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Design and development of magnetic core-shell metal oxide nanofiber by co-axial electrospinning

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Summary

In the present work, we report on pre-formulation and fabrication of magnetic metal oxide core-shell nanofibers with tunable optical properties. Magnetic nanofiber design (iron precursors in core and Ti, Zn, Mo, Mn, Co and Ni precursors in shell), fabrication and annealing have been optimized. Structure properties of the core-shell metal oxide nanofibers have been studied by XRD, SEM/EDX, Raman, and TEM methods. Optical and magnetic properties have been studied by diffuse reflectance and vibration sample magnetometer methods.

Experimental

Fabrication of core-shell nanofibers

Solution A (core): Polyvinylpyrrolidone (PVP) solution in 5 ml of DMF including iron nitrate (0.3 g)

Solution B (shell): Polyacrylonitrile (PAN) in 5 ml of DMF including Co, Mn, Mo and Ni nitrates.

Both solutions A and B was loaded in separate 5 ml plastic syringes and attached to coaxial needle (Linari Engineering, Piza, Italy) with plastic tubes. Coaxial needle have inner diameter of 0.5 mm and outer diameter of 1 mm. Syringes was installed in two independent syringe pumps and setup pump rates 300µL/h (Solution A) and 400µL/h (Solution B). Needle installed into the spinning camera 20cm above collector. Collector was covered by aluminum foil and polypropylene membrane. Collector rotating speed was 200 rpm. Between needle and collector was applied 20kV voltage. Samples were dried in vacuum overnight and annealed at 500 ^{0}C.

Characterization of core-shell nanofibers

The structural properties of the deposited nanofibers were investigated through Scanning Electron Microscopy (SEM) (Hitachi, Japan), Transmission Electron Microscopy with Energy Dispersive X-ray Spectroscopy (TEM/EDX) (JEOL Japan), Renishaw micro-Raman spectrometer (Germany), X-ray Diffraction (XRD (a Bruker D8 diffractometer equipped with CuKa radiation from Germany), FTIR (Bruker II Alfa Germany). Diffuse Reflectance Spectroscopy to study the optical properties of the core-shell nanofibers in the UV–visible range. This analysis was conducted using an Ocean Optics fiber optic light source (DH2000, 250–900 nm, USA), an integrating sphere (Ocean Optics, IS-8, USA), and a fiber optic spectrometer (Ocean Optics HR4000, USA). Magnetic properties have been measured by using home made setup.

Results and discussion

XRD spectra showed that as results of combination Fe/Mn, Fe/Mo and Fe/Co core-shell precursors spinel structures were formed. Fe/Ni core-shell composition showed forming of Fe_3O_4 in the core and NiO in the shell. Therefore, for next studies only Fe_3O_4/NiO core-shell nanofibers have been studied. TEM/SEM images and crossectional mapping showed that average dimensions of the Fe_3O_4/NiO core-shell nanofibers were 400±120 nm, where core was 180±120 nm and shell 230±140 nm. TEM/EDX showed following chemical composition: O at% (53.17%), Fe at% (10.83%), Ni at% (36%). Based on soichiometric composition of Fe_3O_4 and NiO, the fabricated core-shell nanofibers had excess of oxygen. This might be attributed to molecular oxygen, adsorbed on the surface of the nanofibers. Raman and FTIR analysis showed significant difference in core-shell and single metal oxide nanofibers. Formulation of core-shell structure generates new vibrational modes in NiO shell Raman spectrum. Appearance of low mode harmonics points to defects in the crystalline structure of the NiO in core-shell structures. The FTIR spectrum of core-shell nanofibers is likely a superposition of Fe-O and Ni-O bonds vibrations.

Optical properties of the sample showed absorption in the visible range. The calculated band gaps point to forming of iron oxide, defect modified NiO and interface in between Fe_3O_4/NiO.

Magnetic properties of the Fe_3O_4/NiO core shell nanofibers showed higher value of magnetization compared to Fe_2O_3. High Fe/Ni precursor ratio showed higher magnetization values. At the same time, hysteresis loop was suppressed with increase of Fe/Ni precursor ratio. We suppose that the observed phenomenon was due to different orientation of the spin in iron oxide core and increase of the defects at interface.

Conclusions

Fe_3O_4 /NiO core-shell nanofibers have been prepared by using co-axial electrospinning. The developed fibers have separate metal oxide core and shell (not spinel). The fibers have high surface area what reflects in O2 adsorbed excess of the fiber surface. Optical properties show high absorbance in the visible range. Magnetic properties vary from core/shell precursor ratio. The developed fibers have good potential for photocatalysis and magnetic sensor applications.

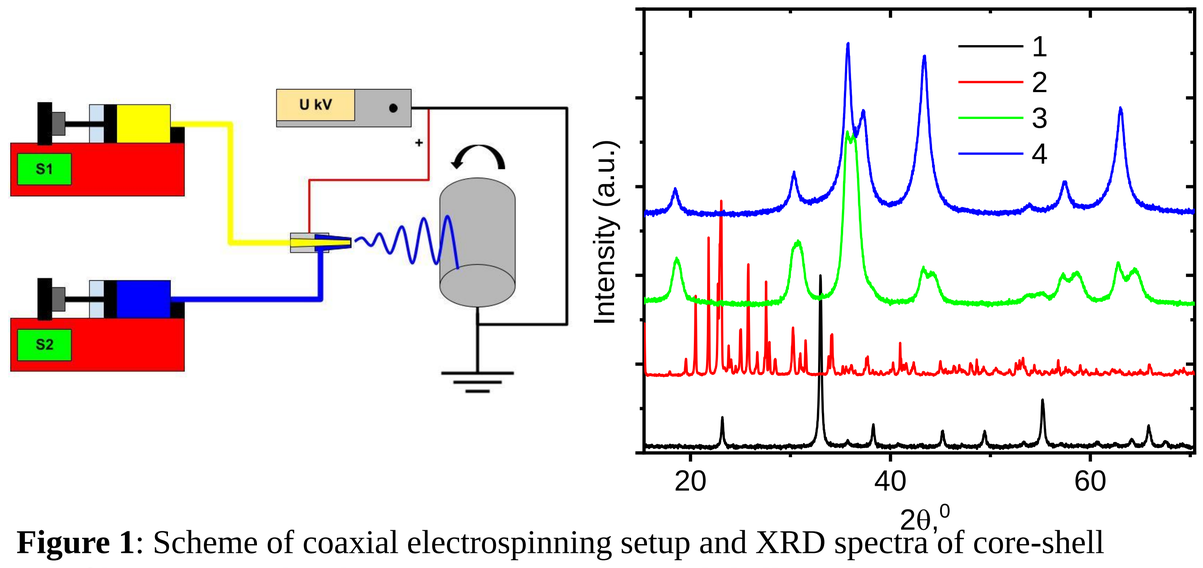

Figure 1: Scheme of coaxial electrospinning setup and XRD spectra of core-shell nanofibers, prepared with iron precursor in core and shell precursor: 1-Mn, 2-Mo, 3-Co and 4-Ni.

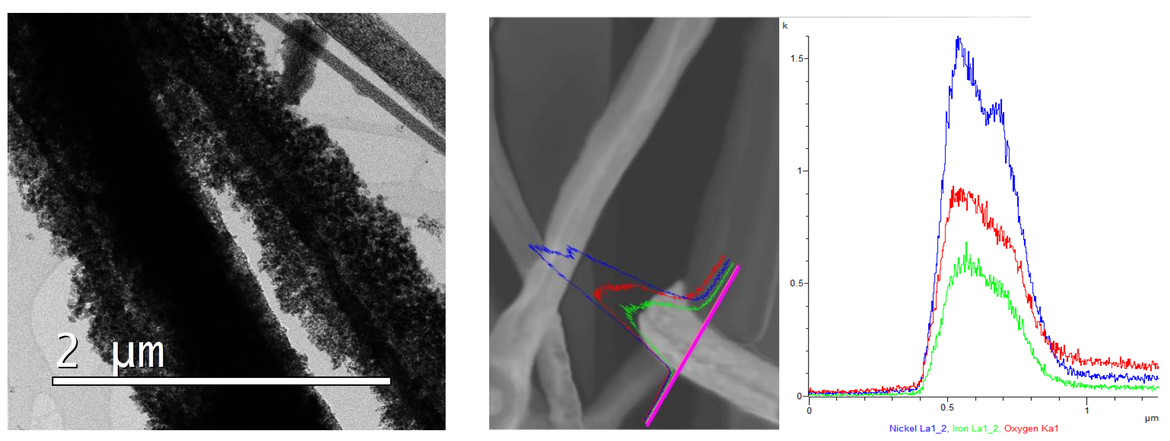

Figure 2: TEM and SEM/EDX profile of Fe3O4/NiO core-shell nanofibers

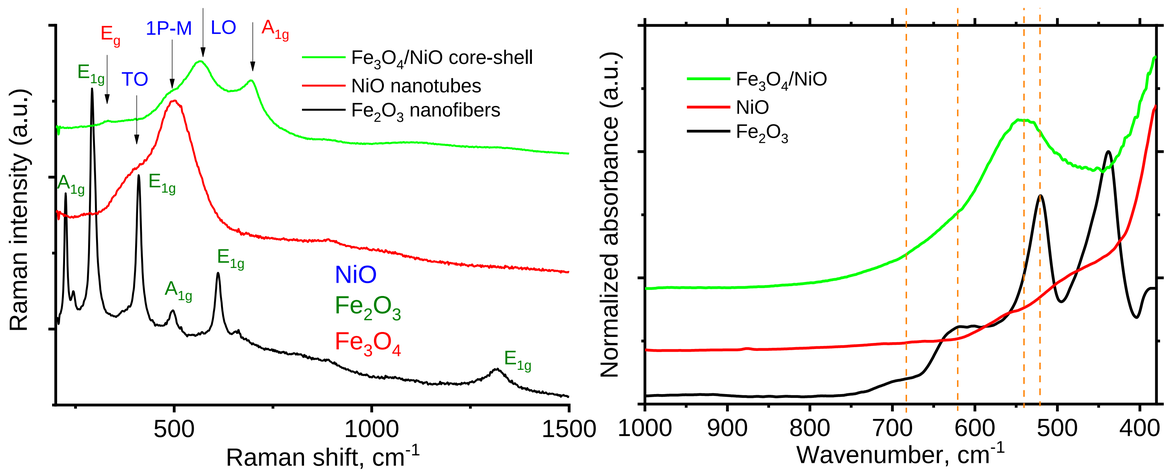

Figure 3: Raman and FTIR spectra of Fe_3O_4/NiO core-shell nanofibers

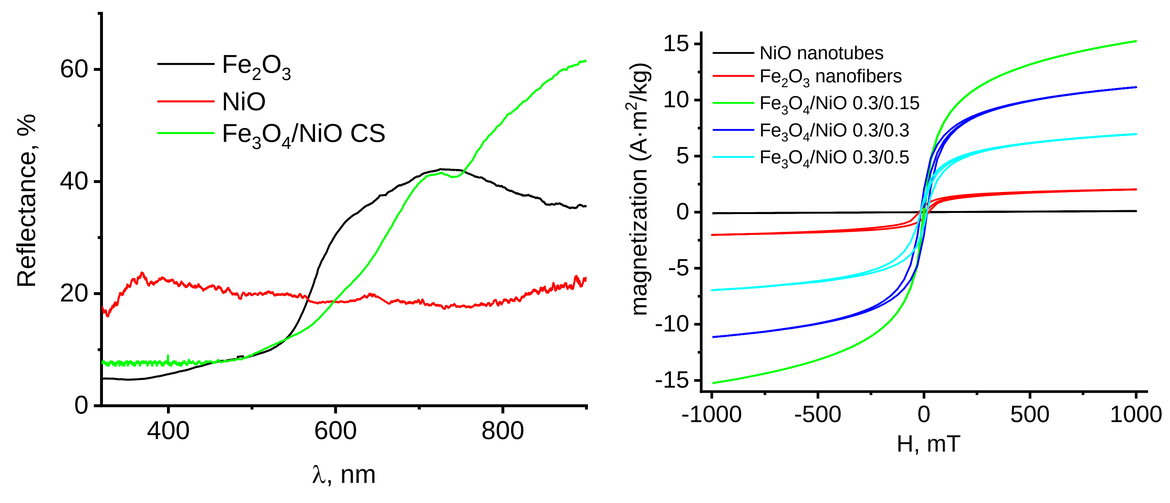

Figure 4: Raman and FTIR spectra of Fe_3O_4/NiO core-shell nanofibers

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