

## PAPER



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## MoS<sub>2</sub>–ZnO nanocomposites as highly functional agents for anti-angiogenic and anti-cancer theranostics

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Due to its excellent properties, 2D-MoS<sub>2</sub> finds potential applications in the fields of electronics, optoelectronics, energy storage and conversion, biomedicine, etc. This work deals with the incorporation of ZnO into 2D-MoS<sub>2</sub>, its structural, morphological, optical, and magnetic studies and its application as an efficient cancer therapeutic agent. The MoS<sub>2</sub>–ZnO nanocomposite exhibits remarkable excitation wavelength dependent down-conversion and up-conversion photoluminescence. The observation of wasp-waisted magnetism in the MoS<sub>2</sub>–ZnO nanocomposite indicates the coupling of ZnO and MoS<sub>2</sub> materials inducing multimodal population. The MoS<sub>2</sub>–ZnO nanocomposite showed cytotoxic properties with a safety index reaching up to ~2. An *in ovo* xenograft assay revealed that the MoS<sub>2</sub>–ZnO nanocomposite retards tumor growth by specifically activating caspase-3 and thereby inducing cellular apoptosis. Moreover, the treatment of xenografts with the MoS<sub>2</sub>–ZnO nanocomposite down regulated the expression of major pro-angiogenic genes such as VEGF, VEGFR2 etc. thereby curtailing vascularization into the tumor intima. Treatment of tumor xenografts with the MoS<sub>2</sub>–ZnO nanocomposite caused reduced expression of mesenchymal specific genes and elevated expression of epithelial specific genes, implying a role of the MoS<sub>2</sub>–ZnO nanocomposite in retarding the process of epithelial to mesenchymal transition (EMT). This study highlights that the introduction of ZnO into MoS<sub>2</sub> nanostructures offers a unique idea to design efficient MoS<sub>2</sub>-based multifunctional nanocomposites that provide opportunities in advanced biomedical and optoelectronic applications.

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## Introduction

The discovery of graphene in 2004 led to a tremendous breakthrough into a whole range of 2D materials which include boron nitride, transition metal dichalcogenides (TMDCs), metal oxides and hydroxides, topological insulators etc., due to their unique, novel functionalities and suitability for a wide range of applications.<sup>1–3</sup> In particular, MoS<sub>2</sub>, a unique class of TMDC having a layered structure, is characterized by strong in-plane bonding and weak van der Waals interaction between the layers, and shows a wide range of mechanical, chemical, thermal, optical and electronic properties.<sup>3,4</sup> Kin Fai *et al.* reported that with decreasing layer thickness, the indirect band gap lying below the direct gap in the bulk material shifts upwards in energy by more than 0.6 eV.<sup>5</sup> Bulk MoS<sub>2</sub> has an indirect band gap of 1.2 eV, which originates from the valence band maximum located at the  $\Gamma$  point to the conduction band

minimum located almost halfway along the  $\Gamma$  and  $K$  points.<sup>6</sup> As the layer number decreases, the lowest band in the conduction band moves upward, increasing the indirect band gap due to the quantum confinement effect in the  $c$ -axis of the crystal. Thus, at monolayer geometry MoS<sub>2</sub> undergoes a transition to a direct band gap of 1.9 eV<sup>7</sup> located at the  $K$ -point of the Brillouin zone different from zero band gap graphene and large band gap hBN. The indirect-to-direct band gap transition in 2D-MoS<sub>2</sub> is strongly evident from the emergence of strong photoluminescence thus presenting an intriguing prospect of scaling all semiconductor technology down to atomic scales. It is well-known that this semiconducting behavior of MoS<sub>2</sub> finds potential applications in lubricants, sensors, batteries, catalysts, LEDs, transistors etc. possessing next generation 2D alternatives to graphene.<sup>7–11</sup> Recent methodologies and research studies based on MoS<sub>2</sub> have indicated the bio-sensing, cell-targeted labelling and anti-cancer properties of these 2D materials, thus unveiling exotic biological applications in addition to their unique electronic and optoelectronic applications.<sup>12–15</sup>

Most interestingly, owing to their large surface area, two-dimensional MoS<sub>2</sub> nanostructures find tremendous applications especially as biosensors, drug delivery systems etc. An MoS<sub>2</sub> based

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