Enhanced electrochemical properties of silver-coated zirconia nanoparticles for supercapacitor application

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\textbf{ABSTRACT}

Silver-coated ZrO\textsubscript{2} and individual ZrO\textsubscript{2} nanoparticles have been synthesized using the simple reduction and co-precipitation methods, respectively. The synthesized products were examined using the X-ray diffraction, energy-dispersive X-ray and UV–visible spectroscopy, which confirmed the successful synthesis of materials. Scanning electron microscopy and transmission electron microscopy revealed the round-shaped nanoparticles of both materials. The cyclic voltammograms revealed the well-defined redox peaks and recommended the pseudocapacitive nature of the electrodes. The silver-coated zirconia showed higher specific capacitance of 792 F/g at 10 mV/s as compared to individual zirconia (10.22 F/g). Silver-coated ZrO\textsubscript{2} also showed good power density of 274.5 W/kg at current density of 5 mA/cm\textsuperscript{2} through the galvanostatic charge discharge profile. Hence, the results suggest that silver-coated ZrO\textsubscript{2} showed improved electrochemical performance as compared individual ZrO\textsubscript{2} due to higher electrical conductivity and specific surface area. Hence, silvercoated ZrO\textsubscript{2} nanoparticles can be employed as an electrode material for supercapacitor applications.

\section{1. Introduction}

Acute climatic variations, restricted fuel and energy resources as well as rapid growth of population have forced the researchers to search out for new tools of energy in order to meet its demand \cite{1,2,3}. Presently, various energy storage devices such as batteries, fuel cells, conventional capacitors and supercapacitors are being employed \cite{4}. Owing to the presence of fast charge-discharge, longer stability and moderate energy density, supercapacitors (SCs) have gained tremendous attention as an alternative to conventional energy storage devices \cite{5}. On the basis of charge storage mechanism, SCs can be classified as Electrical double layer capacitors (EDLCs) and pseudocapacitors. EDLCs mainly consist of carbon based materials (graphene, carbon nanotubes, etc.) which store charge electrostatically and exhibit very good cycling ability \cite{6}. While pseudocapacitors (transition metal oxides (TMOs), transition metal chalcogenides (TMCs) etc.) demonstrate better energy storage properties owing to the large capacitance that results from the reversible redox reaction \cite{7,8}.

Much focus is being paid in tailoring electroactive materials with enhanced electrochemical properties and it has been found that TMOs reveal good pseudocapacitance behaviour \cite{9}. Among various oxides, zirconium oxide (ZrO\textsubscript{2}) finds vast applications due to its features such as high melting point, non-toxic nature and corrosion-free property \cite{10,11,12,13}. However, the instability as well a higher electrical resistance retards its use as an electrode for supercapacitor applications. A promising way to improve the efficiency of TMOs is to coat it with some other conductive material \cite{8}. Metal nanostructures such as copper, silver, nickel, copper and gold find various applications in catalysis and

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optoelectronic devices owing to their intrinsic properties [14–16]. Among these conductive metals, silver receives much attraction because of its good compatibility, electrochemical and electrocatalytic properties. The hybrid nanostructure formed as a result of coating of conductive Ag over TMOs may overcome the drawbacks of bare precursor during electrochemical testing. The loading of silver nanoparticles not only maintains low internal resistance of metal oxid electrodes but also increases ion (Li⁺, Na⁺, K⁺ etc.) diffusion through the electrodes [17]. Aashish et al. fabricated silver NPs decorated polyaniline coated with paper electrode and found good power density and cycling stability [18]. Pandit and Sankapal anchored silver over MCWT and obtained a remarkable capacitance of 757 F/g [19].

Keeping in view the above mentioned findings, the present study envisages the fabrication of ZrO₂ and silver-coated ZrO₂ via the simple and cost-effective co-precipitation and reduction technique. An improved specific capacitance of Ag/ZrO₂ was attained as compared to bare zirconia which may be attributed to the fact that surface modification with some conductive material improves the reaction kinetics of electroactive cavities.

2. Experimental

2.1. Chemicals

The chemicals used to synthesize the materials were ZrOCl₂·8H₂O (Merck, 98%), AgNO₃ (DUKSAN Korea, 99%), NaBH₄ (DAEJUNG 99%), KOH (Sigma-Aldrich, 99.99%), sodium citrate (Sigma-Aldrich, 99%) and ethanol (Sigma-Aldrich, 95%). All chemicals were used as received without any further treatment.

2.2. Synthesis of ZrO₂ nanoparticles

ZrO₂ nanoparticles were synthesized using a simple and cost-effective chemical co-precipitation method. First of all, ZrOCl₂ solution (0.05 M) was prepared in 100 mL of deionized water under continuous stirring. Afterwards, KOH (2.0M) was added dropwise until the pH approached 11 and the white precipitates appeared. The mixture was further stirred for one hour to homogenize it and then centrifuged. The obtained precipitates were washed with deionized water until pH reached 7 and finally with ethanol to remove all unwanted impurities. The product was dried overnight in an oven and the white precipitates thus obtained were annealed at 600 °C for 2 h. The final product was stored in a desiccator for further characterizations and applications.

2.3. Synthesis of silver nanoparticles

Silver nanoparticles were synthesized by the reduction method. For this purpose, 1 mM solution of silver nitrate was prepared in 100 mL of deionized water. The weighed amount of sodium citrate (0.1 mM) as a capping agent was added under vigorous stirring. After 20 min of vigorous stirring, 0.12 g of sodium borohydride was added which acts as a reducing agent. The colour of the solution turned to yellow which confirmed the formation of silver nanoparticles. The yellow coloured colloidal solution was stirred further for half an hour. The formation of the silver nanoparticles was further confirmed by the UV/visible analysis.

2.4. Synthesis of silver-coated zirconia

The weighed amount of silver nitrate (1 mM) was dissolved in 100 mL of deionized water followed by the addition of 0.1 mM of capping agent (sodium citrate). Afterwards, the pre-synthesized zirconia nanoparticles (0.2 g) were added in the silver nitrate solution and the mixture was vigorously stirred for one hour. Then, 0.12 g of the reducing agent (NaBH₄) was added and the mixture was further stirred for half an hour until the white colour of zirconia nanoparticles was transformed to light yellow which confirmed that the silver particles have been coated onto ZrO₂ successfully. The mixture was then, centrifuged and washed with deionized water as well as ethanol. The materials were finally dried in a vacuum oven at 80 °C and stored for further characterization.

2.5. Characterization

The powder X-ray diffraction (XRD) analysis was carried out so as to confirm the crystal structure of the synthesized materials by using a X-ray diffractometer Bruker D8 which uses Cu-Kα as a radiation source while the Ni-filter is used to absorb the Cu-Kβ radiations. The formation of silver nanoparticles was affirmed by UV/Visible spectroscopy using a Lambda 750 UV/visible/NIR spectrophotometer. The morphology and composition of the materials were investigated by field emission scanning electron microscopy (FESEM, Hitachi S4800) coupled with energy-dispersive X-ray (EDX) spectrometer. The morphology of the silver nanoparticles was also confirmed by TEM (Tecnai G2). The surface area, pore size and pore volume of the prepared materials were investigated by the Brunauer–Emmett–Teller (BET) analysis by using Micromeritics, Tristar II 3020. The electrochemical studies such as cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance (EIS) were carried out at room temperature in 2 M KOH solution electrolyte by using an Autolab PGSTAT204 workstation by employing three electrode systems. The working electrodes were prepared onto a nickel foam substrate. The slurry of the materials (5 mg of ZrO₂ and Ag/ZrO₂) was prepared in deionized water. The Ni-foam (NF, area 1 × 1 cm²) substrate was sonicated in deionized water and finally in...
Figure 1. XRD pattern of (a) ZrO$_2$, (b) Ag/ZrO$_2$ and (c) UV/visible spectra of silver nanoparticles.

ethanol. Then the slurry was deposited onto the substrate by using micropipette and the prepared electrodes were dried at 50°C in an electric oven.

3. Results and discussions

3.1. Structural, morphological and compositional analysis

XRD patterns of both the synthesized materials (ZrO$_2$ and Ag/ZrO$_2$) are shown in Figure 1, which revealed the successful synthesis of ZrO$_2$ and silver-coated ZrO$_2$ materials. The XRD peaks that appeared at nearly 2θ positions of 30.43°, 35.42°, 50.87°, 60.70°, 74.71°, 82.43° and 96.10° were well matched with the standard pattern JCPDS card 01-083-0944, confirming the formation of single phase monoclinic geometry of zirconia nanoparticles. However, an additional peak at 38.18° (indicated by $^*$) in Figure 1(b) led to the presence of silver nanoparticles which indicated the successful coating of silver particles on ZrO$_2$. The average particle size calculated by the Scherer formula was found to be 50 nm.

The confirmation for the silver nanoparticles was carried out by UV/Visible spectroscopy and its spectrum is shown in Figure 1(c). A clear broad peak at 426 nm corroborated the formation of silver nanoparticles.

Surface morphology was explored by examining FESEM and TEM micrographs. The images of the synthesized materials are given in Figure 2(a,c). The FESEM image revealed the round-shaped nanoparticles of ZrO$_2$ (Figure 1(a)) and the particle size is in the range of 40–60 nm range which is in good agreement with that obtained from the XRD data. Particles are homogeneously distributed and have clear boundaries. The FESEM image of silver particles is shown in Figure 2(b) where it can be observed that the particles are randomly distributed while some of the particles are agglomerated. In order to further verify the morphology of silver nanoparticles, TEM micrographs were taken (Figure 2(b) inset) which showed that the particles are round shape and homogeneously disturbed. The FESEM image of Ag/ZrO$_2$ is given in Figure 2(c). The particles are narrow and homogeneously distributed.

The EDX analysis has also been carried out to confirm the elemental composition of the synthesized materials as given in Figure 3(a,b) while the area selected for the EDX analysis is shown in Figure S2. The EDX spectrum of ZrO$_2$ showed peaks only for Zr and O (Figure 3(a)) while in silver-coated zirconia, an additional peak of Ag was also observed. The absence of the peak for any other element in the synthesized materials confirmed the purity of these materials. The surface area, pore volume and pore size were determined by the nitrogen adsorption–desorption isotherm. The BET surface area was found to be 46.0992 and 55.849 m$^2$ g$^{-1}$ for ZrO$_2$ and Ag/ZrO$_2$, respectively (representative BET isotherm for silver-coated zirconia is given in supplementary materials as Figure S1). The pore volume (0.137 cm$^3$ g$^{-1}$) and pore size (11.87 nm) were observed for zirconia nanoparticles while for Ag/ZrO$_2$ was 0.164 cm$^3$ g$^{-1}$ and 11.85 nm, respectively. The surface area, pore volume and pore size of the silver-coated zirconia are higher than that of zirconia which is beneficial for electrochemical properties.

3.2. Electrochemical measurements

Electrochemical measurements of ZrO$_2$ and silver-coated ZrO$_2$ were carried out by three electrodes system in 2 M solution of KOH which was used as an electrolyte. The Ag/AgCl, platinum wire and materials under investigation deposited on the nickel foam (NF) substrate were used as reference, counter and working electrodes, respectively. The cyclic voltammetry was employed for both the synthesized materials (ZrO$_2$ and Ag/ZrO$_2$) and their voltammograms are shown in Figure 4(a,b). The appearance of clear redox peaks in CV curves suggested the pseudocapacitive nature of ZrO$_2$ and
silver-coated ZrO$_2$ nanomaterials [20]. However, the silver-coated ZrO$_2$ showed greater redox current and potential than that of ZrO$_2$. The specific capacitance ($C_s$) of ZrO$_2$ and silver-coated ZrO$_2$ was measured using Equation (1) [21]

$$C_s = \frac{\int IdV}{mS\Delta V}$$

where integral is the area of redox CV curves, $m$ is the deposited mass, $S$ and $\Delta V$ is the specific scan rate and potential window, respectively. The measured specific capacitance for ZrO$_2$ was found to be 10.22, 9.75, 8.90, 8.40 and 7.40 F/g, while for silver-coated ZrO$_2$ it came out to be 792, 689, 631, 613 and 610 F/g at a scan rate ($S$) of 10, 15, 20, 25 and 30 mV/s, respectively. Such findings have also been reported by Alves et al. where the incorporation of rGO in ZrO$_2$ enhanced specific capacitance [11]. The electrical conductivity of silver nanoparticles (6.3 × 10$^5$ S/cm) is much higher as compared to that of zirconia (6.5 × 10$^{-5}$ S/cm) [30,31]. Zirconia being unre- active shows lower capacitance values as reported by Song et al. [22] and is also evident from our results. Therefore, it is expected that the electrical conductivity of silver-coated zirconia will be much higher as compared to ZrO$_2$. Secondly, the surface area of silver-coated zirconia is also higher than that of ZrO$_2$ as determined by the BET analysis. The improved specific conductance of silver-coated ZrO$_2$ may be attributed to the fact that silver effectively enhanced the electrical conductivity as well as the specific surface area, which resulted in efficient conduction of charge carriers and hence increased the specific capacitance [23].

### 3.3. Galvanostatic charge and discharge measurements

The galvanostatic charge–discharge measurement was carried out for silver-coated ZrO$_2$ owing to its better CV performance and surface area than ZrO$_2$ as depicted in Figure 5(a). The GCD profile was also well matched with CV curves, indicating the pseudocapacitive nature as showed from the slope region [2,24,25]. The silver-coated ZrO$_2$ followed the possible reversible Faradaic reaction during charge and discharge processes [24,26]:

$$\text{Ag/ZrO}_2 + \text{KOH} \rightleftharpoons \text{Ag/ZrO}_2\text{OH} + \text{K}^+ + \text{e}^-$$

$$\text{Ag/ZrO}_2\text{OH} + \text{OH}^- \rightleftharpoons \text{Ag/ZrO}_2\text{O} + \text{H}_2\text{O} + \text{e}^-$$

The discharge time was observed to be 81, 44, 15 and 9 s at current densities of 0.5, 1, 3, and 5 mA/cm$^2$, respectively. Discharge time decreased linearly with the increase of current density, which might be due to greater excitation of charge carriers which, in turn, increases the collision rate. Resultantly, the electrode material becomes more resistive at higher current densities. The specific capacitance ($C_s$) and energy density ($E_d$) were also calculated from the charge/discharge
profile using Equations (2) and (3) [21]

\[ C_s = \frac{I dt}{m \Delta V} \]  

\[ E_d = \frac{1}{2} C_s \Delta V^2 \]  

where \( I \) is the applied current, \( m \) is the deposited mass of electrodes, \( dt \) is the discharge time and \( \Delta V \) is the applied potential window.

The measured specific capacitance was 16.70, 16.80, 16.33 and 16 F/g, while energy density (\( E_d \)) was found 701.70, 705.60, 686.25 and 686 mWh/kg, at the corresponding current densities of 0.5, 1, 3, and 5 mA/cm², respectively. \( C_s \) and \( E_d \) were found to be greater at a current density of 1.0 mA/cm² and decreased with increased current density. Similar results have also been reported by various researchers [21,27]. The power density (\( P_d \)) was also calculated using Equation (4) [2]

\[ P_d = \frac{E_d t}{m} \]  

Here, \( E_d \) is the energy density and \( t \) is the discharge time. The measured \( P_d \) was 31.20, 57.73, 164.70 and 274.50 W/kg at the corresponding \( E_d \) of 701.70, 705.60, 686.25 and 686 mWh/kg, respectively. Hence, \( P_d \) was greater at higher current density of 5 mA/cm² and observed results suggest that silver coated revealed good electrochemical performance and can be a suitable candidate as an electrode material for supercapacitor applications. It can be inferred from Table 1 that our
fabricated material exhibits superior capacitance than many of the previously reported Ag-coated electrodes.

3.4. Electrochemical impedance spectroscopy

EIS investigation was performed in order to explore the conductive nature of ZrO$_2$ and silver-coated ZrO$_2$ pre-deposited on the NF substrate. The Nyquist plot for individual ZrO$_2$ and silver-coated ZrO$_2$ (shown in Figure S5(b)) revealed that silver-coated NPs-ZrO$_2$ showed less value of equivalent series resistance than that of ZrO$_2$. Small semi-circle at the high-frequency region also showed least charge transfer resistance of silver-coated ZrO$_2$. In the same way, a smaller slope in the lower frequency region also revealed smaller Warburg resistance for silver-coated ZrO$_2$ as compared to ZrO$_2$. So, it can be inferred that silver-coated ZrO$_2$ is more conductive in nature as compared to simple zirconia and stimulates the electrochemical performance [32,33].

4. Conclusion

Silver-coated ZrO$_2$ nanoparticles as an electrode structure were synthesized successfully using two step methods, i.e. simple co-precipitation and the reduction method. The phase, purity as well as the morphology of the materials were confirmed by XRD, UV/Visible, EDX, SEM and TEM techniques. Silver coating effectively improved the electrochemical performance of zirconia nanoparticles, which was due to the enhancement of electrical conductivity and specific surface area of zirconia nanoparticles. Cyclic voltammetry confirmed the pseudocapacitive nature of silver-coated ZrO$_2$ nanoparticles, which showed good specific capacitance of 792 F/g at the scan rate of 10 mV/s. Silver-coated ZrO$_2$ also showed good power density of 274.5 W/kg at the current density of 5 mA/cm$^2$. The results suggested that silver-coated ZrO$_2$ can be a suitable candidate as an electrode material for supercapacitor applications.

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Table 1. Comparison of Csp of various Ag-coated electrodes with our fabricated electrode.

| Electrode          | Electrolyte     | Specific capacitance (F/g) | Reference |
|--------------------|-----------------|----------------------------|-----------|
| Ag NW/MoO$_2$      | 1 M LiClO$_4$   | 500 F/g                    | [28]      |
| PPy/PPA/Ag         | 0.1 M H$_2$SO$_4$ | 226 F/g                   | [29]      |
| SS_CNT/Ag/PANI     | 3 M NaOH        | 615 F/g                    | [30]      |
| Ag@MoS$_2$/WO$_3$  | 2 M KOH         | 95.61 mA h g$^{-1}$        | [17]      |
| Ag-AgO dispersed PPy composite | 0.1 M H$_2$SO$_4$ | 500 F/g                   | [31]      |
| Ag/ZrO$_2$         | 2 M KOH         | 792 F/g                    | Present work |

Disclosure statement

No potential conflict of interest was reported by the authors.

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