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Review

Interactions of π-conjugated polymers with inorganic nanocrystals

Santanu Bhattacharyya, Amitava Patra*

Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata 700032, India

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ABSTRACT

Photophysics of hybrid nanostructures of π-conjugated polymers and inorganic nanoparticles remains a frontier area of research due to the potentials of such structures in the development of optoelectronic, photovoltaic and light harvesting devices. A brief overview of recent developments in the photophysical interactions of π-conjugated semiconducting polymers with inorganic quantum dots and metal nanoparticles is illustrated in this review. To begin with, we describe general synthetic methodologies of π-conjugated polymers and polymer–inorganic hybrid nanostructures. Successively, we emphasize on the fundamental understanding of interfacial charge transfer, energy transfer and electron transfer during the interactions of conjugated polymer with inorganic nanocrystals. The free charge carrier generation at organic/inorganic interface is of crucial importance in the development advanced materials for the above applications. Recent findings reveal that exciton–plasmon interactions in π-conjugated polymer/metal nanoparticle hybrid nanostructures offer exciting opportunities for device technologies. The strong fluorescence quenching in conjugated polymer by Au nanoparticles is assigned to either internal energy transfer or charge transfer processes. Discussions have also been carried out to unveil the local surface plasmon-coupled resonance effect of metal nanoparticles on the properties of π-conjugated polymers. We discuss briefly about their versatile applications in optoelectronics, solar cells and other photovoltaic devices. Finally an outlook on the prospects of this research field is given.

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* Corresponding author. Tel.: +91 33 2473 4971; fax: +91 33 2473 2805.
E-mail addresses: msap@iacs.res.in, amitavapatra.patra@gmail.com (A. Patra).

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Dr. Santanu Bhattacharyya (born 1985) completed his Ph.D. degree from Jadavpur University, India, in 2013 under the supervision of Prof. Amitava Patra. He is currently working as a Research Associate with Prof. Amitava Patra in Indian Association for the Cultivation of Science, India. His research interest is "Spectroscopic properties of semiconducting polymer nanomaterials".

Prof. Amitava Patra (born 1965), received his Ph.D. (1993) from Jadavpur University, India. He is now Professor at the Indian Association for the Cultivation of Science, India. He is a fellow of Royal Society of Chemistry, 2014. He is the recipient of C.N.R. Rao National Prize for Chemical Research, DAE-SRC Outstanding Investigator Award, A.V. Rama Rao Foundation Prize in Chemistry, AsiaNANO 2010 Award, CRSI Bronze Medal, Ramanujan Fellowship, MRSI Medal. He is an Advisory board member of Nanoscale and Journal of Physical Chemistry and others. He is author or co-author of more than 151 scientific papers, 3 book chapters and 2 Indian patents. His research interests include decay dynamics, energy transfer, and electron transfer of QD, Au nanoparticles, polymer and porphyrin based luminescent nanoparticles, and photonic materials using up- and down-conversion luminescence.

1. Introduction

Conjugated polymer based organic–inorganic hybrid nanostructures have recently been emerged as a new class of functional materials because of their modified optoelectronic and photophysical properties which differ from their individual organic/inorganic counter parts [1,2]. These types of hybrid organic–inorganic nanostructures have potential applications in developing efficient light emitting diodes (LEDs), photovoltaics and sensor devices [3–12]. From the fundamental point of view, conjugated polymer is basically multichromophoric systems, in which the π-electrons of every monomeric unit are delocalized over a significant part of the chain and their properties depend on both the chain length and exciton diffusion length and the exciton diffusion length is in the order of 5–20 nm for conjugated polymers [13]. Conjugated polymer possesses large absorption cross-section due to delocalize π-electron transition from ground state (S_0) to excited state (S_n) [14–16]. Furthermore, semiconducting polymer chain exhibits multiple chain conformations and locally variable degrees of order (depicted in Fig. 1) and it causes long red tail of an overall absorption band [17]. The optical properties of conjugated polymer strongly depend on the extent of conjugation as well as electronic delocalization, chromophoric features, inter/intra molecular interactions, etc. Intrachain and interchain; these two types of exciton propagation have been identified in conjugated polymers. Intrachain exciton migration occurs along the polymer segments while interchain exciton migration occurs via coupling through space in the folded and aggregated polymer units. Semiconducting polymer nanostructured materials are formed by coiling of the polymer molecules with altering both inter/intra molecular interactions [13,18–22]. It is evident that conjugated polymer in nano-dimension possesses blue shifted absorption band due to the kinking and bending of polymer back bone [23,24]. However, the red shifting of absorption occurs due to relatively relaxed and ordered conformations [25,26]. Feng et al. have nicely illustrated the preparation, functionalization and biological applications of conjugated polymer nanoparticles [27]. The fundamental properties of conjugated polymer nanoparticles have been discussed by Mecking et al. [28]. Chiu and his co-workers have highlighted the importance of the conjugated polymer dots as efficient fluorescent markers and their recent advancement towards both in vivo and in vitro imaging applications [29]. Furthermore, it is evident that the optical properties of fluorescent polymer nanoparticles can be modified by encapsulating organic fluorophores inside the polymer nanoparticles [30–44]. The energy transfer and excitonic diffusion of dye doped conjugated polymer nanoparticles have been pointed out by McNeill et al. [32]. Additionally, solvatochromic and photochromic dye doped conjugated polymer nanoparticles are also designed to color tuning and photo-switchable properties [42–44]. Extensive studies have been persuaded to understand the host–guest interactions using time resolved spectroscopy and find out potential applications in light harvesting by energy transfer [35–37].

The understanding of the charge carrier generation in π-conjugated polymer/QD composite hybrid nanostructure has been paid significant interest recently, as these materials show great promise for optoelectronic applications. The tuning of electronic energy level alignments of organic–inorganic counterpart by changing morphology, size and shape promote both the charge separation and the energy transfer between organic–inorganic composites upon photo-excitation [45]. Similarly, various semiconductor–metal hybrid materials systems have been fabricated to investigate exciton–plasmon interactions [46,47]. This interest stems from their unexpected electrodynamic properties due to the existence of metal plasmon resonances. Surface plasmon resonance band of metal nanoparticle originates due to coherent excitation of free conduction electrons on the nanoparticle surface and the wavelength of this band depends on size, shape and interparticle dipole interactions [48–50]. However, little focus has been given on photophysical and electrical properties of metal–semiconductor heterostructure. It is evident that surface plasmon of metal nanoparticles can eventually affect the charge transfer process between excited metal nanoparticles and conjugated polymer [51]. Thus, the challenging problem is to design metal–semiconductor heterostructure and understand their photophysical and optoelectronic properties. Optical properties of semiconducting polymer have significantly influenced by metal nanoparticles due to local field enhancement or by energy transfer process [52,53].

To the best of our knowledge, there is no review article on organic–inorganic hybrid nanostructures where photophysical interactions have been discussed. Considering the emerging field of semiconducting polymer, in this review, we overview the photophysical interactions of semiconducting polymer nanoparticles with inorganic (inorganic QDs/metal nanoparticles) nanoparticles. The development of π-conjugated polymer–inorganic hybrid nanostructures remains a frontier area of research to design optoelectronic, photovoltaic and light harvesting devices based on energy or charge transfer process. We highlight the fundamental processes, i.e., charge transfer, interfacial charge transfer, energy transfer and electron transfer during the interactions of conjugated polymer with inorganic nanocrystals. We also discuss the photophysical (photoluminescence quenching, decay dynamics, radiative and nonradiative decay rates and energy transfer) properties of Au/semiconductor polymer hybrid nanostructures. Such understanding will enable us to construct efficient devices for suitable applications. To begin with, we describe the synthesis of π-conjugated polymer - inorganic hybrid nanostructures and highlight the optoelectronic applications of polymer based hybrid nanostructures. Future perspectives of this emerging field of research are given in the end.

2. Synthesis of π-conjugated polymers and fabrication of polymer-nanoparticle materials

A few techniques are commonly used for fabricating hybrid π-conjugated polymer–inorganic nanocrystals systems. The techniques are: (a) blending technique for nonfunctionalized polymer