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Phase identification in binary mixture of nanopowders from deconvoluted valence band spectra using X-ray photoelectron spectroscopy: Case study with iron oxide and titania polymorphs

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ABSTRACT

We propose a new method of quantifying the phases present in a binary mixture of nanopowder from deconvoluted valence band spectra using X-ray photoelectron spectroscopy (XPS). Polymorphs of iron oxide (γ-Fe_2O_3 and α-Fe_2O_3) and titania (anatase and rutile TiO_2) nanopowders containing different weight percentages of the polymorphs were chosen for the present study. Pure iron oxide nanopowder (Fe_3O_4) was prepared by co-precipitation and was air annealed at 250 and 700 °C to obtain γ-Fe_2O_3 and α-Fe_2O_3 phases, respectively. In addition, anatase and rutile TiO_2 were also used in the present study. A linear correlation between the percentage of the phase and the valance band peak area was observed in both the cases. The phase compositions of the nanopowder mixtures identified from the valence band spectra were compared with that of the X-ray Diffraction (XRD) data and the results were found to be in good agreement with each other. For nanoparticles of size > 30 nm, no size dependent effect was observed in determining the phase composition but for particle size below 10 nm, size was found to have a detrimental role. These results showed that the phases of polymorphs can be quantified from XPS valence band analysis.

1. Introduction

X-ray photoelectron spectroscopy (XPS) has been established as an important analytical technique for surface characterization. It provides the elemental information of a solid surface with a sensitivity of < 10 nm and its chemical composition within 0.1–1 at.% for all the elements except H and He [1,2]. XPS is being used for analyzing coatings and thin films, catalysts, ceramics, corrosion, adhesion, polymers, nanomaterials, glasses, ionic liquids, medical & biomaterials, metal, pharmaceutical, petrochemical and semiconductor industrial products, etc [3–7].

In general, the high resolution core level peaks are analyzed to obtain information of the chemical state of the surface probed. The position and shape of the elemental peaks are affected by the oxidation state of the element and its chemical environment, due to the variation in the screening effect of the core electrons. However, the core level peaks are insensitive to the crystal structure and thus do not provide the phase information since the screening is not affected by the crystal geometry. The neighbouring atoms' arrangement can only affect the outermost electron energy levels of an atom, i.e. valence band. Thus, in principle, it is possible to extract the information of the crystal structure or phase of a sample surface by analyzing the valence band using XPS. Determination of the surface phase composition is useful for the applications such as heterogeneous catalysts, photovoltaics, medical implants, etc [8].

At present the most popular phase identification technique being used for thin films is grazing incidence X-ray diffraction (GIXRD). Phase composition of perfectly flat films as thin as 3 nm is possible using GIXRD [9]. However, surface roughness and waviness of the specimen can diffuse the X-ray intensity and introduce artefacts and noise into the data. Hence, in general, GIXRD is not very useful in surface phase identification of specimens whose surface is not flat. Thus, the XPS valence band analysis is being attempted as a potential alternative to GIXRD. On the other hand, ultraviolet photoelectron spectroscopy (UPS) is another technique of choice to analyze the valence band structure of a material surface. However, the surface sensitivity of the UPS is higher than the XPS (i.e. < 5 nm of the surface) and thus provides the information more about the surface adsorbed species than the

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underlying material surface of interest. The UPS data provides band structure of the adsorbates due to the low exiting energies of the UV rays (15–40 eV) and also with much higher energy resolution. Unlike the UPS, XPS provides the density of states (DOS) of the valence band, which can be compared with theoretical studies like density functional theory (DFT) [10,11].

The advantage of the XPS valence band analysis is that it can provide the phase information of the topmost surface layers irrespective of the surface roughness. XPS valence band analysis has been used to calculate the band gap, conduction/valence band offsets, band alignment at the interface of heterojunctions, band bending and valence band maximum [12–15]. However, analyzing the valence band is relatively complex as compared to the analysis of core levels. This is due to the presence of several electron energy levels in a narrow 10–15 eV energy range, together with hybridized orbitals and bonding orbitals of two or more species. Breeson et al. [7] developed a novel method for quantitative surface phase analysis using valence band XPS for the first time. Here, we propose an alternative approach to Breeson's approach by deconvoluting the valence band spectra effectively in quantifying the phases present in a mixed nanopowder containing two polymorphs. To test this, we chose two binary mixtures of iron oxide and titania polymorphs.

Iron oxide and titania nanopowders are among the most widely used materials in many technological applications. Iron oxide nanoparticles are used in magnetic storage, ferrofluids, sensors, medicine, optics, drug delivery, wastewater treatment, photocatalyst, etc [16–18]. Iron oxide nanoparticles exist in different polymorphic phases such as α, β, γ, δ and ε-Fe_2O_3. Maghemite (γ-Fe_2O_3) and haematite (α-Fe_2O_3) nanomaterials are the two prominent polymorphs, extensively used. Titania nanoparticles are used in photo catalysis, antiseptic and antibacterial compositions, as a UV-resistant material, self-cleaning coatings, cosmetic products, paper, pigments, medical devices, gas sensing, purification of air and water, solar cell, construction, oxidation resistance, etc [19–21]. Titania exhibits different polymeric phases among which rutile and anatase find many applications.

2. Materials and methods

Iron oxide nanopowders were synthesized by coprecipitation technique involving Fe^{2+} and Fe^{3+} ions in an alkaline medium under inert atmosphere at room temperature. 0.2 M $FeCl_3{\cdot}6H_2O$ and 0.1 M $FeSO_4{\cdot}7H_2O$ in 1:1 ratio were mixed at a stirring rate of 800 rpm at 60 °C for 5 min, followed by the addition of 30% NH_4OH and increasing the stirring rate to 1200 rpm. The precipitated Fe_3O_4 was separated, washed with water and vacuum dried. To obtain γ-Fe_2O_3 and α-Fe_2O_3, the samples were air annealed at 250 and 700 °C respectively for 2 h.

Titania nanopowders were purchased from Sisco Research Laboratories, India. The average particle sizes (APS) mentioned for anatase and rutile powders were 7 and 250 nm, respectively. Mixed phase samples were produced by combining the desired weight ratio of the powders, followed by thorough mixing. The wt.% of the α-Fe_2O_3 phase in the prepared mixtures of iron oxide nanopowders were 0, 5, 20, 40, 50, 60, 80, 90 and 100 while the anatase wt.% in the titania nanopowders were 0, 5, 10, 25, 40, 50, 60, 75, 90 and 100. Anatase powder of 150 nm particle size was procured from Rankem Pvt. Ltd., India. Anatase nanopowder of average crystallite size of 4 nm APS was purchased from NanoAmor, USA.

Hydrodynamic size and distribution of the iron oxide nanoparticles were measured using Zeta nanosizer (Malvern ZEN3600). It works on the principle of dynamic light scattering, which exploits the Brownian motion of the suspended particles where the spatial arrangement of the suspended particles changes with time, leading to a change in speckle pattern of the scattered light. Time-auto-correlation function was used to measure such scattered intensity fluctuation; $g^2(\delta t) = < I(t)I(t + \delta t) >$ where t is any arbitrary delay time.

Field Emission Scanning Electron Microscope (FESEM, Supra 55, Zeiss, Germany) was used to obtain the morphology of the powder particles and see the homogeneity of mixing of the binary polymorphs in the powder mixtures. The energy of the electron beam was maintained at 5 keV during the imaging of these powders.

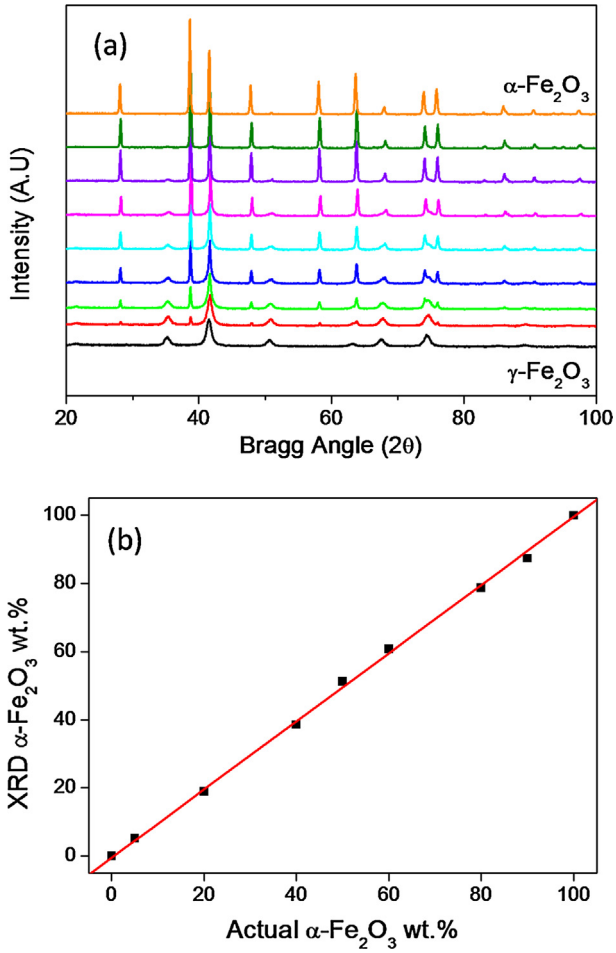

Fig. 1. (a) XRD patterns of iron oxide nanopowders with different compositions of γ-Fe_2O_3 and α-Fe_2O_3 phases where the peak intensities vary with the composition. A.U: Arbitrary Units. (b) The actual wt.% of the α-Fe_2O_3 phase and the wt.% determined from the XRD. The standard deviation (σ) of the linear fit is 1.23 with an R^2 value of 0.999.

X-ray diffraction patterns of the specimens were recorded using Inel make machine (Model – Equinox 2000, France) equipped with Gas Detection Cell (Argon and Ethane) and the intensity measurements were carried out using germanium monochromated Co-Kα radiation (λ = 1.789 Å) in asymmetric (real time) acquisition mode.

X-ray photoelectron spectroscopic (XPS) measurements were carried out using SPECS Surface Nano Analysis GmbH (Germany) make instrument with a 9-channel detector and the electron analyzer axis normal to the sample surface. It was operated in fixed analyzer transmission medium area mode at $< 5 \times 10^{-9}$ mbar ultra high vacuum environment. Monochromated Al Kα X-ray (1486.7 eV @ 55° to the analyzer axis) was used as the source at an anode voltage of 12.5 kV with power level set to 315 W and a spot size of $1 \times 3\,mm^2$. The spectrometer was calibrated for Ag $3d_{5/2}$ peak position at 368.25 eV with a resolution of 0.65 eV at a pass energy of 10 eV and the data were processed by CasaXPS software. The binding energy (B.E.) of C 1s core level from adventitious carbon at 284.8 eV was used as an internal standard of reference to account for any charging of the specimen. Charging of the powder samples during analysis was minimized with the use of low energy (< 10 eV) electron flood gun. The low resolution survey spectra were recorded at a pass-energy of 50 eV with a step size