Effect of RGO- Y_2O_3 and RGO- $Y_2O_3:Cr^{3+}$ Nano Composite Sensor for Dopamine

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Abstract

The RGO-Y₂O₃ and RGO-Y₂O₃: Cr³⁺ (5 mol %) nanocomposite (NC) synthesized a simple hydrothermal technique. The structure and morphology of the synthesized NCs were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Y₂O₃:Cr³⁺ display spherical shaped particles. Conversely, the surface of the RGO displays a wrinkly texture connecting with the existence of flexible and ultrathin graphene sheets. The photoluminescence (PL) emission spectra showed series of sharp peaks at 490, 591, and 687 nm which corresponding to $^4F_{9/2} \rightarrow ^6H_{15/2}$, $^4F_{9/2} \rightarrow ^6H_{13/2}$, and $^4F_{9/2} \rightarrow ^6H_{11/2}$ transitions and lies in the blue, orange, and red region. The prepared NCs were used for the preparation of modified carbon paste electrodes (MCPE) in the electrochemical detection of dopamine (DA) at pH 7.4. Both modified electrodes provide a good electrocatalytic activity for the voltametric detection of DA. Doping is an effective method to improve the conductivity of Y₂O₃:Cr³⁺ and developed a method for the sensor used in analytical applications.

1. Introduction

Now-a-days, one of the most important areas in science is nanotechnology. The nanoparticles (NPs) exhibit unique properties like chemical, physical, and electronic that are different from those of bulk materials. Electrochemical detection plays very important role and attractive for the monitoring of biomolecules [1-4].

Green chemistry controlled and bio-compatible way offers savvy, eco-friendly and scaled up for large quantity and do not need extreme conditions such as high temperature, pressure, and hazardous chemicals to fabricate NPs of metal, metal oxide as well as carbon comprising graphene [5].

As of late, Graphene is one of the developing materials with a single layer of carbon in a closed pressed honeycomb two-dimensional lattice materials having one of kind properties such as large surface area, improved electrical conductivity, unrivaled electrochemical property, and chemically stability make the graphene as profoundly encouraging for a wide range of applications, namely, energy storage, sensor, drug delivery, and optoelectronic devices, etc [6-10].

Nonetheless, a vital task in the fabrication and treating of graphene is that irreversible agglomerates and or restack to frame graphite as a result of van der-waals force interaction. Graphene oxide (GO) is a major by-product of graphene. The exterior of the GO sheets has a huge quantity of oxygen functional groups namely hydroxyl, carboxyl and epoxy groups situated at the edge of the sheets makes the GO sheet powerfully hydrophilic, permitting them to freely scatter in water [11].

Furthermore, the GO sheet is considered to be an electrical shielding material owing to its disordered sp² bonding network and can be reestablished by attainment the reduction of GO. In recent advances, reduced graphene oxide (RGO) is used as the auxiliary for pristine graphene since of its large surface area and superior conductivity, which has been in favor of the precise revealing of the biological analytes.

Additionally, RGO also comprises various types of oxygen vacancies, which make it possible to be altered with other NMs to additional progress its chemical as well as physical properties for the future generation point-of-care biosensors (POC) as well as energy storage devices. Reduction of GO results in the partial restoration of graphitic network conventionally attained using chemical, thermal, and electrochemical pathways [12].

Generally for chemical reduction of GO, reducing agents (RA) such as hydrazine (N_2H_4), hydrazine hydrate, and sodium borohydride (NaBH_4) were used. Conversely, these RA are unsafe to human health and the environment. Further, topological defects and vacancies were created upon thermal reduction of the GO sheet. The presence of these defects which affects the electronic properties of the RGO, resulting in the decrease of ballistic transport path length and introduce scattering sites. Therefore, the execution of a greener reduction route can offer a viable substitute methodology for large production of RGO [13]. Other than the utilization of GO and RGO, these days a lot of consideration for the integration of inorganic phosphor with GO to manufacture composites or hybrids has become a hotly debated issue of exploration because of their upgraded functionalities that can't be accomplished by either part alone. It is well known that the attachment of inorganic NPs onto GO may inhibit the aggregation and improve the significant persuasive effect on electrochemical properties through attaching them onto GO sheets. Amongst the metal oxide NPs decorating RGO, much attention has been given to doped and undoped NPs especially the stable Y_2O_3 host [14, 15].

Till date, many approaches have been utilized for the fabrication of MO/RGO composites namely microwave, hydrothermal, pyrolysis method, etc., [16-20] when the addition of MO NPs to the GO matrix, an upsurge in porosity happens and the GO-MO attains the properties that are dissimilar from those exhibited by each distinct component. On the other hand, Y_2O_3 NPs are chemically steady and have a narrow bandgap that enables electron transfer and offers excellent electrochemical sensitivity.

The present work describes the electrochemical study of DA by using hydrothermal synthesized RGO- Y_2O_3 and RGO- Y_2O_3 : Cr^{3+} NCs. The prepared NCs were well characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). NCs were used as the electrochemical sensor for voltametric determination of DA by using a modified carbon paste electrode.

2. Experimental Section

2.1. Reagents & Investigation techniques

The sodium hydroxide, Dopamine hydrochloride, Uric acid, Na_2HPO_4 & NaH_2PO_4 was from nice chemicals. The graphite powder (Loba Chemie), silicon oil (Himedia) & all other required solutions were prepared from distilled water. The electrochemical experiments were performed on a voltammetric instrument of model CHI-660c (CH Instrument-660 electrochemical workstation). The Shimadzu made diffractometer provided with $\text{CuK}\alpha$ radiation was utilized for structural characterization. Surface morphology and particle size were studied with the help of a field emission scanning electron microscope

(FESEM, TESCON) and transmission electron microscope (TEM, H-600, Hitachi, Japan) respectively. The Horiba made spectrofluorimeter (Jobin Yvon) was used for Photoluminescence (PL) with a 450 W Xenon lamp as an excitation source.

2.2. Preparation of RGO-Y₂O₃ composite hydrothermal synthesis

The chemicals procured in the present work are analytical grade and used without further purification. The modified Hummers method has been used for the synthesis of GO [21]. The obtained GO solution was sonicated for about 25-30 min, centrifuged to wipe off the unreacted GO.

A single step hydrothermal route was utilized for the fabrication of pure Y₂O₃ and Cr doped Y₂O₃ in RGO. In a typical synthesis, stoichiometric quantities of yttrium chloride (YCl₃·6H₂O) and chromium chloride (CrCl₃·6H₂O) were dissolved to 120 mL of mixed liquid, encompassing 60 mL of C₂H₅OH and 60 mL of GO aqueous dispersion before stirred for 25-30 min to get a clear solution. Then the resulting solution was shifted to a 180 mL Teflon-lined stainless-steel autoclave and treated thermally at 175 °C for 12 h. Afterward, the autoclave was natural cooling down to room temperature. The final yield was washed away several times with distilled water and then ethanol, separately, and then centrifugation. The as-obtained products were dried at 80 °C for 12 h in air, and annealed at 500 °C for 2 h in Ar and subsequently 200 °C for 12 h in the air to form the RGO/Y₂O₃:Cr³⁺ NCs. Pure Y₂O₃ and a series of RGO-Y₂O₃:Cr³⁺ NCs with the GO contents of 2, 4, 6, 8, and 10 mg were synthesized by changing the concentration of GO aqueous dispersion.

2.3. Modification of RGO-Y₂O₃ and RGO-Y₂O₃Cr³⁺ NCs

The BCPE was prepared according to the literature [22, 23]. The CPE was modified by taking different weights of NCs (2, 4, 6, 8, and 10mg) in silicon oil and graphite powder. Then this mixture was thoroughly mixed in an agate mortar for about 30 min and packed into a homemade Teflon cavity current collector and polished using soft paper(scheme-1)[24].

3. Results And Discussion

3.1 Characterization of RGO-Y₂O₃ and RGO-Y₂O₃Cr³⁺ NCs

Fig. 1 shows the PXRD patterns of GO, RGO, and Y₂O₃:Cr³⁺/RGO respectively. As obtained GO exhibits a distinctive (001) peak at 10.8° (JCPDS No. 89-8490). Further, GO was exposed to the HT route, a well-defined (002) peak was acquired at ~25° (JCPDS No. 89-7213) which indicates that the reduction of GO sheets. Further, Y₂O₃:Cr³⁺/RGO NCs (Fig.1b) were dominated by the Y₂O₃:Cr³⁺ reflections (JCPDS file no. 83-0134). A feeble and expansive diffraction peak obtained at 24.31°, conforming to the interlayer spacing (d) of 0.37 nm, and the peak located at ~ 12.11° vanishes, signifying that the reduction and the exfoliating of GO into thinner RGO with lesser size. No obvious reflections, including the (001) GO are perceived specifying the creation of highly pure Y₂O₃:Cr³⁺ NPs. Most of the XRD peaks of the

$\text{Y}_2\text{O}_3:\text{Cr}^{3+}/\text{RGO}$ hybrids were similar to those of the $\text{Y}_2\text{O}_3:\text{Cr}^{3+}$ NPs with minor variations in the peak positions (broadening, change in the intensity of the diffraction profiles, which showed that $\text{Y}_2\text{O}_3:\text{Cr}^{3+}$ is effectively anchored onto RGO which was auxiliary proved by the absence of a sharp (002) diffraction peak in the $\text{Y}_2\text{O}_3:\text{Cr}^{3+}/\text{RGO}$ hybrid. Hence, the restacks of RGO are inhibited by the control of $\text{Y}_2\text{O}_3:\text{Cr}^{3+}$ NPs.

The FE-SEM results of $\text{Y}_2\text{O}_3:\text{Cr}^{3+}$, RGO, and $\text{RGO}/\text{Y}_2\text{O}_3:\text{Cr}^{3+}$ NCs are shown in Fig. 2a. The as can be evident from the figure, $\text{Y}_2\text{O}_3:\text{Cr}^{3+}$ NPs exhibit spherical shaped particles. However, the surface of the RGO exhibits wrinkled texture connecting with the occurrence of flexible and ultra-thin GO sheets (Fig. 2b). The SEM image of $\text{RGO}/\text{Y}_2\text{O}_3:\text{Cr}^{3+}$ indicated a uniform distribution of $\text{Y}_2\text{O}_3:\text{Cr}^{3+}$ NPs on the wrinkled RGO (Fig. 2c). The TEM image of the $\text{Y}_2\text{O}_3:\text{Cr}^{3+}/\text{RGO}$ show the distribution of $\text{Y}_2\text{O}_3:\text{Cr}^{3+}$ NPs on the GO sheet (Fig. 3)

3.2 Photoluminescence analysis

Fig. 4a shows the excitation spectrum of $\text{Y}_2\text{O}_3:\text{Cr}^{3+}$ (5 mol %) NPs monitored at 689 nm emission wavelength. The excitation spectrum consists of peaks at 361nm 419nm corresponding to the transitions ${}^6\text{H}_{15/2} \rightarrow {}^4\text{P}_{7/2}$ and ${}^6\text{H}_{15/2} \rightarrow {}^4\text{M}_{21/2}$ respectively. Typical PL emission spectra of $\text{Y}_2\text{O}_3:\text{Cr}^{3+}$ (5 mol %) NPs under 361nm excitation wavelength are shown in Fig. 4b The emission spectra displays sharp peaks at ~ 490, 591, and 689 nm corresponding to ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$, ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$, and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$ transitions which lie in the blue, orange and red region. As can be seen from the figure, it is apparent that the red emission was dominating when compared to blue and orange emissions. The transition corresponding to orange emission is magnetically allowed and hardly differs with the crystal field strength around the Cr^{3+} ion. Whereas, the transition corresponding to blue emission belongs to the hypersensitive electric field (forced electric dipole) transition with the selection rule $\Delta J = 2$, which is strongly influenced by the outside surrounding environment. When Cr^{3+} is located at a low – symmetry local site (without inversion center), red emission is often dominant. In the present study, since the red emission is dominant, the Cr^{3+} ions occupy lower symmetry local site in the Y_2O_3 host matrix.

3.3 Characterization and Optimization of $\text{RGO}-\text{Y}_2\text{O}_3$ and $\text{RGO}-\text{Y}_2\text{O}_3:\text{Cr}^{3+}$ MCPE

Fig. 5a establishes the CVs response of 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ in the KCl at the modified electrodes. The NCs MCPE displayed increment in the redox peak current (I_p) with the decrease ΔE_p compared to BCPE and $\text{RGO}-\text{Y}_2\text{O}_3:\text{Cr}^{3+}$ MCPE exhibit highest I_p . The total active surface area of electrodes calculated by Randles-Sevick's equation (1) [25]. The area calculated that of greater value for NCs MCPE (0.0412 cm^2 and 0.0456 cm^2) compared to BCPE (0.031 cm^2).

$$I_p = (2.69 \times 10^5) n^{3/2} A D_0^{1/2} C_0 \nu^{1/2} \text{-----} 1$$

To optimize the quantity of amount of RGO-Y₂O₃ and RGO-Y₂O₃Cr³⁺ were used as a modifier, CPEs modified with different quantities of the RGO-Y₂O₃ and RGO-Y₂O₃ composites were used to determine 10 μM of DA (PBS at pH 7.4). Fig. 5b depicts the plot of I_{pa} versus the different quantities of RGO-Y₂O₃ and RGO-Y₂O₃Cr³⁺ NPs respectively. As a result, the MCPEs modified with 6 mg were used as optimized electrodes for further electrochemical investigations.

3.4. The electrochemical response of DA at RGO-Y₂O₃ and RGO-Y₂O₃: Cr³⁺ MCPE

Fig. 6 shows the current response of 10 μM DA at the BCPE and RGO-Y₂O₃ and RGO-Y₂O₃: Cr³⁺ MCPEs (0.2 M PBS at pH 7.4) at SR of 50 mVs⁻¹. In BCPE, the CVs of DA showed a minimum current response, and a peak potential was noted at 142mV and 86 mV, respectively and their corresponding redox peak potential differences (ΔE_p) were computed to be 56 mV. Similarly, RGO-Y₂O₃ and RGO-Y₂O₃:Cr³⁺ MCPE showed good I_{pa} with decreased ΔE_p value 54 mV and 52 mV respectively as compared to the BCPE. It exhibits clear proof of the catalytic effect of the expected sensor towards DA investigation.

3.5. Response of speed rate at RGO-Y₂O₃ and RGO-Y₂O₃Cr³⁺ MCPE

The speed rate (ν) was inspected by CV using 10 μM DA in 0.2 M PBS at RGO-Y₂O₃ and RGO-Y₂O₃: Cr³⁺ MCPE. Fig. 7a & b show the I_p increment with a slight positive shift in the peak potential when the ν was a hike in the range from 50-500 mVs⁻¹. The kinetics of the electrode was evaluated by plotting of ν v/s I_{pa} present marvelous linearity (Fig.7c). The ν^{1/2} v/s I_{pa} (Fig.7d) also shows good linearity. This suggests the adsorption- controlled phenomena on electrode [26]. The heterogeneous rate constant (k⁰) (Table-1) of RGO-Y₂O₃ and RGO-Y₂O₃Cr³⁺ MCPEs was calculated by using Eq. (2). [26]

$$\Delta E_p = 201.39 \log (\nu / k^0) - 301.78 \text{ ————— (2)}$$

3.6. Success of concentration

Fig. 8 a&b depicted the CVs of DA at RGO-Y₂O₃ and RGO-Y₂O₃Cr³⁺ MCPEs. The concentration of these biomolecules varied 10 to 60 μM (a- j) in 0.2 M PBS at pH 7.4. The I_p of DA hikes with a hike the concentration. The plot of I_{pa} v/s DA concentration exhibits the correlation coefficient value was found to be 0.9954 and 0.9986 respectively (Inset of Fig. a&b). The limit of detection (LOD) and limit of quantification (LOQ) was a determination by using the equations [27]:

$$\text{LOD} = 3 \text{ S/M ————— (3)}$$

$$\text{LOQ} = 10 \text{ S/M ————— (4)}$$

To determine, the LOD for DA was 6.01 and 3 μM. & LOQ was 20.04 and 10.88 μM for DA at the RGO-Y₂O₃ and RGO-Y₂O₃Cr³⁺ MCPEs respectively. The comparative analytical performance electrode for DA is designed in Table 2. [28-37].

3.7. Influence of pH

The effect of pH on the electrochemical response of the overoxidized dopamine film towards DA at the RGO-Y₂O₃ and RGO-Y₂O₃Cr³⁺ MCPEs was carefully examined in the pH series of 6.2–7.8 show Fig. 9 a& b respectively. The peak potential shifts to a negative side with hike pH in the MCPEs. The anodic peak potential (E_{pa}) versus pH graph (Inset of Fig. 9 a& b) clearly illustrates. The getting slopes of 57 mV/pH and 60 mV/pH are very close to the Nernstian value of 59 mV for an equal number of electron and proton transfer reactions.

3.8. Selectivity& Stability

Selectivity & stability are also key indicators for practical use. The CVs were recorded for the mixture of 10 µM DA with 10 µM UA, in 0.2 M PBS of pH 7.4 at BCPE, RGO-Y₂O₃, and RGO-Y₂O₃Cr³⁺ MCPEs (Fig. 10). The CVs responses for analytes with low current intensities were seriously overlapped, demonstrating the poor selectivity & sensitivity of the BCPE. However, in identical conditions, the MCPE can separate the oxidation potential of all analytes in the mixture. This result was identifying selectivity MCPE. The stability of RGO-Y₂O₃ and RGO-Y₂O₃Cr³⁺ was also investigated after being stored in a dry state for seven days at room temperature. It was found that the current signals retained 95.6 % and 96.18% of the initial current response & the peak potentials were unchanged.

3.9. Interference study

Lastly, to evaluate the feasibility of the proposed method, the interference of possible chemicals in the determination of DA was conducted, the interference study was performed in the mixture of samples of DA & UA at the RGO-Y₂O₃, and RGO-Y₂O₃Cr³⁺ MCPEs by differential pulse voltammetry (DPV). The RGO-Y₂O₃MCPE (Fig. 11a) shows the I_p of UA was increased with increased concentration from 5 to 30 µM by keeping the constant concentration of 5 µM DA, Similarly, DA concentration was varied and its I_p is increased with the concentration (Inset Fig. 11a). The same procedure also adopted for RGO-Y₂O₃Cr³⁺ MCPE and varying the concentration UA and DA shows in Fig. 11b&Inset Fig. 11b respectively. This result shows higher current sensitivity and absence of background current and this result helps in the accurate and precise determination of DA and UA at RGO-Y₂O₃ and RGO-Y₂O₃Cr³⁺ MCPEs.

3.10. The analytical application of the proposed sensor

To verify the success of the proposed sensor in the dopamine hydrochloride injection. The injection was procured from VHB Medi Sciences Ltd with a specified content of DA 40.0 mg/mL (suitable dilution in 0.2 M PBS). The samples were analyzed by the standard addition method. The results have been shown in Table 3. Therefore, the proposed modified electrode could be applied for the real sample analysis with satisfactory results.

4. Conclusion

In the present work, the RGO-Y₂O₃ and RGO-Y₂O₃: Cr⁺³ NCs were synthesized and used as sensors for DA. The prepared RGO-Y₂O₃ and RGO-Y₂O₃: Cr⁺³ MCPEs marvelous current response towards DA. We successfully studied the selectivity and stability of RGO-Y₂O₃ and RGO-Y₂O₃: Cr⁺³ MCPEs with the influence of pH. The RGO-Y₂O₃: Cr⁺³ MCPE show good linearity with the lower LOD compares to other electrodes. Thus, the facile green synthesized RGO-Y₂O₃: Cr⁺³ NCs is a promising electrode material for sensor applications.

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Tables

Table.1. Rate constant values for DA at different speed rates.

u/mV/s	ΔE_p /mV		k° (s ⁻¹)	
	RG0-Y ₂ O ₃	RG0-Y ₂ O ₃ ;Cr ³⁺	RG0-Y ₂ O ₃	RG0-Y ₂ O ₃ ;Cr ³⁺
50	74	53	0.68083	0.86559
100	74	53	1.36166	1.73119
150	76	54	1.99631	2.56726
200	78	60	2.60157	3.19606
250	82	63	3.10659	3.86037
300	86	65	3.56126	4.52771
350	90	71	3.96907	4.93211
400	97	71	4.18718	5.6367
450	102	74	4.44884	6.12746
500	108	75	4.61542	6.73089

Table.2. Comparative analytical performance electrode for DA

Sl. No	Electrode	Detection limit (μM)	Method	References
01	Au/Gr-Au	30	SW	[28]
01	Pt–Au hybrid	24	CV	[29]
02	CTAB/CPE	11.0	DPV	[30]
03	Fc-MCPE	9.4	CV	[31]
04	poly (sudan III)/MCPE	9.3	CV	[32]
05	SWCNT/GCE	7.0	DPV	[33]
06	RG0-Y₂O₃ MCPE	6.01	CV	Present work
07	Metallothioneins self-assembled gold electrode	6.0	CV	[34]
08	LDH/CILE	5.0	DPV	[35]
09	Ag-reduced GO/GCE	5.4	LSV	[36]
10	Ag/Ag ₂ S-CNT-Nafion	4.7	DPV	[37]
11	RG0-Y₂O₃Cr³⁺ MCPE	3.26	CV	Present work

Table.3. Detection of DA in the real sample (n=2)

Electrodes	Sample added (μM)	Found (μM)	Recovery (%)
RGO-Y ₂ O ₃ MCPE	20	19.48	97.4
	30	29.92	99.6
RGO-Y ₂ O ₃ Cr ³⁺ MCPE	20	19.5	97.8
	30	29.96	99.8

Figures

Figure 1

PXRD patterns of (a) rGO (b) rGO/ $Y_2O_3:Cr^{3+}$ NCs (c) $Y_2O_3:Cr^{3+}$ NPs

Figure 2

Schematic representation of the stepwise fabrication of electrode.

Figure 3

SEM images of a) Y2O3:Cr3+ NPs b) rGO c) rGO/ Y2O3:Cr3+ NCs

Figure 4

TEM images of a) rGO b) rGO/ Y2O3:Cr³⁺ NCs c) HRTEM Image

Figure 5

a) PL excitation spectrum b) Emission spectrum of rGO/Y₂O₃:Cr³⁺

Figure 6

a) CVs of 1 mM potassium ferrocyanide in 1 M KCl solution at speed rate 50 mVs⁻¹. b) Plot of I_{pa} v/s weight of NCs.

Figure 7

CVs of 10 μM DA in 0.2 M PBS solution of pH 7.4 at speed rate 50 mVs⁻¹.

Figure 8

a) CVs of 10 μM DA (0.2M PBS of pH 7.4) at RGO-Y2O3 MCPE at various speed rate b) CVs of 10 μM DA (0.2M PBS of pH 7.4) at RGO-Y2O3; Cr³⁺ MCPE at speed various rate. c) Plot of I_{pa} ν/s ν . d) Plot of I_{pa} ν/s $\nu^{1/2}$.

Figure 9

CVs of DA (0.2M PBS of pH 7.4) at RGO-Y2O3 MCPE with various concentrations. b) CVs of 10 μM DA (0.2M PBS of pH 7.4) at RGO-Y2O3; Cr^{3+} MCPE with various concentrations. The inset Fig a& b shows the graph of I_{pa} versus concentration of DA.

Figure 10

CVs for different pH of 10 μM DA in 0.2 M PBS at RGO-Y2O3 MCPE b) CVs for different pH of 10 μM DA in 0.2 M PBS RGO-Y2O3; Cr^{3+} MCPE. The inset Fig a& b shows the graph of E_{pa} v/s pH.

Figure 11

CVs for selectivity analysis for 10 μM DA & 10 μM UA at BCPE & MCPE at a speed rate of 50 mVs⁻¹

Fig. K

Figure 12

DPVs got for different concentration 10-60 μM DA in PBS (pH 7.4) with 10 μM UA at RGO-Y2O3 MCPE (a) & RGO-Y2O3; Cr³⁺ MCPE (b). The inset figure DPVs got for different of concentration 10-60 μM UA in PBS (pH 7.4) with 10 μM DA at RGO-Y2O3 MCPE (Inset a) & RGO-Y2O3; Cr³⁺ MCPE (Inset b).