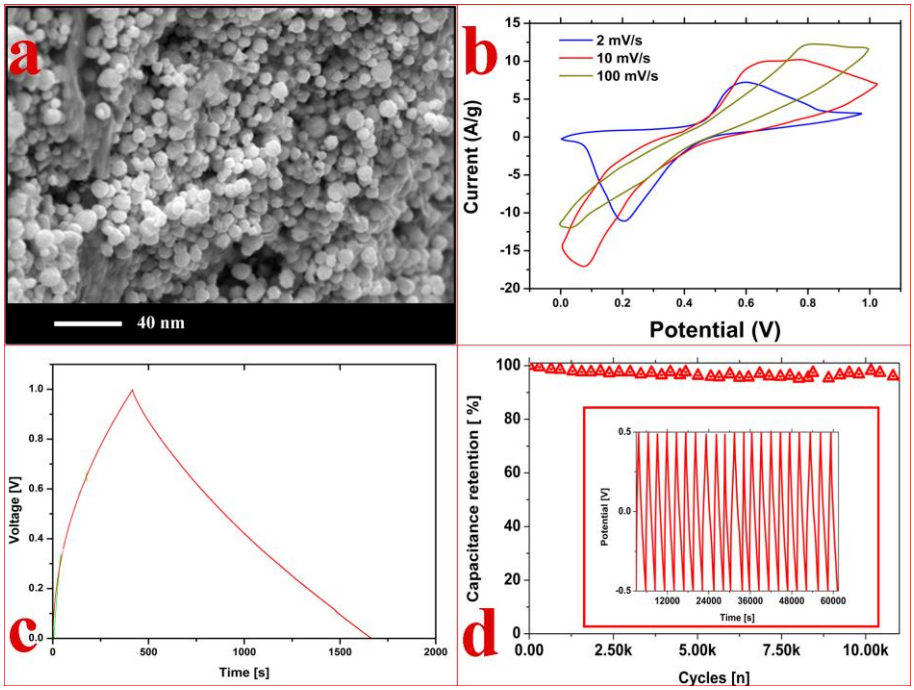

Figure 1. a) SEM image of rGO_Ag; b) Cyclic voltammograms of rGO_Ag; c) Galvanostatic charge-discharge curves of rGO_Ag; d) Specific capacitances at different current density for rGO_Ag

4. Conclusions

In this work reduced graphene oxide decorated with silver nanoparticles was obtained through a fast, easy and 'green' one step method. The morphological studies reveal that rGO_Ag is composed of a highly exfoliated graphene (few overlapped layers) and silver nanoparticles, 10 ±1.6 nm size, densely covering the graphene surfaces. The silver nanoparticles have multiple features, they: act as spacers hindering the graphene restacking, improve electrolyte diffusion and material conductivity, and allowing to total exploitation of the graphene surface. The electrochemical behavior and specific capacitance was investigated. We believe that the excellent performances reached for rGO_Ag can be ascribed to a combination of factors: the synergy arising from the redox activity or Faradaic process of the Ag NPs combined with the non-Faradaic behavior, the electrodes surface easy to be wetted by the electrolyte due to their hydrophilic nature and the electrode high conductivity.

References

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Keywords
Reduced graphene oxide; silver; green synthesis; supercapacitor.