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Synthesis of stable cesium superoxide nanoparticles for gas sensing application by solution-processed spray pyrolysis method

K. R. Nemade[1] · S. A. Waghuley[2]

Abstract In the present work, we synthesized cesium superoxide (CsO_2) nanoparticles by solution-processed spray pyrolysis technique. The as-synthesized CsO_2 nanoparticles were characterized through Raman spectroscopy, X-ray diffraction, scanning electron microscopy and ultraviolet–visible spectroscopy. The CsO_2 nanoparticle-based gas sensor is more selective towards the carbon dioxide (CO_2) gas. The sensor shows good gas sensing performance for CO_2 gas. Gas sensing mechanism is dominated by the adsorption and desorption process. Through this paper, we studied another dimension of gas sensing process by employing superoxide for gas sensing. The sensing mechanism for cesium superoxide is explained by newly designed "bridging oxygen-free mechanism".

Keywords Spray pyrolysis · Cesium superoxide · Gas sensing

Introduction

The superoxides have been a subject of growing interest because of its extraordinary characteristics resulting from superoxide ion (O_2^-) (Budanur and Khan 2014). The study of superoxide ion can facilitate understanding its role in metal–oxygen batteries. Ren et al. reported the metal–oxygen battery application of potassium superoxide

nanoparticles. This study successfully confirms formation and removal of KO_2 in the battery cycle test. Moreover, without any catalysts, a low discharge/charge potential gap of the order of 50 mV was observed (Ren and Wu 2013). Bryantsev et al. (2011) reported the predicting solvent stability of aprotic electrolyte Li–air batteries by the superoxide anion radical. This experimental study provides competent qualitatively screening solvent stability in Li–air batteries. Hartmann et al. (2013) reported the rechargeable room-temperature battery application of sodium superoxide. This study shows that exchange of lithium by sodium may offer an unforeseen route towards rechargeable metal–air batteries.

Inspiring from the extraordinary characteristics resulting from superoxide ion (O_2^-) in superoxide, we planned to study the gas sensing application of cesium superoxide nanoparticles. A very small number and scattered reports found in the literature of material science on superoxide. Thus, through this work, we make an attempt to explore gas-sensing performance of cesium superoxide nanoparticles. As the superoxide itself contains the superoxide ion (O_2^-), therefore, we developed "bridging oxygen-free mechanism" for superoxide.

The core objective behind the development of "bridging oxygen-free mechanism" for gas sensing materials are that it will result in fast sensing, selectivity and fast response and recovery time. This is due to the traditional gas sensing material-bridging oxygen forms layer between target gas molecules and sensing surface, but the superoxide-based sensing materials itself contain superoxide ion (O_2^-). Generally, in resistive gas-sensing method, bridging oxygen forms layer on sensing material, through which electron transfer takes place (Alwan and Dheyab 2017). The transfers of electrons result in resistance change through which sensing response is measured (Muhsien et al. 2014).

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The formation of bridging oxygen layer acts as a barrier between target gas and sensing surface for rapid detection of target gas. In addition, formation of bridging oxygen layer on sensing surface increases response and recovery time of sensor. Therefore, UV light exposure is given to sensor surface to achieve baseline value of resistance (Chinh et al. 2016). This increases the operation cost and decreases the life of sensor.

Experimental

In the present work, cesium superoxide (CsO_2) was prepared by solution-processed spray pyrolysis technique. For the synthesis of CsO_2 nanoparticles, cesium chloride (CsCl) and hydrogen peroxide (H_2O_2) was used as starting chemicals. The 1 M of cesium chloride was dissolved in H_2O_2 under rapid magnetic stirring in distilled water of resistivity not less than 18.2 MΩ cm for 15 min. Subsequent to this step; solution was kept for probe sonication. After this step, solution was loaded in spray pyrolysis setup of specification (Nemade and Waghuley 2014a). This solution was allowed to spray and deposit on chemically clean glass substrate maintained at temperature 100°C. The complete process was conducted in dry oxygen-rich environment under constant flow. By considering the highly reactive nature of cesium, the complete process was handled in an atmosphere of water below 0.1 ppm.

The highly conducting silver paste was used as ohmic contacts to determine the film surface resistance change measurements. The as-deposited CsO_2 nanoparticles on chemically cleaned SiO_2 substrate of dimensions 25 mm × 25 mm used for gas sensing action. The gas sensing performance of chemiresistor was checked in air as reference gas. The sensing response (S) is defined as $S = |R_a − R_g|/R_a$, where R_a is the resistance in air i.e., baseline resistance and R_g represents the resistance in CO_2 gas.

Results and discussion

Figure 1 shows the Raman spectrum of as-synthesized CsO_2 nanoparticles at room temperature (303 K). The spectra exhibit the sharp intense peak at 1134 cm^{-1}, which can be assigned to the stretching mode of the superoxide dumbbell. This reflects as-synthesized CsO_2 nanoparticles acquire hyperoxide state. The inset of Fig. 1 shows XRD pattern of CsO_2 nanoparticles, indicates the presence of a very low concentration of peroxide anions, which might result from incomplete oxidation (Bates et al. 1972). The CsO_2 acquires the space group I/4mmm with lattice
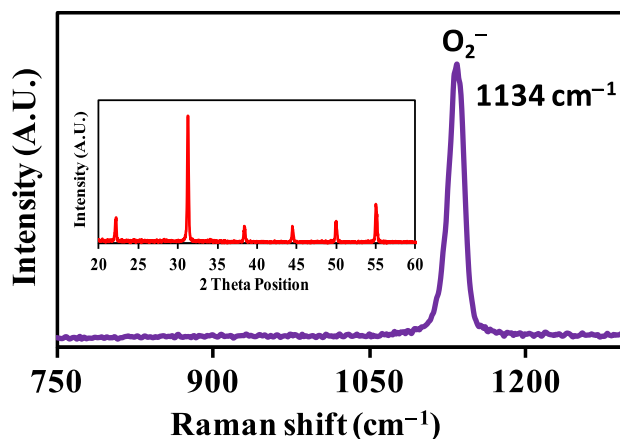

Fig. 1 Raman spectrum of as-synthesized CsO_2 nanoparticles at room temperature. The sharp peak at 1134 cm^{-1} is attributed to the superoxide anion that is O–O stretching mode. Inset shows XRD pattern of intermediate phase CsO_2 nanoparticles obtained from incomplete oxidation

parameters at temperature 303 K, $a = b = 4.461$ Å and $c = 7.331$ Å. Generally, superoxides have the largest lattice parameters, which is consequential to larger distance between the dioxygen dumbbells and cesium. Therefore, lower cationic field experienced by the dumbbells. Thus, even in oxygen-rich reaction environment, superoxides do not merge entirely superionic state (Zumsteg et al. 1974). The average crystallite size of as-synthesized CsO_2 nanoparticles was estimated using Debye–Scherrer formula (Nemade and Waghuley 2013a, 2014b), $D = 0.89\lambda/\beta\cos\theta$, where 0.89 is Scherrer's constant, λ is the wavelength of X-rays, θ is the Bragg diffraction angle, and β is the full width at half maximum. The average particle size of the CsO_2 nanoparticles was found to be 21.39 nm.

Figure 2 represents the SEM image of as-synthesized CsO_2 nanoparticles. This image substantiates the irregular shape of the nanoparticles, and most of the particles exhibit small amount of agglomeration. From the image, it is observed that the size of the nanoparticle is around 22 nm, which was in good agreement with the particle sizes (21.39 nm) calculated from the Debye–Scherrer formula.

The UV–VIS absorption spectroscopy is used to analyze the optical properties of CsO_2 nanoparticles. The as-synthesized CsO_2 nanoparticles exhibit excitonic absorption tail around 225 nm. The monodisperse nature of the CsO_2 nanoparticle distribution reflects from sharp increase in absorbance value (Zhang et al. 2002). The optical band gap of as-synthesized CsO_2 nanoparticles was determined by applying the energy-wavelength relation (Nemade and Waghuley 2013b). The optical band gap is determined by extrapolating straight line at $R = 0$ to the curve $(\alpha h\nu)^2$ vs. $(h\nu)$ is shown in inset of Fig. 3. This extrapolation intersect energy axis at 5.3 eV. This is optical band gap of CsO_2

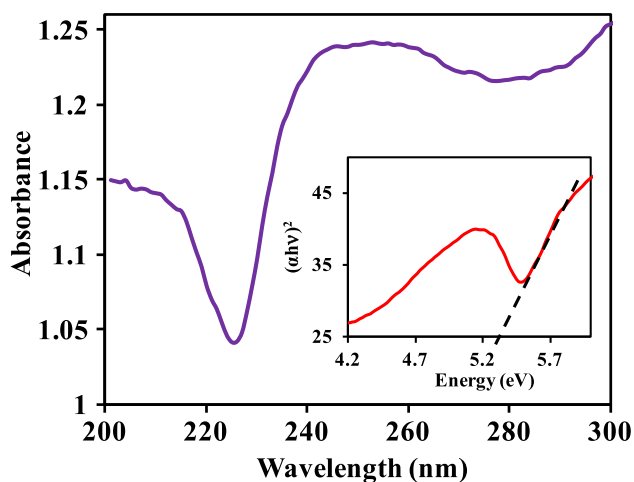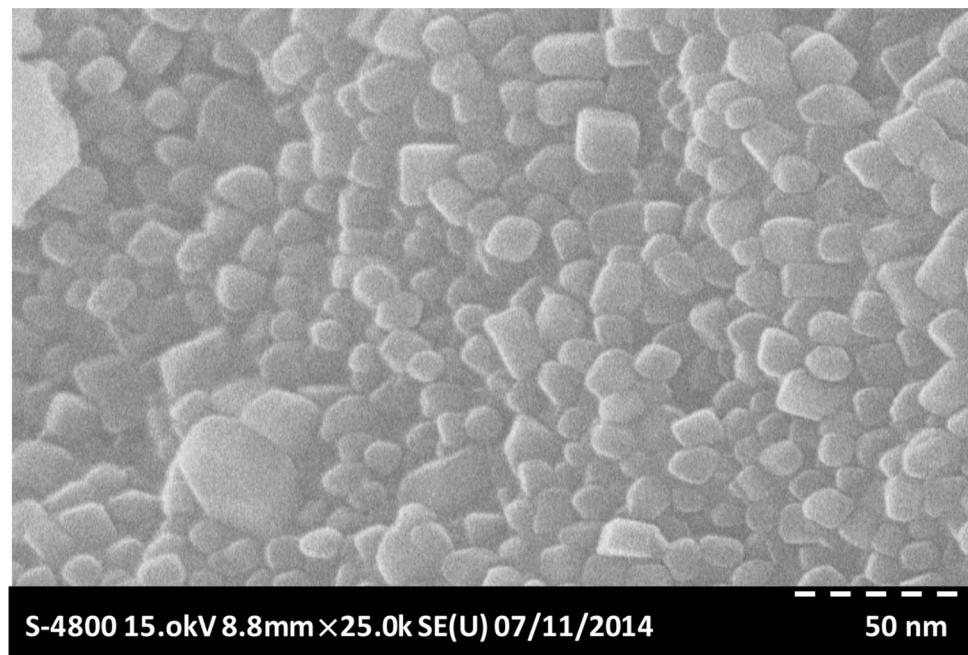**Fig. 2** FE-SEM image of as-synthesized CsO_2 nanoparticles

S-4800 15.okV 8.8mm×25.0k SE(U) 07/11/2014   50 nm

Fig. 3 UV-VIS spectrum of CsO_2 nanoparticles and inset shows the optical band gap plot showing CsO_2 nanoparticles have band gap 5.3 eV

Fig. 4 Selectivity performance of CsO_2 nanoparticles against LPG and CO_2 gas

nanoparticles. The intense absorption around the 225 nm indicates the presence of quantum confinement (Nemade and Waghuley 2013c).

The selectivity is the ability of a sensor to measure only one gas with maximum response (Morrison 1987). To check selectivity response of CsO_2 nanoparticles-based sensor, we investigate sensing response towards the LPG and CO_2 gas at 250 ppm at room temperature as shown in Fig. 4. Plot clearly shows that CsO_2 nanoparticles exhibits higher sensing response towards the CO_2 gas. Therefore, as-synthesized CsO_2 nanoparticles are more selective for CO_2 gas. Thus, the future study focused on CO_2 gas sensing.
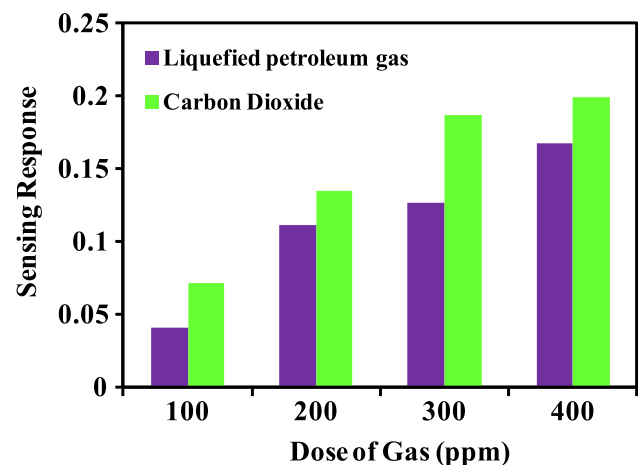
Figure 5 depicts the gas sensing response of CsO_2 nanoparticles towards the CO_2 gas at room temperature (303 K). The plot clearly shows the good dependence on the CO_2 concentration. Sensing response curve has nearly linear fitting ($R^2 = 0.9933$) with CO_2 gas concentration. The resistance of CsO_2 nanoparticles increases in the presence of CO_2 gas. This reflects the n-type behavior of as-synthesized CsO_2 nanoparticles (Nemade and Waghuley 2013d, 2015b). The increase in resistance is also indicating the oxidizing nature of CO_2 gas. The oxidizing gases have tendency to inject electron for sensing surface. This results in reduction of electron density in conduction band of sensing surface (Nemade and Waghuley 2015a). Therefore, resistance of CsO_2 sensing surface is increase in the presence of CO_2 gas.
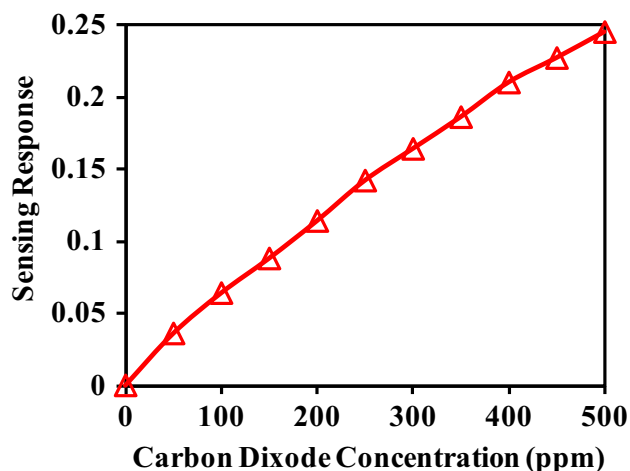
Fig. 5 Sensing response of CsO_2 nanoparticles towards the CO_2 gas at room temperature (303 K)

Fig. 7 Operating temperature performance of CsO_2 nanoparticles towards 250 ppm CO_2

Generally, gas sensing mechanism is dominated by the adsorption and desorption process through oxygen species (Fig. 6a). This is known as oxygen bridging mechanism. But in case of the materials, which itself contains superionic species such as O_2^-, that is superoxide oxide, oxygen bridging mechanism laps. This may be due to adsorption of oxygen is not necessary for superoxide oxide. Therefore, it is necessary to develop mechanism for gas sensing by superoxide oxide. Through this paper, we proposed this mechanism, which is termed as "bridging oxygen-free mechanism" (Fig. 6b). According to this mechanism during the gas sensing, CO_2 directly converted into the surface carbonates, without adsorption of oxygen molecules, which is generally observed in another materials.

Figure 7 shows that the operating temperature response of CsO_2 nanoparticle-based sensor was studied towards the 250 ppm CO_2 gas. The sensing response value increases up to 448 K. Beyond 448 K, sensing response starts to decrease. This is the operating temperature (448 K) for as-fabricated sensor. This decrease in sensing response may
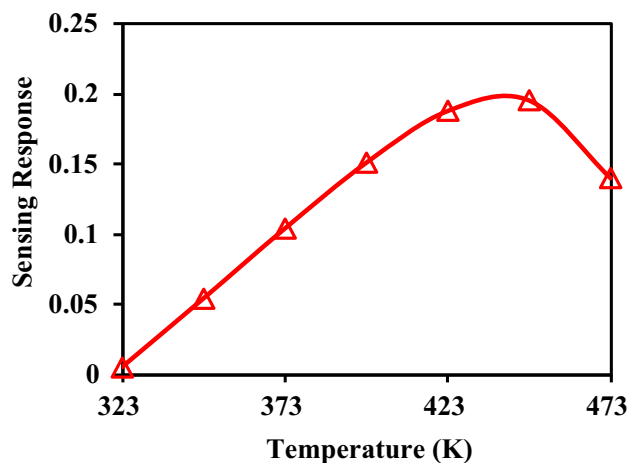
attribute to desorption of gas molecules. Beyond fixed temperature, the response value starts to decrease, which is assigned to desorption of adsorbed oxygen molecules from sensing surface. At higher temperature, due to increase in internal thermal vibration adsorbed oxygen is detached from the sensing surface (Nemade and Waghuley 2013e).

Figure 8 shows transient response of CsO_2 nanoparticles towards 250 ppm CO_2 gas at room temperature. The plot shows sensor-exhibited fast response time around 50 s and recovery time 40 s. This shows that sensors have good practical applicability. The fast response and recovery time attributed to fast interaction between target gas molecules and superoxide-based sensing material. The fast interaction between gas and sensing surface is due to absence of bridging oxygen layer as CsO_2 nanoparticles itself contains superionic species such as O_2^-.

Figure 9 shows the stability performance of CsO_2 nanoparticles against 250 ppm CO_2 gas at room temperature. The sensing curve shows nearly stable response for the entire month.

Fig. 6 Comparison of gas sensing mechanism between metal oxide and superoxide based resistive gas sensor
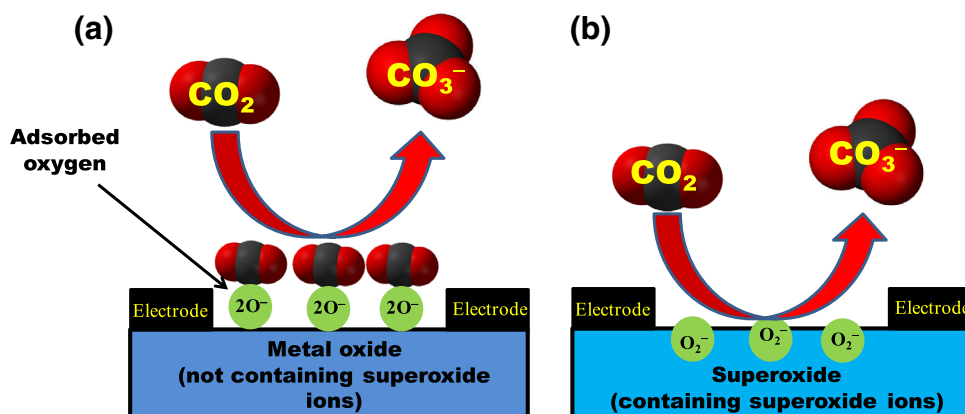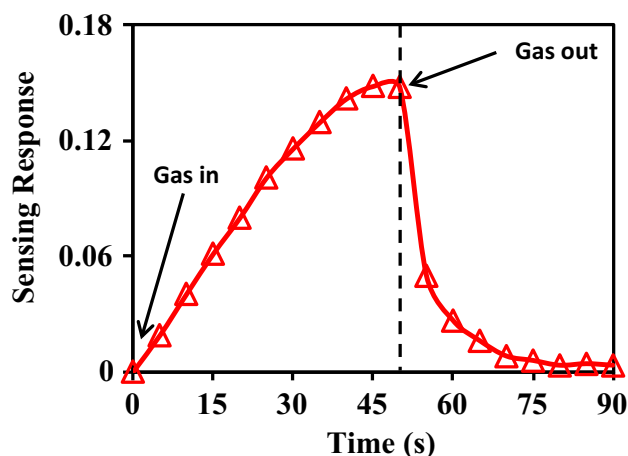
Fig. 8 Transient response of CsO_2 nanoparticles towards 250 ppm CO_2 at room temperature 303 K
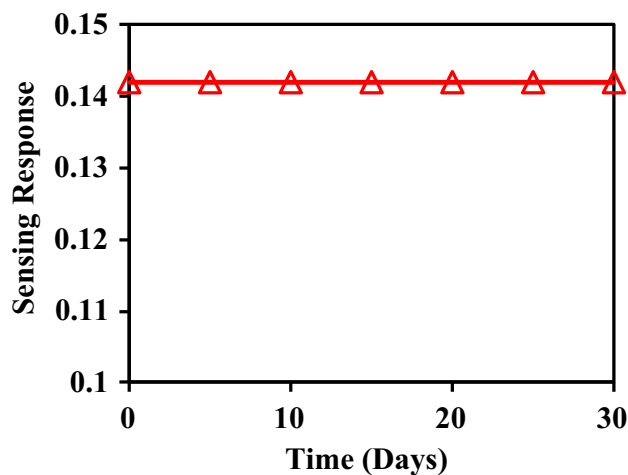

Fig. 9 Stability response of CsO_2 nanoparticles towards 250 ppm CO_2 at room temperature 303 K

Conclusions

Stable CsO_2 nanoparticles were prepared by solution-processed spray pyrolysis method. The prepared particles were characterized by various techniques to confirm structural, chemical and optical purity. The Raman spectroscopy directly shows that as-synthesized nanoparticles contain the superoxide ions. The gas sensing performance of CsO_2 nanoparticles towards the CO_2 gas quite fit for practical application. The operating temperature was found to be 448 K. The as-fabricated sensor shows good stability and rapid response and recovery time. The fast response and recovery time characteristic of sensor is attributed to "bridging oxygen-free mechanism". The study towards further development of "bridging oxygen-free mechanism" is currently underway in our lab.

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