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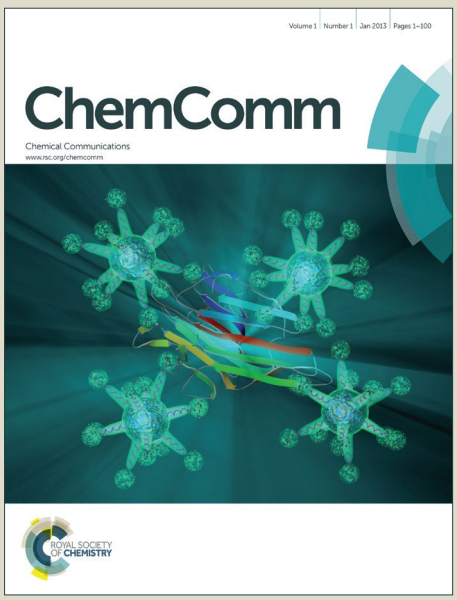

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ARTICLE TYPE

Intrinsic magnetic characteristics dependent charge transfer and visible photo-catalytic H_2 evolution reaction (HER) properties of Fe_3O_4@PPy@Pt catalyst

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A ternary nano-architectural photocatalyst has been designed to investigate whether the intrinsic magnetic property of photo-catalysts have effect on the charge transfer and its photo-catalytic H_2 evolution reaction (HER) properties under visible light irradiation. The electron transfer and the visible-light-driven hydrogen evolution were remarkably enhanced by regulating the electro-magnetic interaction between the magnetic catalysts and the photo-generated electrons.

With the improvement of society, it is urgent to search for efficient, clean and renewable energy resource to solve the energy crisis caused by over-consuming fossil fuel and accompanied environmental pollutions[1]. Hydrogen has been acknowledged as an ideal sustainable energy for the future because of its higher combustion enthalpy than conventional fuels and "zero-pollution" (avoiding the production of greenhouse gases)[2]. Splitting water by solar energy is a promising strategy for hydrogen generation.[3] Plenty of advances have been reported to enhance the efficiency of visible-light-driven H_2 evolution, including the application of high active catalysts, improving the charge separation by the aids of carbon materials, expanding the photo-responsive range by dye sensitization and modify the dispersion of catalyst in reactive system to improve the reactive interface area between the catalyst and the solution[4-8].

In order to accomplish scale-up photocatalytic hydrogen manufacture, easy separation is needed to realize recycle operation of the catalyst, thus using catalyst with a magnetic core to build a composite magnetic photocatalyst is an excellent option for visible-light-driven hydrogen evolution and photo-catalytic decomposition of organics[9-12]. However, developing composite magnetic photocatalyst with HER efficiency is still challenged by limited understanding of the magnetic influence on charge transfer in the composite structure. In fact, it has been found that the magnetic field could affect the redox process of water electrolysis significantly by Lorentz force or Kelvin force[13-16]. An appropriate magnetic field can effectively enhance the electron-transfer rate, promote the reaction of water electrolysis, and even affect the catalytic activity by regulating the surface Spins of catalysts[17]. Since the photo-catalytic hydrogen evolution reactions involves the separation and transfer process of photo-generated charges, it is reasonable to speculate that the magnetic field can influence the movement pathway of photo-generated electrons in a catalyst with a magnetic core, accelerate or retard the H_2 evolution efficiency over these photo-catalysts.

Nevertheless, recovering of the magnetic effect on charge transfer in those catalysts has not been fulfilled because of the absence of appropriate catalysts which are simultaneously equipped with a magnetic core, electron in-put molecule and a charge transfer medium. To accomplish this purpose, dye sensitized conjugated compounds, especially the graphene and conductive polymers, could be a nice study model because the conjugated compounds exhibits high conductivity, superior electron mobility and extremely high specific surface area, while the dye offers in-put electron high efficiently. By strategy of assembling the dye sensitized conjugated compounds with a Pt co-catalyst, a dye molecule, as well as a Fe_3O_4 magnetic core to build a magnetic architecture, one can easily study the HER efficiency dependence on magnetic properties under every designed wavelength of irradiation and magnetic field intensity, so as to understand the mechanism of charge movement in those assembled magnetic catalysts.

In this work, we report, for the first time, a new result of the electro-magnetic coupling effects on the dye-sensitized H_2 evolution under the irradiation of visible light ($\lambda \geq 420$ nm). By a dedicated core-shell structural catalyst (Fe_3O_4@PPy@Pt) with ternary functional components, (1) Fe_3O_4 hollow sphere as core to provide the catalyst with super-paramagnetic property and sufficient hydrophilic groups; (2) Polypyrrole (PPy) shell works as the conductive medium to transfer the photo-generated charge, as well as compensates the surface defects of Fe_3O_4 spheres; (3) Pt quantum dots which are dispersed into the PPy shell acts as the co-catalysts. The dependence of charge transfer on intrinsic magnetic field was recovered by such nano-architecture. It is interesting to find that the intrinsic magnetic characteristics of Fe_3O_4@PPy@Pt catalyst remarkable affected their hydrogen generation activity by deflecting the photo-electron transfer in the charge transfer medium. The deflection of photo-electron could be regulated easily by tuning the magnetic nature of photo-catalysts.

Fe_3O_4 spheres with different saturation magnetization (*Ms*) was used as the core of Fe_3O_4@PPy@Pt, thus the Fe_3O_4@PPy@Pt ternary photo-catalysts exhibiting different saturation magnetization, as shown in Fig. 1 (a). The photo-catalysts are respectively marked as Fe_3O_4@PPy@Pt-A (Ms=44.8 emu·g^{-1}), Fe_3O_4@PPy@Pt-B (Ms=47.2 emu·g^{-1}), and

Fe_3O_4@PPy@Pt-C (Ms=47.2 emu·g^{-1}). Hydrogen evolutions over different photo-catalysts are measured under visible light irradiation, with Eosin Y dye (EY) as the sensitizer and tri-ethanolamine (TEOA) as the sacrifice reagent. As shown in Fig. 1 (b), in the first run, the Fe_3O_4@PPy@Pt ternary catalysts exhibit higher photo-catalytic activity than the Fe_3O_4@Pt catalyst. After 3h photo-catalytic reaction, H_2 evolution over the Fe_3O_4@PPy@Pt-A, Fe_3O_4@PPy@Pt-B, Fe_3O_4@PPy@Pt-C and Fe_3O_4@PPy@Pt-D are respectively 3.6, 2.8, 2.0 and 1.8 times higher than that over the Fe_3O_4@Pt catalyst. As shown in Fig. 1 (a) and (b), the hydrogen generation over those catalysts is closely related to their saturation magnetization (*Ms*). H_2 evolution rate over the Fe_3O_4@PPy@Pt-A and Fe_3O_4@PPy@Pt-B are respectively 1.8 and 1.4 times higher than that over the Fe_3O_4@PPy@Pt-C after 3h visible light irradiation.

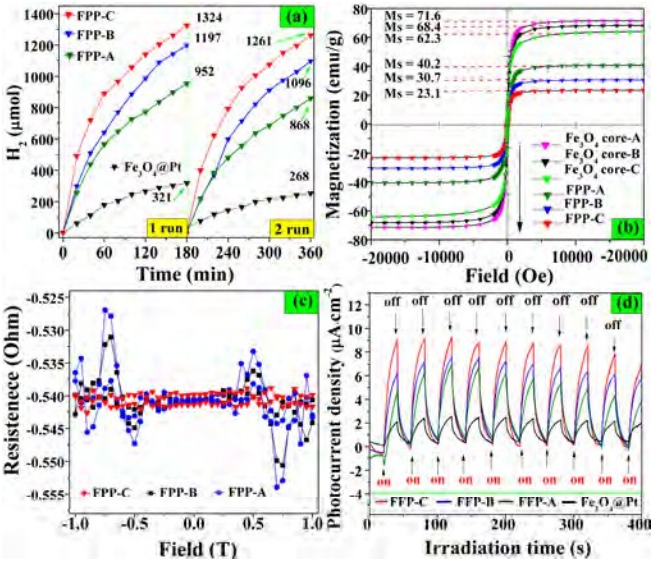


Fig. 1 (a) H_2 evolution (C_{EY} =1.0*10^{-3}mol/L, λ⩾420 nm, EY as sensitizer, TEOA as sacrifice reagent) (b) Magnetic hysteresis curves (c) Hall-effect and (d) Transient photocurrent-time profiles of the Fe_3O_4@PPy@Pt-A (FPP-A), Fe_3O_4@PPy@Pt-B (FPP-B), and Fe_3O_4@PPy@Pt-C (FPP-C) photo-catalysts at room temperature

In order to reveal more clues to explain that phenomenon, the Hall effects are measured for those catalysts as the hydrogen evolution reaction is intrinsically an electron transfer process. The catalysts exhibit different response to the external magnetic field which varied from -1.0 to 1.0 Tesla (Fig. 1 (d). Photo-generated electrons endure higher Lorentz force in Fe_3O_4@PPy@Pt-A but less Lorentz force in Fe_3O_4@PPy@Pt-C under magnetic field, because the Hall resistance originates from the Lorentz force acting on the electrons. The charge transfer process for the photo-catalytic HER over Fe_3O_4@PPy@Pt is closely associated to different magnetic-electronic coupling effect caused by the intrinsic magnetic characteristics of catalyst: the electrons in Fe_3O_4@PPy@Pt-C are less likely to be deflected from their original motion path, whereas the electrons endure more resistance when they transmitted in the Fe_3O_4@PPy@Pt-A. Furthermore, it has been found that the magnetic field could control the space-charge density of electrons beam in materials, but the maximum current could only be obtained at a suitable optimum magnetic field [18]. Fig. 1 (a) and (c) indicates that in the reactive system, the Fe_3O_4@PPy@Pt-C with weaker Hall effects could provide suitable magnetic nature for enhancing the space-charge density of photo-generated electrons. The electrons then have higher migration rate when they are transferred from the excited dye to Pt active sites for proton. Owing to such effective magnetic-electronic coupling, the Fe_3O_4@PPy@Pt-C catalysts exhibits better charge-separation efficiency and higher hydrogen production. In addition, even some electrons close to the Pt dots may be deflected from the Pt dots if the Lorentz force is too large, thus further decreasing the proton reduction efficiency over the Pt dots. The Hall effects of ternary catalysts could also be supported by their photo-current (Fig. 1 (d)) that the catalyst with higher *Ms* value exhibits lower photo-current. Fe_3O_4@Pt catalyst is also prepared in this work to compare with the properties of Fe_3O_4@PPy@Pt photo-catalysts. In consistent with the Hall effect results, the Fe_3O_4@PPy@Pt-A exhibits higher photo-current than the Fe_3O_4@PPy@Pt-B and Fe_3O_4@PPy@Pt-C photo-catalysts, indicating larger scale of electron transferring from the PPy to Pt dots inside the PPy layer (Fig. 1 (d)). So the Fe_3O_4@PPy@Pt-A doesn't exhibit higher photo-catalytic performance though it has stronger magnetic characteristic.

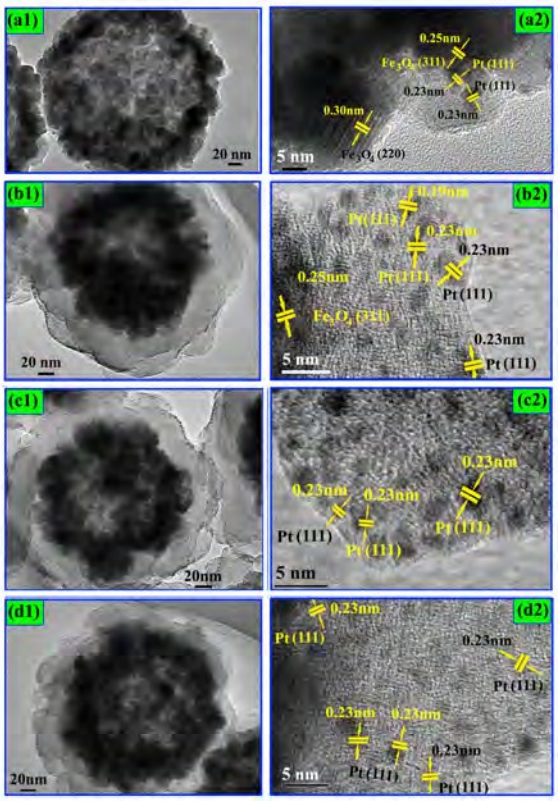


Fig. 2 TEM image and HRTEM image of (a) Fe_3O_4@Pt, (b) Fe_3O_4@PPy@Pt-A, (c) Fe_3O_4@PPy@Pt-B, and (d) Fe_3O_4@PPy@Pt-C

As shown in Fig. 2 (b1, c1, d1)), Fe_3O_4 hollow microspheres are encapsulated by the polypyrrole (PPy) matrix to build the core-shell structure of photo-catalysts. The Pt nano-dots locate inside the PPy matrix to form a PPy@Pt composite layer. Pt NPs in PPy shell were all synthesized at the same reaction condition by microwave method to make the Pt NPs have approximate

particle size, as shown in HRTEM images (Fig. 2 (b2, c2, d2)). The dots are less than 3 nm and they distributed uniformly in the PPy layer to form a homogeneous metal-polymer network.

It is interesting to find that the Pt dots mainly expose their (111) crystal plane in the PPy layer, as shown in Fig. 2 (b2), (c2), (d2). The oriented growth of Pt nano-crystals has also been found in the graphene-based catalysts[19]. It seems that the matrix with abundant delocalized electron (such as the graphene and PPy) could induce the Pt nano-crystals growing preferentially to expose their (111) facets. Compared with the Pt (200) facets, the (111) facets of Pt have higher energy and better photo-catalytic performance for visible-light-driven H_2 evolution[20,21].

The HRTEM results are well supported by their XRD patterns (Fig. 3 (a)) and XPS spectra (Fig. 3 (b)). Due to their small size, the diffraction of Pt dots is not obvious in the XRD pattern (Fig. 3 (a)). The Fe_3O_4@PPy@Pt-A, Fe_3O_4@PPy@Pt-B and Fe_3O_4@PPy@Pt-C have approximate Pt 4f binding energy, indicating that the Pt dots in the three catalysts are in similar chemical environments. The Raman spectra reveal more structural information for recovering the magnetic influence on charge transfer in the composite structure (Fig. 3 (c)). The strong band at 1560 cm^{-1} is assigned to the C=C conjugated bonds, which could provide the PPy layer with abundant delocalized electrons[22]. C 1s spectra of the catalysts also indicate that the surface of PPy shell are mainly composed of C=C conjugated bonds (Fig. S7). The PPy layer could therefore act as the transfer medium for the photo-generated electrons in dye-sensitized hydrogen evolution reaction. Besides, in this work, the PPy molecules are synthesized by oxidative polymerization of pyrrole molecule. In Fig. 3 (c), the bands at 981 cm^{-1} is assigned to the bipolaron groups, which clearly confirm the oxidation state of PPy layers[23]. The oxidization could further improve the electrical conductivity of PPy layers[23,24]. Due to effective interfacial electron transfer from the excited EY* to the PPy@Pt shell, the EY luminescence quenched obviously in the presence of ternary catalysts (Fig. 3 (d)).

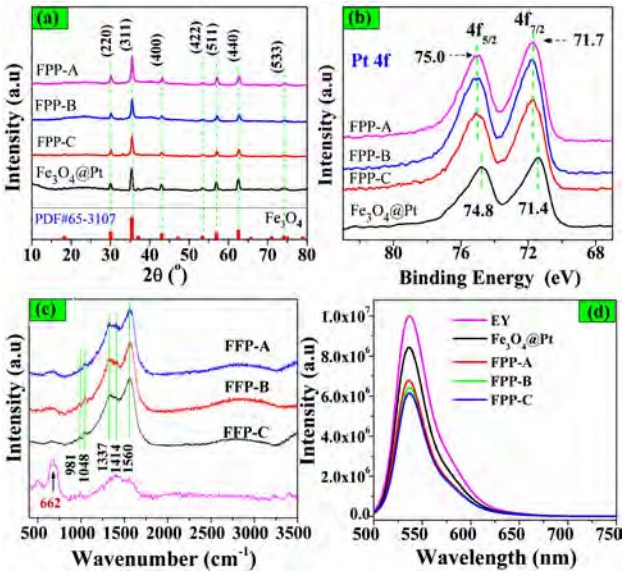
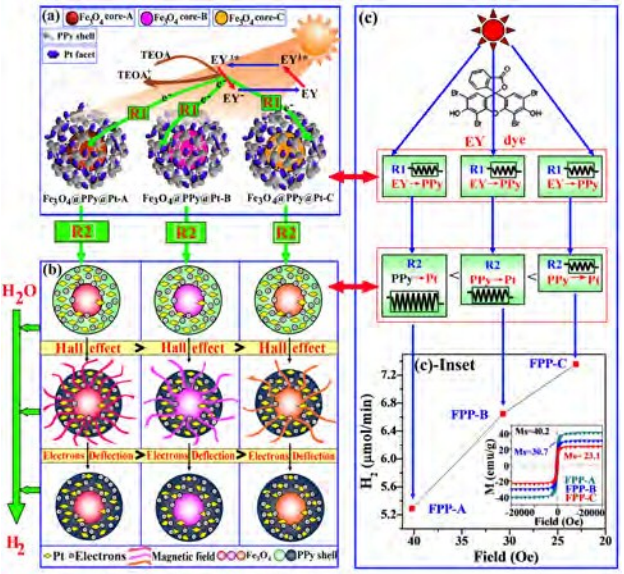


Fig. 3 (a) X-ray diffraction (XRD) patterns (b) Pt 4f spectra, (c) Raman spectra of Fe_3O_4@Pt, Fe_3O_4@ PPy@Pt-A, Fe_3O_4@ PPy@Pt-B, and Fe_3O_4@PPy@Pt-C (d) Photo-luminescence of EY, EY-Fe_3O_4@Pt, EY-Fe_3O_4@PPy@Pt-A (FPP-A), EY-Fe_3O_4@PPy@Pt-B (FPP-B), and EY-Fe_3O_4@PPy@Pt-C (FPP-C)

The PPy@Pt layers play an important role in improving the photo-catalytic activity of the ternary catalysts. The Raman spectra also indicate the PPy@Pt shell could "hide" the Fe_3O_4 core as the Fe-O stretching vibration at 662 cm^{-1} becomes much weaker than the Fe_3O_4@Pt catalyst (Fig. 3 (c)). It has been found that the surface defects of Fe_3O_4 microspheres could quench the photo-generated electrons and lead to poor hydrogen evolution efficiency of Fe_3O_4@Pt catalyst[18]. In consequence, higher catalytic activity of the ternary catalysts could also be attributed to the insulation effect of PPy@Pt layer because the layer can protect the photo-generated electrons from being quenched by the surface defects of Fe_3O_4. In the 2nd run, hydrogen evolution over the Fe_3O_4@PPy@Pt-C catalyst revived to 95.2% while that over the Fe_3O_4@Pt only recovered to 83.5%. Better catalytic stability of the Fe_3O_4@PPy@Pt could also be assigned to the advantages of PPy@Pt layer. The PPy@Pt layer is able to protect the Fe_3O_4 core from acid or alkali corrosion. In addition, the Pt dots could be fixed more stably on the catalysts as they are “grasped” by the PPy shell.



Scheme 1 Charge transfer in the Fe_3O_4@PPy@Pt catalysts (a) **Process 1**, the electron transferring from EY* to PPy layer (Photo-catalytic dye sensitization mechanism); (b) Magnetic disturbance on the electron transferring from PPy to Pt dots (Process 2); (c) Equivalent circuit of photo-catalytic reaction; (Inset of c) Relationship between the saturation magnetization and H_2 evolution

`As illustrated in Scheme 1, there exist two electron transfer process during the hydrogen evolution, including the electron transferring from EY* to PPy layer (**Process 1**, EY*→PPy, scheme 1 (a)), and then the electron transferring from the PPy to Pt dots inside the PPy layer (**Process 2**, PPy→Pt, scheme 1 (b)). The photo-currents from the two electron transfer processes will encounter various disturbances, which could be regarded as the electronic resistance for electron transferring. Those resistances are marked as “**R1**” and “**R2**” respectively for **Process 1** and

Process 2. As shown in scheme 1 (c), the **R1** and **R2** are connected in series. In Fig. 1 (c), quenching efficiency is 68.5%, 64.5%, and 61.7% for Fe_3O_4@PPy@Pt-A, Fe_3O_4@PPy@Pt-B and Fe_3O_4@PPy@Pt-C catalysts, respectively. The approximate quenching efficiency indicates that in **Process 1**, the three catalysts have approximate electron-transfer efficiency and electrical resistance (**R1**). The variation of photo-currents (Fig. 1 (d)) could be assigned to different electron-transfer efficiency of **Process 2**. In **Process 2**, the photo-generated electrons are transferred from PPy layer to the Pt dots for hydrogen evolution. The photo-catalyst with larger *Ms* value has stronger Hall effects on the photo-generated electrons. Higher Lorentz force could slow down the migration speed of electrons by higher Lorentz force and aggravate the deflection of electrons from their original transfer path, thus depressing the transfer efficiency of electrons. So the photo-currents encounter larger resistance (**R2**) when they move in the Fe_3O_4@PPy@Pt-A and Fe_3O_4@PPy@Pt-B than in the Fe_3O_4@ PPy@Pt-C catalysts. In addition, even some electrons close to the Pt dots may be deflected from the Pt dots if the Lorentz force is too large. As a result, intrinsic magnetic characteristic of the photo-catalysts become the key factor in regulating the electron-transfer process and H_2 evolution efficiency.

In summary, super-paramagnetic ternary catalysts have been prepared for dye-sensitized H_2 evolution visible light irradiation ($\lambda \geq 420$ nm). Due to the electron transfer effect of PPy shell, the Fe_3O_4@PPy@Pt catalyst exhibited higher activity for hydrogen evolution than the catalyst without conductive shell. Moreover, this is the first time to build an appropriate architecture to detect whether the magnetic property of the catalysts have effect on their hydrogen generation in the research field of dye-sensitized hydrogen generation. Intrinsic magnetic characteristics of the Fe_3O_4@PPy@Pt catalyst have remarkable effect on the hydrogen generation by accelerating the photo-electron transfer in the charge transfer medium. Only an appropriate magnetic nature can effectively enhance the electron-transfer rate and promote the reaction of water electrolysis. The deflection and migration of photo-electron could be regulated easily by tuning the magnetic nature of photo-catalysts. Such electro-magnetic coupling could effectively enhance the visible-light-driven H_2 evolution over the magnetic photo-catalysts.

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Notes and references

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