Indian Journal of Chemistry
Vol. 57A, May 2018, pp. 605-609

Rapid Communication

Unusual redox activity of composite alkaline earth metal oxides and reduced graphene oxide system

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Received 24 March 2018; revised and accepted 26 April 2018

Reduced graphene oxide (rGO) impregnated on Group 2 alkaline earth oxides (CaO, SrO, BaO) matrix following mechanical mixing, thermal annealing and subsequent cold shock has yielded a new electrochemical material. Material characterization has been done by Fourier transform infrared spectroscopy, scanning electron microscopy and powder X-ray diffraction patterns in micrometer dimension. Thermal stability has been checked by thermal gravimetric analysis and differential scanning calorimetry. Cyclic voltammetry of the composites shows anodic peak potential in the order –0.6 V (rGO-CaO) < –0.4 V (rGO-SrO) < –0.3 V (rGO-BaO), which also follows the ordering of ionic size, Ca^{2+} (100 pm) < Sr^{2+} (118 pm) < Ba^{2+} (135 pm). They exhibit unexpected inherent redox activity with an amazing chemical reversibility. This characteristic becomes more prominent on moving down the group. Thermal stability of these coupled systems also increases down the group.

Keywords: Coupled systems, Composites, Reduced graphene oxide, Oxides, Metal oxides, Alkaline earth metal oxides, Electrochemical activity, Redox activity

In recent times, nanoparticles have become increasingly important in different fields of science[1-4]. Over the last decade, nanoscience dealing with graphene and graphene oxide (GO) have become extremely popular considering their wide range of applications[5-8]. These carbon allotropes can be functionalized or coupled with various other substances leading to new materials with unique properties[9-14]. Variation of these properties mainly depends on non-covalent interactions[15]. Sun *et al.*[16] have reported excellent electrochemical catalytic activity of graphene supported transition metal oxide catalysts in Oxidation Reduction Reaction (ORR) compared to unsupported ones. Recently GO has been reported as an electroactive material by Ambrossi *et al.*[17] Reduced graphene oxide (rGO) with most of oxygen functionalities removed, are more promising toward electrolytic activity[18-20]. Here we report electrochemical properties of rGO and rGO supported by the matrix of alkaline earth metal oxide (EMO) nanoparticles. Coupled rGO-EMO systems were synthesized and characterized by X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy, thermogravimetric analysis and differential scanning calorimetry. Analysis of electrochemical properties of rGO and coupled rGO-EMO systems were carried out using cyclic voltametry. The coupled GO systems supported by the matrix of alkaline earth metal oxide nanoparticles (such as CaO, SrO, BaO) show impressive electrochemical performances in cyclic voltammetric time scale.

Experimental

All the chemicals were purchased from Merck India.

Initially GO was prepared according to the Hummer modified method[21] from graphite flakes. To obtain the reduced graphene oxide (rGO), the GO was calcinated in a muffle furnace for 6 h at 500 °C. The alkaline earth oxide nanoparticles were synthesized using the chemical route which involved precipitation reaction followed by calcination at 400 °C. The general scheme of the reaction is given below.

$$\mathrm{M(NO_3)_2 + 2NaOH \longrightarrow M(OH)_2 + 2NaNO_3}$$

$$\mathrm{M(OH)_2 \xrightarrow{400\ ^\circ C} MO + H_2O}$$

The coupled nanosystems with rGO impregnated on the surface of the metallic oxide nanoparticles were synthesized by mixing rGO and EMO at 1:1 (*w/w*) ratio followed by thermal annealing at 400 °C and subsequent cold freezing at –20 °C, the process was repeated three times. Finally, the resultant powder was collected, dried, homogenized using a mortar passel and stored for further experiments.

XRD measurements were made using a X-ray diffractometer (UltimaIII Rigaku, Japan) with a Cu target (slit 10 mm and using a Cu Kα radiation of 1.54 Å wavelength). For the FTIR analysis the nanoparticle samples were dried and ground with KBr pellets and analyzed on a Nicolet IR 200 (Thermo Electron Corp, USA). For SEM analysis, a droplet of the nanoparticle solution was transferred to a clean glass slide (1 cm × 1 cm) and micrographs were taken randomly at various locations with the help of a scanning electron microscope (Carl Zeiss S50, Germany) at an accelerating voltage of 15 kV after gold coating. Thermal gravimetric studies were done using a Pyris Diamond TG/DTA instrument from Perkin Elmer (Singapore) operating under a nitrogen atmosphere (150 mL/min). Platinum crucible was used with α-alumina powder as reference.

Electrochemical measurements were performed using a computer-controlled CH-Instrument electrochemical workstation (model no. CHI 600D (SPL)) with Pt-disk electrodes. All measurements were made under nitrogen environment at 298 K with reference to Ag/AgCl electrode in acetonitrile using tetrabutylammonium perchlorate ([nBu$_4$N]ClO$_4$) as supporting electrolyte.

Results and discussions

X-ray diffraction pattern of rGO shows an intense peak at 26.58° corresponding to the (002) and two additional small peaks corresponding to (101) and (004) planes. All these peaks are in agreement with reports from other researchers[22] (Fig. 1a).

FTIR spectra of rGO show diminished intensity of almost all the functional groups probably due to removal of most of oxygen functionalities during thermal calcination. Small peaks ~1100-1050 cm^{-1} are suggestive of C-O stretching and the peak ~500 cm^{-1} is due to the C=C bond stretching (Supplementary data, Fig. S1).

X-ray diffractrogram (XRD) of the alkaline earth metal oxides shows presence of systematic crystalline planes that strongly confirms the formation of crystalline particles (Fig. 1(b), (c) and (d)), most of the peaks were assigned to certain definite planes. Interestingly for all the coupled systems, the peak of rGO at 26.58° almost overshadows all other peaks from metallic oxides (data not shown). This may be because during the coupling process the rGO actually forms an adsorbed layer on the surface of the alkaline earth metal oxides and thus renders itself more sensitive and available to X-ray detection.

FTIR spectrum of CaO exhibits a broad peak at 3326 cm^{-1}, which is probably due to O-H stretching from water molecules. The spectrum shows two consecutive small peaks at 1678 cm^{-1} and 1538 cm^{-1} respectively (Fig. 2a) due to calcium oxygen

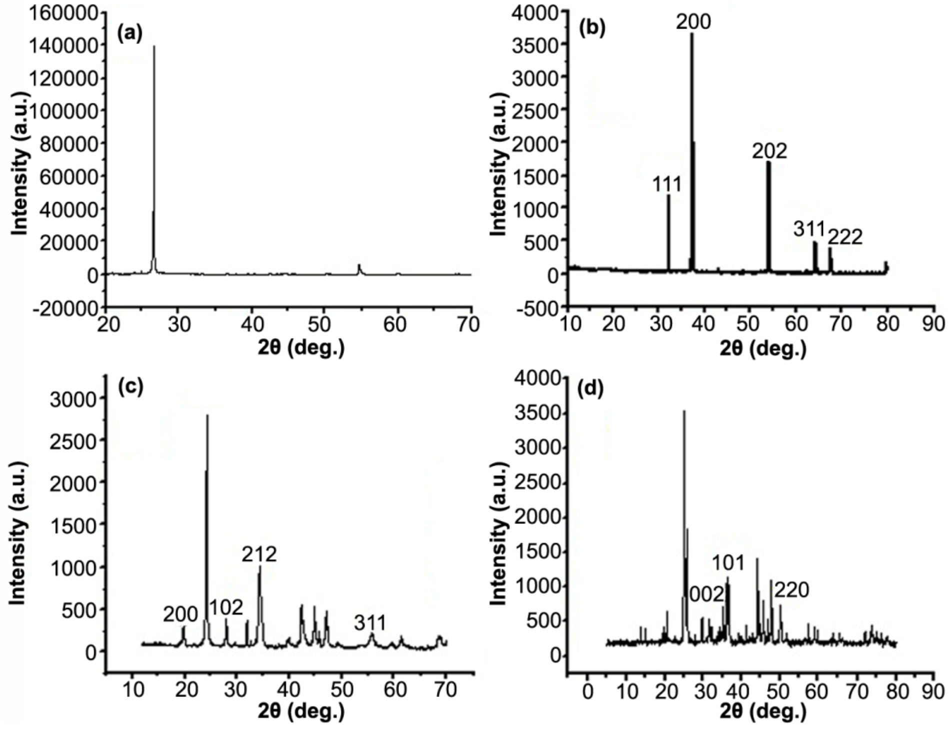

Fig. 1 — (a) X-ray diffraction pattern of reduced graphene oxide (rGO), and, XRD profiles of (b) CaO, (c) SrO, and, (d) BaO.

vibrations. The FTIR of CaO-rGO system is almost identical with that of CaO with negligible shifting of Ca-O stretching peaks (Fig. 2a′). This suggests only non-covalent and physical interaction of the coupled system with no chemical modification. FTIR spectrum of SrO shows a broad –OH stretching at 3300 cm^{-1} and two peaks at 1610 cm^{-1} and 1124 cm^{-1} which can be accounted for SrO stretching vibrations (Fig. 2b). However, in the coupled system, the Sr-O stretching peaks shift to a significantly lower wave number (1470 cm^{-1}). Some unusual upward humps become prominent and significant for this SrO-rGO coupled system. The humps are at 3512, 2910 and 1660 cm^{-1} respectively (Fig. 2b') and their origin is difficult to explain. The reason may be the effect of heterogeneous adsorption, which becomes more pronounced as the matrix becomes heavier. FTIR spectrum of BaO shows two sharp distinct peaks at 1435 cm^{-1} and 608 cm^{-1}, owing to Ba-O stretching vibrations (Fig. 2c). The spectrum of the BaO-rGO system shows a bathochromic shift for the BaO stretching peaks to 1457 cm^{-1} and 612 cm^{-1}. These changes may be attributed to a stronger non-specific interaction between rGO layer and the BaO matrix. However, here also FTIR of the BaO-rGO coupled system shows similar unusual upward humps at 3490 cm^{-1}, 1639 cm^{-1} and 1114 cm^{-1} (Fig. 2c'). These observations suggest enhancement of the non-specific interactions of the heavier alkaline earth metal oxides with the reduced graphene oxide (rGO) layer.

HR-SEM pictures of all of these coupled rGO-EMO systems show similar cubic morphology with size roughly in the range of 700-800 nm (Fig. 3).

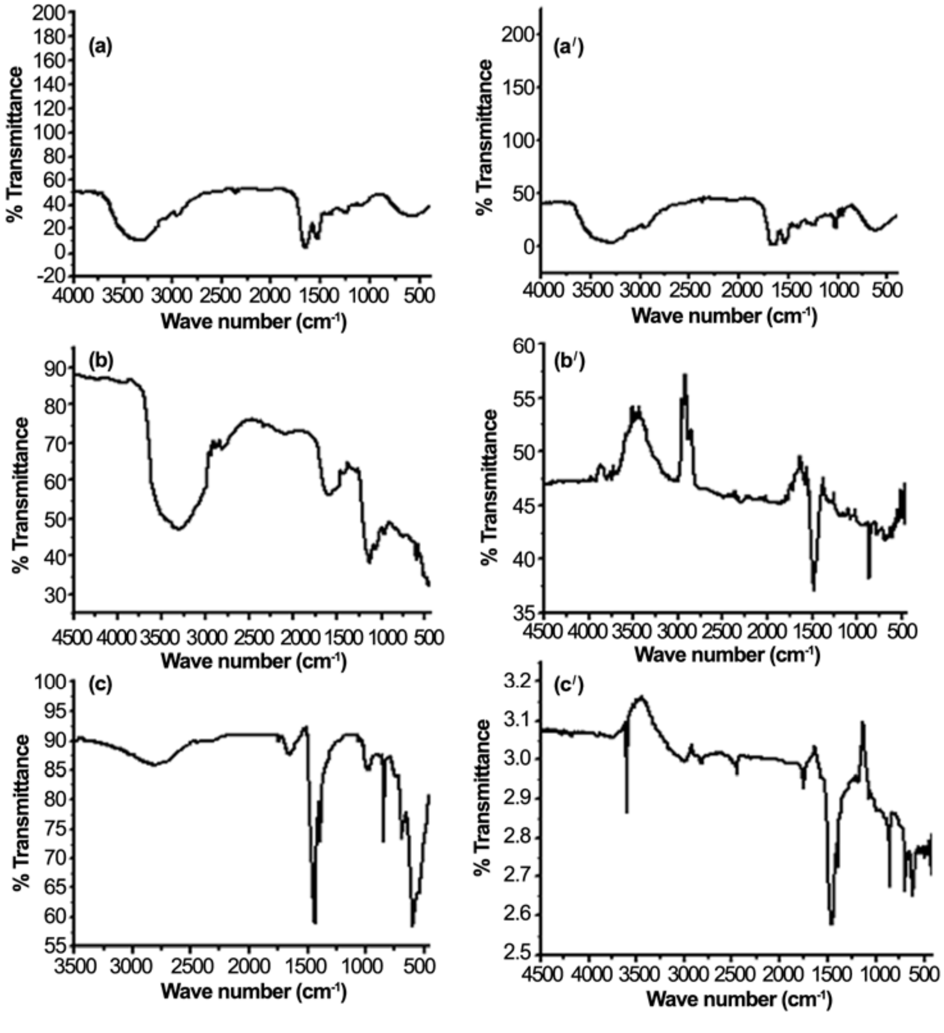

Fig. 2 — FTIR spectra of (a) CaO, (b) SrO, and, (c) BaO, and, FTIR spectra of the coupled systems (a') CaO-rGO, (b') SrO-rGO, and, (c') BaO-rGO.

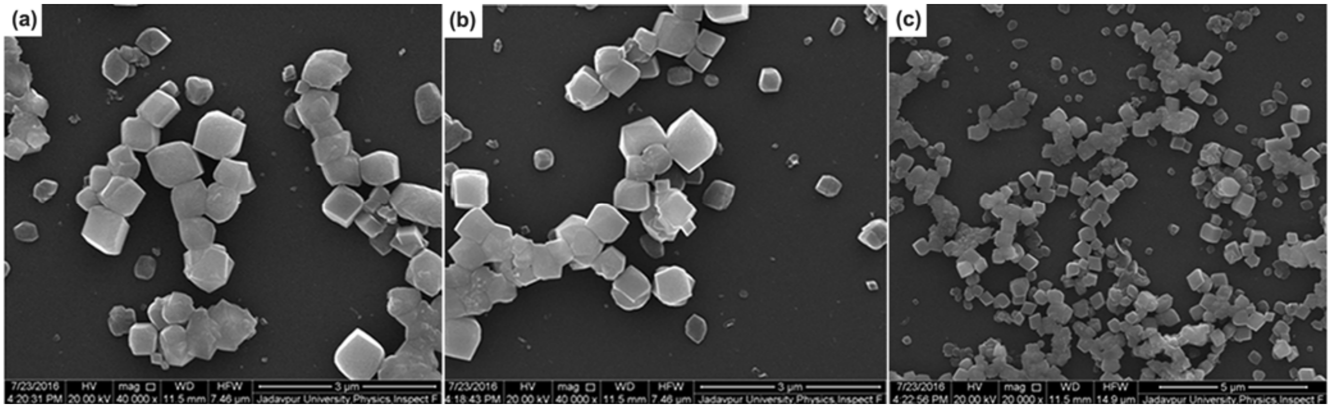

Fig. 3 — Scanning electron micrographs of (a) CaO-rGO, (b) SrO-rGO, and, (c) BaO-rGO.

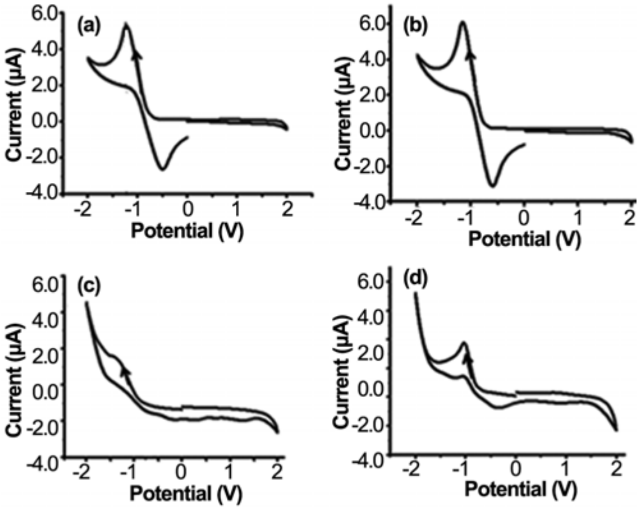

Fig. 4 — CV profiles of (a) reduced graphene oxide (rGO), (b) rGO-CaO, (c) rGO-SrO, and, (d) rGO-BaO in MeCN solution. [Working electrode: Pt-disk; reference electrode: Ag/AgCl, Cl$^-$ auxiliary electrode: Pt-wire; supporting electrolyte: tetrabutylammonium perchlorate].

TGA-DSC analysis of coupled rGO-EMO systems reveal that thermal stability increases as we move down towards heavier alkaline earth metal oxide (Supplementary data, Fig. S2). It can be seen that rGO-CaO system loses 8% of its initial weight ~400 °C and at 700 °C it loses 30% of its initial weight (Fig. S2(a)). The rGO-SrO system shows higher thermal stability and it loses only about 8% initial weight ~700 °C, it loses only 25% of its initial weight ~975 °C (Fig. S2(b)). The increasing trend of thermal stability is carried over for rGO-BaO system, which becomes highly stable and loses only 6% of its initial weight up to 700 °C and at ~975 °C it shows only 15% of its initial weight loss (Fig. S2(c)). DSC curves for all these systems show a similar pattern, comprising a steep consistent decrease up to 200 °C, then an intermediate flat region followed by a steady decrease. DSC curve of rGO-CaO shows two small exothermic peaks at about 400 °C and 700 °C (Fig. S1(a), rGO-SrO exhibits only one small exothermic peak at 900 °C (Fig. S2(b)), whereas the rGO-BaO system shows one small exothermic peak at 850 °C followed immediately by another endothermic peak at 900 °C (Fig. S2(c)). All of these peaks may be attributed to the possible phase transitions.

Electrochemical properties of the coupled reduced graphene oxide-alkaline earth metal oxide (rGo-EMO) systems show an unexpected inherent redox activity and chemical reversibility. The rGO modified with *p*-block elements such as CaO, SrO and BaO in nano regime shows impressive electrochemical performances in cyclic voltammetric time scale.

Representative cyclic voltammograms of rGO shows the cathodic peak potential (E_{pc}) at –1.22 V followed by (E_{pa}) (anodic peak potential) at –0.50 V (Fig. 4a). Repeated potential sweeping did not show any change in the peak or symmetry of the pattern, which indicates the stability of the rGO surface in electrode field. On impregnation of *p*-block metal oxides (CaO, SrO, BaO) imperative changes are seen in the voltammogram pattern and peak positions. In the CV of rGO-CaO, E_{pa} is shifted by 0.1 V to more negative values (–0.6 V) as compared to that of rGO while E_{pc} remains almost at the same position (–1.20 V) (Fig. 4b). This implies that rGO remains inert to electrochemical reduction. Voltammograms of rGO-BaO (–0.3 V) and rGO-SrO (–0.4 V) are significantly changed as compared to that of rGO pattern. The rGO impregnated BaO and SrO do not show well defined anodic peak (E_{pa}: –0.4 V (rGO-SrO) and –0.3 V (rGO-BaO)), while the cathodic peaks appear at –1.12 V and –1.35 V for rGO-SrO and rGO-BaO respectively (Fig. 4(c & d)). Ionic size follows the order: Ca^{2+} (100 pm) < Sr^{2+} (118 pm) < Ba^{2+} (135 pm), which also supports E_{pa} ordering of metal oxide impregnated rGO surface.

Herein we report the synthesis, characterization and electrochemical activity of novel coupled rGO systems impregnated on the matrix of alkaline earth metal oxides. These systems become more and more thermally stable and electrochemically reversible as the matrix becomes heavier down the group. These findings will certainly add on to the ever increasing knowledge base for potent applications of reduced graphene oxide and the unusual electrochemical reversibility and thermal stability of these systems indicate their possible application as catalysts and in other fields.

Supplementary data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_57A(05)605-609_SupplData.pdf.

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