



Sn and Ag doped ZnO quantum dots with PMMA by *in situ* polymerization for UV/IR protective, photochromic multifunctional hybrid coatings



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ARTICLE INFO

Keywords:

NIR reflectance
Hybrid coatings
ZnO quantum dots
Photochromic
Microwave assisted sol-gel
UV/IR shielding

ABSTRACT

A facile multilayer hybrid coating with multifunctional characteristics like UV shielding, IR reflectance, photochromic and photoluminescence are designed with doped ZnO quantum dots [ZQDs] in PMMA polymer and proposed to fabricate solar radiation control active-interface layers. Sn and Ag doped ZnO quantum dots [ZQDs] were initially synthesized *via* a simple microwave assisted sol-gel strategy in the presence of 3-aminopropyl trimethoxy silane, a known organic capping agent. Doped ZQDs were assessed for the size, morphology, chemical nature, crystallinity and optical qualities. ZQDs were subsequently dispersed in methyl methacrylate monomer and polymerized *in situ* to obtain PMMA/ZQDs coating precursor sol. Multilayer hybrid coatings were then fabricated and examined for NIR shielding and UV absorbance efficiencies. Results indicated that the doped ZQDs/PMMA hybrid coatings have blue emission under UV light. With regard to NIR reflectance, the undoped PMMA/ZQDs hybrid coatings exhibit only < 14% NIR reflectance. It is enhanced to 30% and 23% upon doping with Ag and Sn in PMMA/ZQDs hybrids. The hybrid is redesigned with the inclusion of rare earth phosphate dispersoids by which the NIR reflectance is wisely enhanced to ~ 36%. A photochromic organic dye, *spiropyran*, is introduced in the doped ZQDs/PMMA hybrids, to display photochromic functionality with red emission. It is concluded that ZQDs doped with Sn and Ag ions once treated with organic dye molecule and inorganic co-activators, can result in an innovative photochromic, UV/NIR shielding solar-control interface coatings.

1. Introduction

The solar radiation control coatings designed with doped semiconductor materials, which are further revamped and offers desirable multiple functions like UV shielding, photoluminescence, visible light transmission and significant IR reflectance [1,2]. The aforesaid nanoscale semiconducting metal oxides out of Sn, In and Zn are recommended to develop spectrally selective thin films on glass and polymer substrates [1,3–5]. Earlier reports show that, low emissivity coatings are possible with indium tin oxide, antimony tin oxide and lanthanum hexaboride [1,6]. However, in these kinds of semiconducting nanostructured coatings only a limited success is realized since the doping level could not be made as high as to provide large reflectance in the IR part of the solar spectrum [7]. One of the widely accepted coating designs is fabricated by the sequential deposition of appropriate metal/dielectric/metal oxide multilayers on the substrate, where the thickness of the individual films is carefully controlled to have maximum IR reflective quality [8].

Studies of direct deposition of semiconducting metal oxides and

high refractive index materials on the substrates were also reported earlier [8]. Sol-gel [9], sputtering [10] and physical vapour deposition [11] techniques were widely employed for such thin film depositions. In fact, silver has been extensively considered as the best choice for the metal layer assembly because of its high infrared reflectivity and comparatively low absorption capability in the visible region [1,2,12,13].

In recent days, application of active interface layers capable of shielding UV/IR waves effectively is preferred from polymer based low temperature coatings. For the assembly of such active-interface layers, polymer is modified with nanostructured metal oxides. However, uniform dispersion of nanometric metal oxides in polymer hybrids that too with high refractive index is still very critical and technologically challenging. *In situ* sol-gel polymerization is a dominant approach for making metal oxide/polymer hybrid coatings [14]. A high IR reflectance is within reach with polymer hybrid coatings when nanolevel, high refractive index materials such as TiO₂, ZnO, CeO₂ and ZrO₂ are chemically reinforced [15–17]. Poly(methyl) methacrylate [PMMA] is a model system widely reported for hybrid coatings [16–18]. In our

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earlier work, we have shown morphologically varied nano ZnO can improve the IR reflectance quality of PMMA [19]. In this work, we proposed a hybrid coating with Sn and Ag doped ZnO quantum dots in *in situ* polymerized PMMA films. A rare earth phosphate and an organic dye molecule were also employed as co-activators to make the coating multifunctional. The characteristics such as UV shielding, NIR reflectance, photochromic and photoluminescence behaviours of the ZQDs/PMMA hybrid have been studied with respect to the dopants and co-activators.

2. Experimental section

2.1. Materials and reagents

Tin (II) acetate [Sn (CH₃COO)₂, Sigma-Aldrich, CAS#: 638-39-1], Silver nitrate GR [AgNO₃, Extra pure-Merck Specialities Private Limited, Mumbai, India, CAS#: 7761-88-8], Zinc acetate dihydrate, Zn (CH₃COO)₂·2H₂O, [Extra pure-Merck Specialities Private Limited, Mumbai, India, assay 99%, CAS#: 5970-45-6], 3-Aminopropyltrimethoxy silane [APTMS, H₂N(CH₂)₃Si(OCH₃)₃, Sigma-Aldrich, 97%, CAS#: 13822-56-5], Methyl methacrylate [MMA, CH₂=C(CH₃)COOCH₃, Merck], α , α' -Azobisisobutyronitrile [AIBN, [(CH₃)₂C(CN)]₂N₂, Spectrochem. Pvt. Ltd. Mumbai, India], 2-Methoxyethanol AR [HOCH₂CH₂OCH₃, SDFCL, 99.5%], Monoethanolamine (for synthesis) [CH₃CH₂ONH₂, Merck, \geq 99.0%], Zinc oxide nanoparticle [ZnO, < 100 nm, Sigma-Aldrich, CAS#: 1314-13-2], Spiropyran [SP, CSIR-NIIST, Trivandrum, India], and Lanthanum Phosphate [LaPO₄, Indian Rare Earth Ltd., India] were used to fabricate inorganic-organic hybrids. Monoethanolamine and 2-methoxyethanol were used as a stabilizer and solvent, respectively. Blue stars[®] microslides [PIC-1, Polar industrial corporation, Mumbai, India] was used as substrates. Toluene and double distilled water were also employed as solvents wherever necessary.

2.2. Microwave-reflux assisted sol-gel synthesis

Doped and undoped ZnO quantum dots were processed by microwave-reflux assisted sol-gel synthesis. In a typical synthesis, zinc precursor of 2.7 g zinc acetate dihydrate and 30 mL of 2-methoxy ethanol (CH₃OCH₂CH₂OH) were homogeneously mixed under constant stirring. To this solution the dopant precursor Sn(CH₃COO)₂ (2 mol%) was then added followed by the addition of 0.25 mL 3-aminopropyltrimethoxy silane (APTMS). A white colloidal dispersion was obtained at this stage. It became a transparent, clear sol upon the addition of monoethanolamine (MEA). The reaction mixture was maintained at pH 10. The prepared homogeneous, transparent sol was refluxed at 70 °C in a microwave reactor [Sineo Microwave Chemistry Technology (Shanghai) Co., Ltd., MAS-II Plus microwave synthesis/extraction reaction workstation] with the microwave power of 300 W. The reaction was continued for 30 min and then removed and aged for 24 h at room temperature. At the end, a pale yellow coloured transparent Sn doped ZnO quantum dots sol was obtained. The same procedure was repeated for obtaining Ag doped ZnO quantum dots sol using AgNO₃ (2 mol%) as dopant precursor. For a comparative study, the typical synthesis undoped ZnO quantum dots procedure was repeated without any dopants.

The above three sols received from Sn doped, Ag doped and undoped ZnO quantum dots were stored at 4 °C in order to prevent any further particle growth and aggregation. The Sn doped, Ag doped and undoped ZnO quantum dots sols were represented by Sn@ZQDs, Ag@ZQDs and Un@ZQDs, respectively.

2.3. Synthesis of ZQDs/PMMA hybrids sol for coatings

The doped and undoped sol was further treated with 1:1 ethanol-water mixture and to harvest the ZQDs by centrifugal filtration. The product was washed several times with ethanol and then used for

making the hybrids.

0.25 g of AIBN initiator was first ultrasonically dissolved in 20 mL of MMA monomer and 30 mL of 2-methoxyethanol was further added and stirred well. To this reaction mixture 0.5 wt% of Sn doped ZQDs was added and sonicated for 15 min. A stable, translucent colloidal dispersion was finally obtained. It was *in situ* polymerized by conventional refluxing technique for 4 h at 70 °C. The polymerization reaction produced metal doped ZQDs dispersed PMMA hybrid precursor. The precursor was further diluted with adequate amount of toluene that resulted in semi transparent hybrid colloid. The procedure was repeated for obtaining the Ag doped ZQDs/PMMA hybrid colloids and the undoped hybrid colloid was obtained with the same procedure without the inclusion of any dopants. They were further used for fabricating hybrids coatings on glass substrates.

2.4. Fabrication of ZQDs/PMMA hybrid coatings

Glass slides with a size of 75 mm long; 25 mm width, and thickness of 1.35 mm were boiled in concentrated HNO₃, cleaned and washed thoroughly with ethanol. The slides were dried at 80 °C in a vacuum oven and then used for making coatings. The coating was fabricated using a computer controlled dip-coater [KSV Instruments, Netherlands]. The cleaned glass substrate was dipped into the doped (Sn or Ag) and undoped ZQDs/PMMA hybrid colloids with an advancing and receding rate of 85.5 mm min⁻¹. A neat thin coating on both sides of the glass slide was obtained by giving a residence time for about a minute. The glass substrate once coated was cured prior to any successive dip-coatings. The coating process was repeated for obtaining 3, 5, 7, 12 and 20 layers of coatings. We have summarized the experimental steps schematically and shown in Fig. 1.

2.5. LaPO₄ modified ZQDs/PMMA hybrid coatings

The doped ZQDs/PMMA colloid was ultrasonically blended with LaPO₄/PMMA sol prepared separately. 1 wt% LaPO₄ was used for obtaining the LaPO₄/PMMA precursor sol. The ZQDs/PMMA hybrid coated glass (20 times coatings) was further employed for a top-coat with LaPO₄/PMMA sol in which the coating was developed for 3 times.

2.6. Preparation of photochromic ZQDs/PMMA hybrid coatings

ZQDs dispersed PMMA precursor sol was treated with the organic dye molecule, *spiropyran* to obtain light sensitive hybrid coatings. 0.005 g of spiropyran (SP) was added to the doped ZQDs/PMMA hybrid colloid and stirred homogeneously for 30 min under dark condition. It was carefully coated on glass substrate, in the absence of light, via a similar dip coating technique, under identical coating conditions.

2.7. Characterizations

2.7.1. Analysis of ZnO quantum dots

In order to ensure the doping, the as prepared Sn and Ag doped ZnO quantum dots were first examined using Confocal Raman, Ultraviolet-visible (UV-vis) and Photoluminescence (PL) spectroscopic techniques in addition to the powder X-ray diffraction (XRD) and TEM/EDAX analysis. Raman spectra were measured using WI-Tec Raman microscope (Confocal Raman Microscope (alpha300R, WITec Inc. Germany)) with a wavelength of 633 nm laser excitation. Prior to every measurement, a calibration with a silicon standard (Raman peak centered at 520 cm⁻¹) was performed. WI-Tec Project plus (v 4.1) software package was used for the data evaluation. The confocal micro Raman spectra of undoped and doped ZQDs were recorded in the range of 200–1500 cm⁻¹. The spectra of Aldrich ZnO (bulk ZnO) was also obtained to compare the nature and the structural modifications in ZnO quantum dot with the bulk ZnO. Raman scattering is a powerful technique for studying the doping characteristics and lattice disorders about

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