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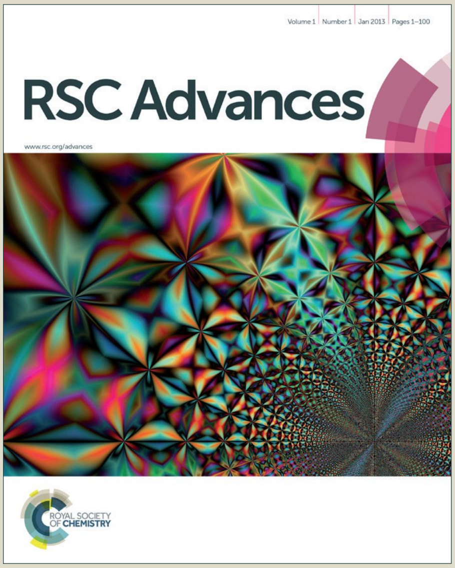

Journal Name

COMMUNICATION

Poly(3,4-ethylenedioxythiophene)/germanium organic-inorganic hybrid thin films: substrate-induced synthesis, enhanced photoelectrochemical and photocatalytic properties

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The unique optoelectronic properties and promising photovoltaic applications of hybrid organic-inorganic composites have driven the exploration of facile design and fabrication of hybrid materials and corresponding devices. As a step toward both expanding the library of morphological diversity of organic conducting polymers and increasing the species diversity of hybrid organic-inorganic materials that utilized in optoelectronic devices, we report here the fabrication and enhanced potoelectrochemical properties of a newly hybrid organic-inorganic composite consisting of poly(3,4-ethylenedioxythiophene) (PEDOT) nanoflowers and Germanium (Ge) nanoparticles. Aliquot studies revealed that dissolution and deformation of the nanoparticles induced the initial formation of flower-like PEDOT. Furthermore, enhanced photoelectrochemical and photocatalytic properties of hybrid films are realized compared to the bare Ge and PEDOT films, which resulted from the enhancement of the separation of electron-hole pairs photoinduced by the hybrid interface between Ge and PEDOT. The hybrid organic-inorganic composite is promising for cost-effective photovoltaic devices and the design principle provides future opportunities for fabrication of other organic conducting polymers.

1. Introduction

Hybrid organic-inorganic composites are attracting increasing attention as potential candidates for optoelectronic applications.[1-3] Integrating the stability and tunable carrier mobility properties of inorganic semiconductors with the large functionality and strong light absorption ability of organic materials offers the possibility to generate a variety of new materials with interesting and unique additional optical and electronic properties. In the field of optoelectronics, hybrid organic-inorganic light-emitting,[4] photovoltaic,[5, 6] and photodetector devices[7] with remarkably broader spectral response and better performance than those of purely inorganic counterparts have been demonstrated.[7] Thus, developments of novel hybrid polymeric composites could be of interest to explore properties suitable for potential application in advanced optoelectronic components.

Germanium is an amazing inorganic semiconductor utilized in lots of the state-of-the-art optoelectronic devices.[8] Bulk Ge not only has a band gap of 0.67 eV at 300 K, a high carrier mobility (3900 $cm^2/V \cdot s$ for electrons and 1900 $cm^2/V \cdot s$ for holes), it also exhibits strong quantum confinement effects and a size-tunable band gap.[9, 10] Due to these inherent properties, Ge is drawing special attention as a potential alternative material for applications in different areas, including photodetectors, field-effect transistors, lithium-ion batteries, and solar cells.[10] However, hybrid structures of Ge based nanomaterials exhibited large interface area for charge separation, giving rise to ideal effects for the enhancement of photoresponse under illumination. For example, Wan et al constructed a hybrid device based on the conjunction of Ge nanocrystals and poly(3-hexylthiophene), and the device exhibited high performance for photodetectors applications.[11] Besides, Ge nanoparticles exhibited a chemical reductive ability, which is evidenced by the rapid degradation of organic dyes.[12]

Among organic conducting polymers, polyaniline and polythiophene are widely used for the construction of conducting polymer-inorganic hybrid materials.[13,14] As a derivative of polythiophene, PEDOT has been exploited in organic electronic and energy conversion devices because of its unique optical and electrical properties, including reduced bandgap, and high stability in the conducting form, as well as its larger electroactive potential window and higher cycling stability than polyaniline.[15,16] Therefore, nanostructured PEDOT can be used as alternative materials for the design and fabrication of hybrid devices and may result in interesting properties. Recently, Chen et al fabricated Si/PEDOT core/shell nanowire photoanode by vapor-phase polymerization of PEDOT and the resulting device exhibits better photoresponse and improved stability.[17] Lee et al reported on the enhanced thermoelectric properties of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate)/Ge composite films prepared by drop-casting of a solution of Ge

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powder in polymers.[18] However, to the best of our knowledge, there have been almost no reports for the application of PEDOT/Ge for photovoltaic devices and organic pollutants photodegradation.

Various 0D, 1D and 2D nanostructures of PEDOT, including nanospheres, nanotubes, nanofibers, and nanorods have been controlled prepared or developed. To our surprise, few reports have studied on more complicated polymer materials such as 3D nanostructures, which should be favorable by virtue of their unique morphologies and fascinating physical and chemical properties. 3D nanostructures enabled high surface area, so that greatly assist in the penetration of electrolyte and reactants into the whole electrode. Recently, Wang et al[19] employed carbon nanotube network as working electrode for the polymerization of a honeycomb-like 3D structure of PEDOT at water-CH_2Cl_2 interface. Ho et al[20] used a film of ZnO microflowers as the template for the growth of PEDOT/ZnO microflowers composed of PEDOT nanosheets. Moreover, PEDOT with a unique 3D macroporous structure was prepared by a facile electrodeposited approach in a mixed solvent of CH_2Cl_2 and water by Xu.[21] Unfortunately, the fabrication of 3D nanostructures of PEDOT requires surfactants which make the preparation complex and the use of organic solvents is not satisfied with the need for green chemistry.

Here, we report the fabrication of hierarchical 3D PEDOT nano-flowers/Ge nanoparticles using a Ge nanoparticles substrate-induced growth strategy from aqueous solutions. To our knowledge, this represents the first report of PEDOT/Ge organic-inorganic hybrid composites and is one of only a few examples of newly 3D flower-like fine structures of PEDOT. In addition to synthesis and characterization, the enhanced photoelectrochemical and photocatalytic performance of the PEDOT/Ge hybrid films were interrogated. The results suggest that the novel PEDOT/Ge hybrid film could be a candidate for solar energy conversion and the design principle gives a promising strategy to other semiconductor materials.

2. Experimental section

Electrodeposition of Ge films: thin films of Ge nanopaticles were grown on ITO-coated glass substrates (sheet resistance: 15Ω) by an electrodeposition process similar to that reported in the literature.[22] ITO-coated glass substrates (8mm × 15 mm) were cleaned by successive sonication in acetone, ethanol and deionized (DI) water. Clean ITO substrates were then dried under flowing nitrogen gas. Ge was electrodeposited in a conventional three-electrode cell using ITO as the working electrode, platinum sheet as the counter electrode, and an Ag/AgCl (3M KCl solution) reference electrode. The electrodeposition solution contained 0.05 M GeO_2 and 0.01 M $Na_2B_4O_7$. Ge films were deposited in chronoamperometry mode using an electrochemical station (CHI 760D, USA) with an applied potential of -1.3V vs Ag/AgCl for a duration of 300 s. As-deposited Ge films were thoroughly rinsed with DI water and dried under flowing nitrogen gas.

Electrodeposition of PEDOT films: polymerization reactions of the 3,4-ethylenedioxythiophene (EDOT) monomer were performed by following a previous procedure suggested by Ringer.[23] The deposition of PEDOT on the surface of cleaned ITO electrodes was carried out by means of cyclic voltammetry using 0.01 M EDOT as the monomer in a KCl electrolyte. Nitrogen gas was bubbled into the electrolyte for 15 min before electropolymerization and continued during the whole PEDOT deposition process to remove oxygen gas. PEDOT film was formed within the potential range of +1.4 to 0 V (vs. Ag/AgCl) for 10 potential cycles. Once the electropolymerization was completed, the work electrode covered with sky blue PEDOT and rinsed with water, dried under flowing nitrogen gas.

Synthesis of PEDOT/Ge hybrid thin films: Ge films were deposited first on the ITO substrates, and then a PEDOT layer of varying thickness was deposited onto the Ge nanoparticles modified ITO film for different number of potential cycles (1-10) by cyclic voltammetric electropolymerization as described above. As-prepared PEDOT/Ge films were washed with deionized water and dried under flowing nitrogen gas prior to characterization and photo-electrochemical tests.

Characterization: The morphology and energy dispersive spectroscopy (EDS) of Ge films, PEDOT films and PEDOT/Ge hybrid films were determined by field emission scanning electron microscopy (JSM-6700F) and EDS was carried out during SEM measurements. UV–visible diffuse reflectance spectra of the films were recorded on a Cary 5000 UV-visible spectrophotometer equipped with a PTFE-coated integration sphere (Varian technology Co., LTD).

Photo-electrochemical measurements: Photo-electrochemical measurements were carried out with an electrochemical station (CHI 760D, USA) using a three-electrode configuration with a PEDOT/Ge film as the working electrode. Platinum and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. 0.1M Na_2SO_4 aqueous solution was used as a supporting electrolyte and 1 cm^{-2} area of PEDOT/Ge was exposed to light illumination. A light emitting diode (LED) operating at 365 nm (max. 80 mW) and a 532 nm laser diode (100mW) were employed as the light source. Transient photocurrent measurements were performed for the as prepared films during ON/OFF cycles under illumination at -0.5V vs Ag/AgCl for 400 s.

Photocatalytic activity test: The catalytic activity of PEDOT/Ge films were evaluated using methylene blue (MB) as model pollutant under irradiation with a 300 W Xe lamp. 2 × 3 cm area of PEDOT/Ge photoelectrode was immersed in 10 ppm of MB solution and the adsorption/desorption equilibrium for the dye on catalyst surface was achieved by kept in a dark environment for 1 h. Then the solution with PEDOT/Ge film was illuminated for 180 min. The change in concentration of MB solution was monitored using Cary 5000 UV-visible spectrophotometer for every 60 min by detecting the maximum absorption wavelength (653 nm) for MB. For the sake of comparison, Ge films and PEDOT films were tested under the same conditions.

3. Results and discussion

The Ge nanoparticles modified ITO films were fabricated through a method based on a reduced ITO as working electrode for the reduction of Ge reported by Jay and co-workers.[22] The morphology and structure of Ge films were first determined by scanning electron microscopy (SEM). Typical SEM images (Fig. 1a) demonstrated that the Ge nanoparticles films were successfully synthesized with an average Ge particle size of 50 nm. The Ge films consisted of numerous, uniformly dispersed Ge nanoparticles with a screes-like morphology (Fig. 1a). The inset in Fig. 1a showed the morphology of as-received ITO that was smooth, and did not show any evidence of structures on the surface. In a similar fashion, pure PEDOT film with a well-defined and cross-linked 3D pore framework can be deposited. The flexible PEDOT in hierarchical structural overlapped or coalesced with each other, leading to the formation of cross-linking 3D framework ultimately (Fig. 1b). This cross-linking 3D framework with a large contact area would be helpful for solution diffusion in photoelectrochemistry and photodegradation.

For the preparation of the organic-inorganic hybrid film, 3D PEDOT was deposited after growth of Ge nanoparticles on ITO glass. The morphology of PEDOT/Ge was observed using SEM (Fig. 1c and d). SEM images showed the 3D flower-like PEDOT grew on the Ge film while the screes-like morphology of the Ge nanoparticles substrates changed to relatively spherical particles after such a substrate-induced electropolymerization. The quasi-spherical flower-like 3D structures have a size of 4-5 μm, which were assembled by the identical intertwined nano-petals with a thickness of about ca.40 nm. Additionally, it was found that the nano-petals entwined with each other and constructed plenty of diminutive gaps among adjacent petals, which were positive to the communication of solute.

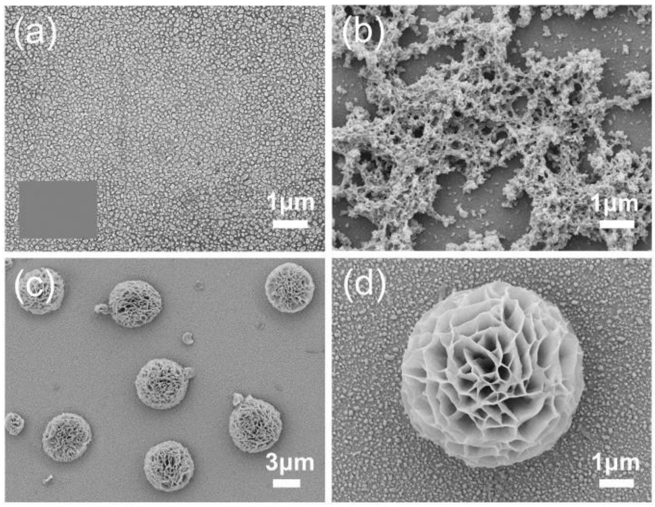

Fig. 1 SEM images of thin films. (a) Ge nanoparticles thin film (the inset was ITO substrates), (b) PEDOT thin film, (c) PEDOT/Ge hybrid thin film, (d) HRSEM images of PEDOT/Ge hybrid thin film.

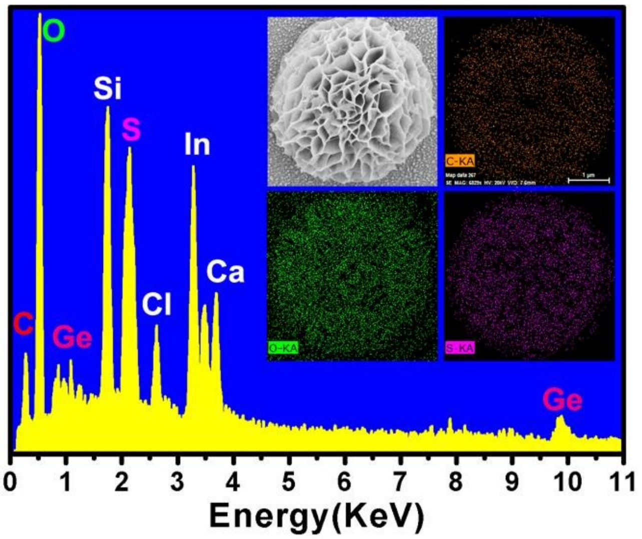

Fig. 2 EDS spectrum for a representative sample of PEDOT/Ge hybrid film. The inset shows an SEM image and corresponding EDS mapping data for an ensemble of PEDOT nanoflowers.

Furthermore, the point-scan energy-dispersive X-ray spectroscopic analysis (EDS) spectrum for an ensemble of the PEDOT/Ge film, shown in Fig. 2, indicated the hybrid films were composed of C, O, S and Ge, as expected for PEDOT nano-flowers/Ge nanoparticles. Si, In and Ca were also presented and they were from the ITO-coated glass substrates. The presence of small amounts of Cl was attributed to residual KCl. A representative SEM image with corresponding EDS mapping data, illustrated in the inset to Fig. 2, gave further evidence for the formation of PEDOT by identifying the homogeneous distribution of C, O and S in the nano-flowers. These results clearly demonstrated that the newly found PEDOT nano-flowers have been successfully polymerized onto Ge nanoparticles films.

To understand the mechanism of the electro-polymerization of PEDOT nano-flowers onto Ge nanoparticles films, SEM analyses were adopted. The morphological evolution process was illustrated by investigating the intermediates collected at different potential cycles of the cyclic voltammetric electropolymerization. After one potential cycle of electropolymerization of PEDOT, the morphology of the Ge nanoparticles changed from sharp screes to relatively spherical particles under a positive potential (Fig. 3a). In the meantime, there is formation and deposition of initial crystals of PEDOT on the electrode via the oxidation of EDOT.[24] SEM images (Fig. 3a) showed that the primary crystals of PEDOT exhibited a silk-like morphology covered on the relatively spherical particles, the release and deformation of sharp screes of Ge led to the formation of PEDOT silk-like sheets. Additionally, due to the poor solubility of EDOT in an aqueous electrolyte, the precursor EDOT could form micelle droplet in aqueous and the droplets played a key role in the formation of silk-like morphology.[21] With an increasing potential cycles of the electropolymerization process of PEDOT (4 and 7 cycles), the 3D growth contributed on silk-like PEDOT, resulting in the

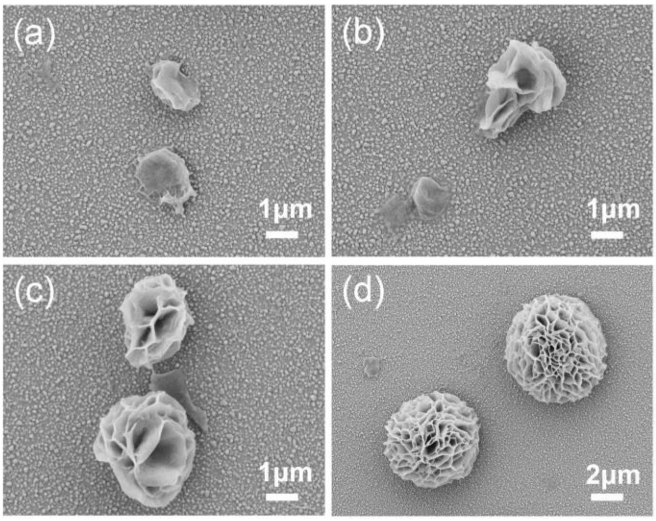

Fig. 3 SEM images of the PEDOT intermediates polymerized on the Ge films for different number of cycles: 1(a), 4(b), 7(c), 10(d).

formation of separate PEDOT petals (Fig. 3b and c). Those primary crystals formed petals at the electrode based on the Ge nanoparticles substrates and the precipitation solubility equilibrium.[25] The precipitation and deposition over the flowers increased as the potential cycles reached to 10, which filled the gaps among adjacent petals led to the formation of flower-like morphology (Fig. 3d). Under the influence of polymerized parameters and the anisotropic arrangement, the new petals deposited on the films tend to join with each other to decrease anisotropic energy and surface energy. Therefore, hemispherical petal-built aggregates with smooth surfaces were exhibited.[26, 27] The mechanism for the formation of PEDOT nano-flowers on Ge nanoparticles involves a substrate-induced polymerization accompanied with 3D growth of PEDOT. We expect that this substrate-induced polymerization may be extended to the fabrication of other conducting polymers nanostructures.

Recently, organic-inorganic hybrid hetero-structures have been identified as promising materials for future solar cells, light-emitting diodes, lasers, ferroelectrics, and fluorescence probes.[28,29] Thus, to demonstrate the potential application of our PEDOT nanoflowers/Ge nanoparticles in solar harvesting, the potoelectrochemical behavior of the PEDOT/Ge film was investigated. We measured the UV-vis absorption spectra of a bare Ge film, pure PEDOT film, and PEDOT/Ge hybrid film, respectively (Fig. 4a). The results indicated that the integration of PEDOT onto Ge nanoparticles film significantly broadened the absorption spectrum of PEDOT/Ge hybrid film. While the spectrum of the pure PEDOT film showed a characteristic wide peak in the range of 500–800 nm, the absorption spectrum of the PEDOT/Ge hybrid film exhibited a significant absorption in the range of 350–800 nm as well as a stronger absorption at wavelengths shorter than 450 nm. These results suggested the existence of a synergistic effect between Ge nanoparticles and PEDOT nanoflowers.

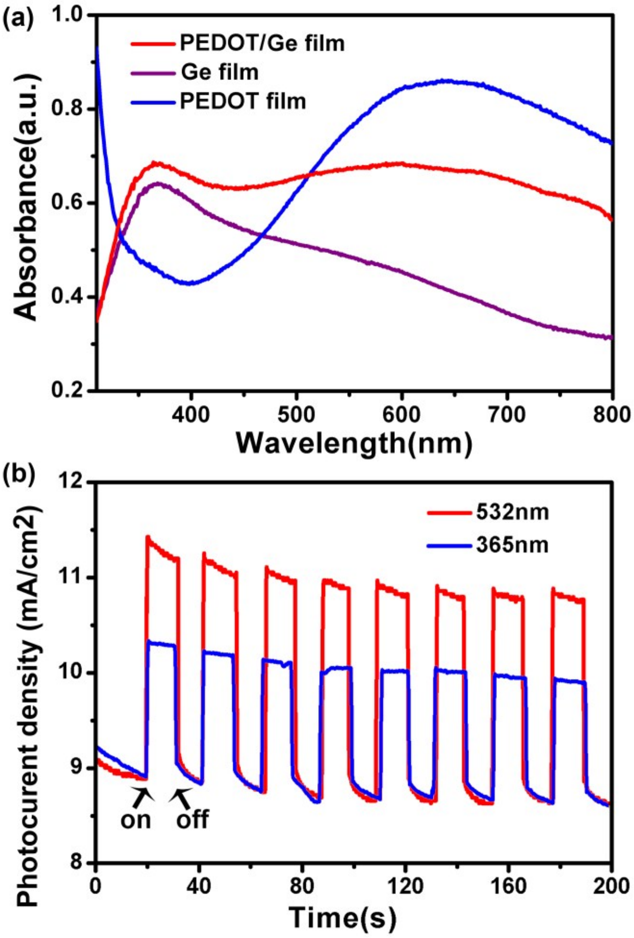

Fig. 4 (A) UV–vis diffuse reflectance spectra of PEDOT film, Ge film, and PEDOT/Ge hybrid film. (B) Transient photocurrent of PEDOT/Ge hybrid films under irradiation: 365 nm and 532 nm. Bias voltage:-0.5V.

Then, the potoelectrochemical behaviors for the films were studied under dark condition and irradiation of various light sources covering UV-vis region; 365 nm (max. 80 mW, LED) and 532 nm (100mW, laser diode). As shown in Fig. 4b, the comparison of photocurrents for the films was detected at negative potentials of -0.5V. The PEDOT nanoflowers/Ge nanoparticles hybrid film responded sensitively over the UV−vis wavelength range and irradiation with light of a wavelength of 532 nm led to a superior photocurrent response. Enhanced photoelectronic response was observed with the integration of PEDOT nanoflowers with Ge nanoparticles. The photocurrent density of the hybrid films under irradiation of UV light increased evidently from 0.034 to 1.32 μAcm^{-2} with the introduction of PEDOT onto the Ge nanoparticles (Fig. S1, ESI†). Moreover, the photocurrent density of the PEDOT/Ge film (2.4 μAcm^{-2}) was 6 times higher than that of PEDOT film (0.4 μAcm^{-2}) (Fig. S2, ESI†) upon illumination with a 532 nm laser diode. Besides, the poto-stability of the photocurrent responses of the PEDOT/Ge film was assessed under many times on/off irradiation cycles for 800 s (Fig. S3, ESI†). Negligible change of photocurrent response was recorded, indicating that the hybrid film possessed excellent poto-stability.

The promising optoelectronic performance of the PEDOT/Ge film may be associated with the PEDOT nanoflowers/Ge nanoparticles configuration, enhanced light absorption, and the unique nature of the Ge nanoparticles or PEDOT nanoflowers. As reported, exciton dissociation can occur efficiently at the interface of two semiconductors, such as in the system of an inorganic semiconductor of Ge and an organic conjugated polymer of P3HT in a hybrid film because of their different natures.[11] Similarly, in the present system, the Ge nanoparticles acted as the photoelectron acceptor due to its high electron affinity, while the PEDOT served as a hole acceptor as well as an electron donor upon photoexcitation. In addition, the interface between the Ge nanoparticles and PEDOT nanoflowers induced charge separation resulted in high transport and long-lived charge separation in the hybrid devices. It is expected that to anticipate the 3D framework geometry and optoelectronic performance of PEDOT/Ge hybrid heterostructures are promising materials for applications in photocatalytic degradation and optoelectronic device.

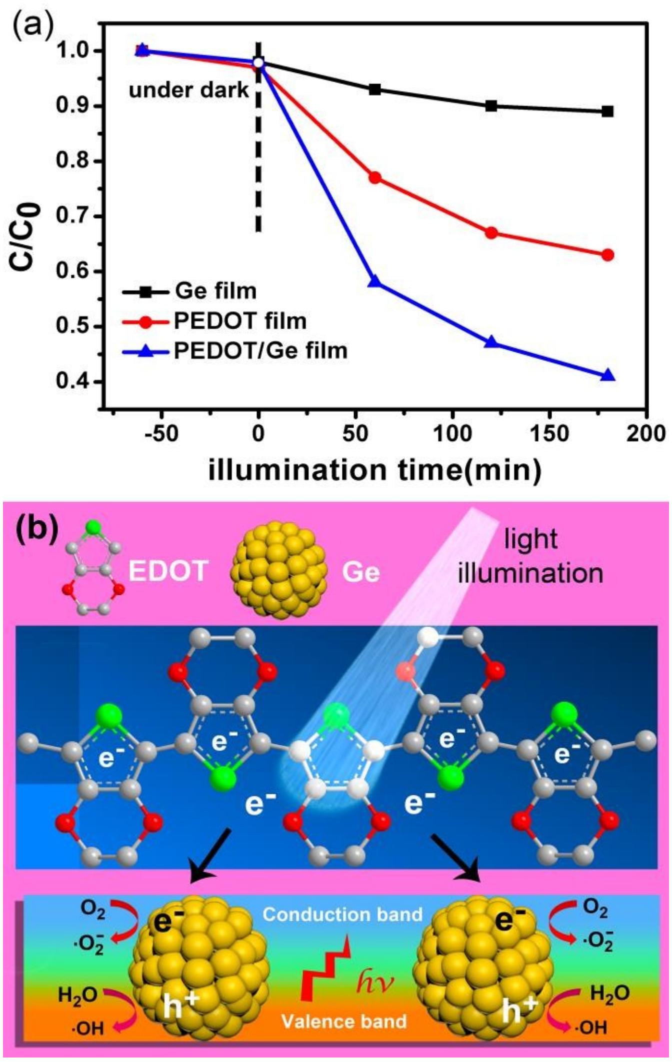

Fig. 5 (A) Time profiles of MB dyes photodegradation with light illumination. (B) A schematic illustration of the photocatalytic activity of PEDOT/Ge hybrid films.

It is well known that a higher photocurrent indicates a higher efficiency in the separation of the photon-generated electrons and holes, and thus suggests a better photo-catalytic activity.[30] To evaluate the photocatalytic performance of PEDOT/Ge film, the decomposition of methylene blue (MB) was examined upon irradiation with visible light. For the sake of comparison, Ge film and PEDOT film were tested also. The degradation spectra and the time profiles of MB degradation with the pure PEDOT film, Ge film, and PEDOT/Ge film nanocomposites under visible light were shown in Fig. S4 and Fig. 5a. As can be seen, After 180 min of visible light illumination, 58% of MB was decomposed by PEDOT/Ge film, whereas only 11% and 37% for Ge film, pure PEDOT film, respectively. The above results demonstrated that the PEDOT/Ge film exhibited the highest degradation activity. The schematic mechanism of the enhanced photocatalytic properties of PEDOT/Ge hybrid nanostructures was demonstrated in Fig. 5b. Upon illumination, the hybrid nanostructures of PEDOT/Ge with a contact interface aroused a rapid photo-induced charge separation and contributed to the decrease the charge recombination rate in the electron transfer process, and thus increased in photocurrent density.[17, 31] The accumulated photoelectrons in the conduction band of Ge nanoparticles transferred to the dissolved oxygen, which will lead to the formation of active oxygen species (e.g. $\cdot O^{2-}$, $\cdot OH$). The highly reactive oxyradical resulted in the degradation or mineralization of MB molecules to desired products (H_2O and CO_2) under visible light.[30, 32-35] Additionally, the 3D framework of PEDOT nano-flowers and the gaps between adjacent petals enabled high surface area that has been illustrated to be beneficial for the efficiently transformation of holes to the electrolyte, so that the holes straightly reacted with organic dye MB to form intermediates or mineralized products.[36] In a word, the PEDOT/Ge hybrid films demonstrated enhanced photocatalytic performance.

4. Conclusions

In conclusion, PEDOT 3D nanoflowers/Ge nanoparticles organic-inorganic hybrid thin films have been synthesized using a green electrochemical method from aqueous solutions. Enhanced photoelectrochemical and photocatalytic performance of the hybrid film were obtained in comparison with the bare Ge film and pure PEDOT film. Integrating of organic conducting polymers and inorganic materials formed hetero-junctions and then decreased the recombination of electron-hole pairs. The successful synthesis and assembly of PEDOT nanoflowers/Ge nanoparticles is an important step toward utilizing organic-inorganic hybrid materials in optoelectronic devices and performing additional in-depth studies of its photoelectrochemical and photocatalytic properties. Moreover, the novel hierarchical 3D PEDOT nanoflowers are a significant addition to the limited library of existing PEDOT and related nanostructures. The hybrid film PEDOT/Ge demonstrated here may find a broad spectrum of applications in the photoelectric nanodevices and environmental protection.

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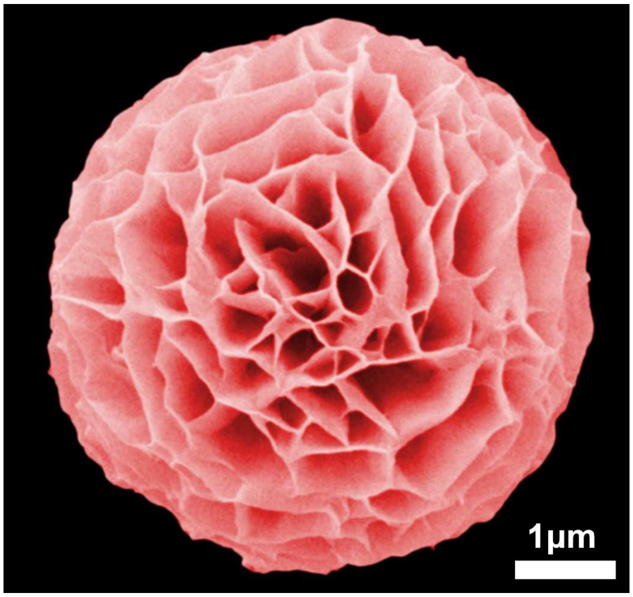
Graphical Abstract



We demonstrate here a facile synthesis of 3D PEDOT nano-flowers/Ge nanoparticles organic-inorganic hybrid film with enhanced photoelectrochemical and photocatalytic performance.