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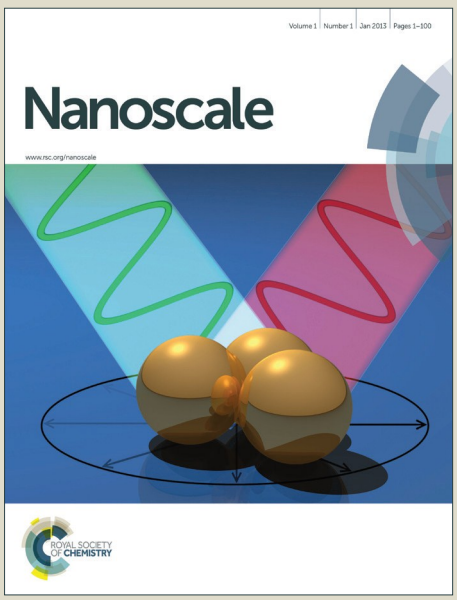

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White-Light-Emitting Magnetite Nanoparticle-Polymer Composites: Photonic Reactions of Magnetic Multi-Granule Nanoclusters as Photothermal Agents

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Magnetite nanoparticles combined with polymers produce white light emission under multiphoton laser irradiation. Understanding the photonic reaction in magnetite-polymer composites is critical for application of the magnetite NPs as photothermal agents. Laser irradiated magnetite nanoparticles-poly(methyl methacrylate) (PMMA) composites exhibit fluorescence due to the carbon double-bond formation resulting from the oxidation of the PMMA.

Magnetic nanoparticles (NPs) are emerging as important multifunctional agents for various applications in nanobiotechnology, as well as memory devices due to their good superparamagnetism, favorable water dispersion properties, potentially good biocompatibility, and tailored surface chemistry.[1-4]

Since most research efforts have been focused on the unique electromagnetic properties of magnetic NPs, their behavior under an electromagnetic field has been studied in detail.[5,6] However, the response of magnetic NPs to laser irradiation is not yet fully understood, since only a few studies on the phenomenological analysis of the photothermal and photodynamic therapies in the biomedical field have been reported to date.[3,7-9]

Recent research regarding the photothermal therapy has been focused on investigating reagents for the simultaneous therapy and *in vivo* imaging, most of which employ plasmonic NPs.[10-13] The materials properties of efficient and stable photothermal agents must satisfy three conditions: large photon absorption cross-section, strong intraparticle interactions, and strong bonding to any surfactant.[14] Therefore, plasmonic gold (Au) NPs have been used in many systems as photothermal agents due to their adjustable optical characteristics, efficient heat generation, and potential biocompatibility.[3,15-19] However, Au NPs have a low luminous efficiency at a relatively strong absorption, and exhibit poor thermal stability due to the relatively weak metal-metal interactions at the high temperatures generated by the photothermal effect. These issues can cause variations in the NP distribution and morphology, as well as the destruction of the ligands attached to the Au NP surface, which will ultimately result in a loss of heat control at a molecular level from the photothermal Au NP-containing systems.[14,20,21] Moreover, nanosized Au can be a potential risk factor due to its accumulation inside the human body,[22] and thus, semiconductor NPs have been proposed as an alternative to Au NPs.[23-25] In particular, magnetite NPs exhibit better stability and *in vivo* compatibility than Au NPs at high temperature, and satisfy the required conditions for photothermal agents described earlier.[14] A recent study confirmed that magnetite NPs could be used as excellent photothermal agents due to their strong heat generation under NIR irradiation.[8] In a previous study, we reported the preparation of multifunctional magnetic NPs such as Fe_3O_4-ZnO core-shell NPs, self-assembly of Fe_3O_4-coordination polymer nanochains, and magnetic NPs conjugated with a photosensitizer.[26-28] Magnetic-PMMA composites are mainly used for the thermosensitive drug delivery and cell separation systems. They possess a high drug delivery efficiency due to their enhanced permeability, simple surface modification, surface stability, low toxicity, and *in vivo* biocompatibility.[29,30] In addition, PMMA-containing photodynamic systems produce photonic reactions due to a thermal effect. Therefore, understanding the characteristic variations of the magnetite NP-PMMA composites produced by the photothermal effect is essential.

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Electronic Supplementary Information (ESI) available: Detail experimental process and additional results of photonic reactions are presented. See DOI: 10.1039/x0xx00000x
‡These authors made equal contributions to this study.

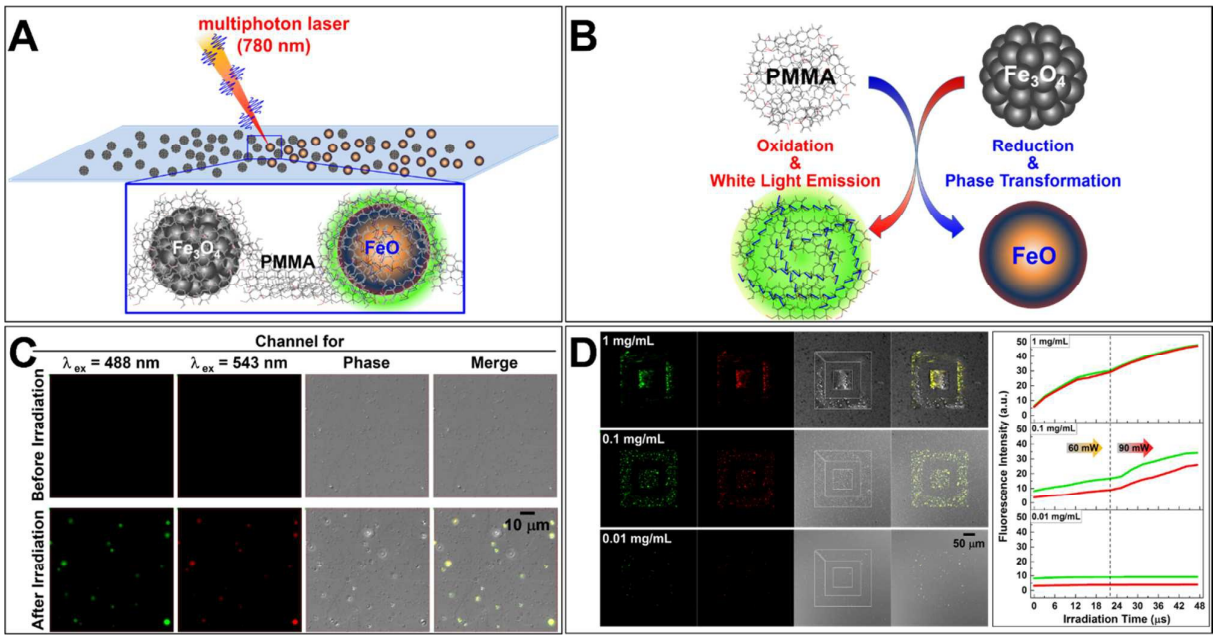

Fig. 1 White light emission by the MGNC–PMMA composites under 780 nm multiphoton laser irradiation photonic stimulus. (A) A schematic representation of the photonic reaction of the MGNC–PMMA composites. (B) A diagram illustrating the photonic reaction in magnetite and PMMA polymers induced by the photothermal effect. (C) Fluorescent images of the MGNC–PMMA composites (concentration: 0.1 mg/mL) before and after the 780 nm multiphoton laser irradiation. (D) Emission intensity depends on the MGNC concentration. The fluorescent images depicted in panels C and D are measured at the magnifications of 100X and 20X, respectively; the areas inside the white boxes in panel D were partially subjected to irradiation by a 780 nm multiphoton laser.

PMMA is a well-known polymer that can undergo structural modifications due to thermal stimulus and electron irradiation. However, there are only a few studies on the stability and properties of the magnetite-PMMA composites subjected to photonic irradiation, while the investigation of the photonic reactions of the magnetite-PMMA composites could be beneficial for theranostic applications.[7]

In this study, we report the photothermal effects produced by NIR-sensitive magnetic MGNC NP-polymer nanocomposites, which result from the interaction between the magnetic multigranule nanoclusters (MGNCs; 100 nm in diameter) and the 780 nm multiphoton laser irradiation. We demonstrate for the first time the generation of a strong luminescence by photothermal effect-induced thermal degradation and oxidation of the PMMA chains.

Multiphoton confocal microscopy (LSM 710 NLO confocal microscope, Carl Zeiss) was used to investigate the MGNC-polymer complexes. UV-visible spectroscopy (UV-Vis: UV-Vis-NIR spectrophotometer, Cary 5000, Agilent Technologies), Raman spectroscopy (LabRam ARAMIS IR2, Horiba Jobin Yvon), X-ray photoelectron spectroscopy (XPS: X-Tool, ULVAC-PHI), transmission electron microscopy (TEM: JEM-2100F, JEOL), and X-ray diffraction (XRD: D/Max-2500, Rigaku) were used to study the structural modifications of the nanocluster-polymer complexes.

Figures 1A and B schematically describe the experimental setup used for the white-light-emitting systems and the photonic reactions (including oxidation of the PMMA polymer and reduction of the MGNC) of the nanocomposites through the magnetite-based photothermal effect. The photothermal effect of magnetite induced by the 780 nm multiphoton laser irradiation results in a continuous heat generation; and the oxidation, resulting in thermal degradation of the PMMA polymer around the particles, leads to the emission of green and red luminescence (Figure 1C). Figure 1D displays the differences in luminescence intensity using different particle concentrations indicating that the latter is an important factor in determining the light emission intensity under multiphoton laser irradiation with a constant power intensity. After different compounds were tested under these conditions, the obtained fluorescence intensity in the visible range increased with the PMMA degradation, which indicates that the white-light emitted by the PMMA is due to the creation of new luminescence centers formed by the photothermal and photochemical reactions. In order to investigate this previously unknown phenomenon, various conditions were studied. However, no significant emission was observed for both the PMMA and Au NP-PMMA composites using low-power multiphoton laser irradiation (Figure 2A and B). In particular, the MGNC-PMMA composites present a green and red fluorescence intensity 10 times stronger than that of the Au NPs-PMMA composites and PMMA after 60 mW irradiation using a 780 nm multiphoton laser.

The Au NPs also emit luminescence due to the photothermal effect, but they require significantly higher levels of multiphoton laser irradiation (10 times stronger or more). These results indicate that the white-light emission originates from the thermal degradation and oxidation of the PMMA depending on the heat generation of the laser-irradiated sample. In addition, the light emission shown by the

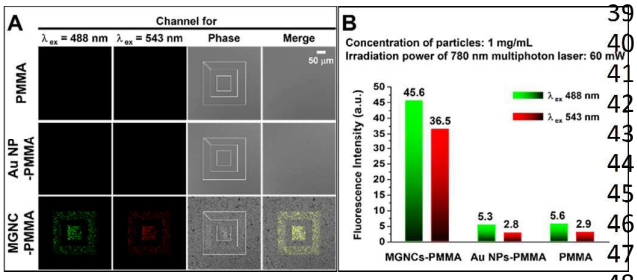

Fig. 2 Comparison of the fluorescence emission properties for various composite materials. (A) In contrast to the PMMA and Au–PMMA composites, the MGNC–PMMA composites were luminous in the entire visible range under identical irradiation conditions (780 nm multiphoton laser power: 60 mW) (top row: PMMA, mid row: 1 mg/mL of the Au–PMMA composites, bottom row: 1 mg/mL of the MGNC–PMMA composites). (B) Fluorescence intensities of the MGNC–PMMA composites, Au NP–PMMA composites, and PMMA polymer, respectively, under identical conditions.

PMMA and Au NP-PMMA composites is produced by the multiphoton laser irradiation, which requires higher energies than those for the MGNC-PMMA composites (see Electronic Supporting Information, Figure S1). Thus, magnetite NPs can be used as efficient heat-generating agents due to their ability to accumulate energy under low-power 780 nm multiphoton laser irradiation.

The heat generation due to the photothermal effect of the magnetite NPs and the reduction of Fe ions in magnetite NPs together with the oxidation of PMMA polymer imparted morphological and crystal structure modifications to the granule cluster particles from magnetite (Fe_3O_4) to wüstite (FeO). The transformation of the metastable wüstite phase after the 780 nm multiphoton laser irradiation was confirmed using XRD analysis (Figures 3A and B). The TEM measurements reveal a morphological and crystallographic structural modification in the MGNCs (Figure 3A), showing that the MGNC characteristics corresponding to the multi-granule geometric and polycrystalline structures disappear after the 780 nm multiphoton laser irradiation, which is possibly due to a modification of the MGNCs phase or composition. The observed crystallization results from the conformational changes due to sintering at high-temperature. The XRD analysis (Figure 3B) shows a noticeable increase in the (200) peak intensity and decrease in the (311) peak intensity after irradiation, which correspond to the wüstite and magnetite phases, respectively.[31] This is consistent with the heat generation by the MGNCs due to the low-power 780 nm multiphoton laser irradiation (the overall relative intensities of the other XRD peaks remained mostly unchanged). The temperature near the focusing area was elevated high enough to cause sintering and phase transformation when the magnetite MGNCs absorbed laser energy. As previously known, the phase transformation from magnetite to wüstite requires high temperature, and sintering process of magnetite granules can occur below the phase transformation temperature.[32] In case of our experiments, PMMA polymer which covers the surface of magnetite nanoparticles can induce reduction of magnetite nanoparticles to wüstite nanoparticle with phase transformation.

Furthermore, the observed luminescence can be explained by the fact that the excitation wavelength-dependent luminescence spectra reflects the distribution of the emission sites interacting with the carbon chains of the thermally deformed PMMA polymers. It has been recently reported that the white-light emission originates from the band gap created by possible modifications or recombination of the carbon chains.[33-35]

It has been reported that carbon nanostructures are characterized by high fluorescence quantum yields produced by irradiation in the ultraviolet region, and thus exhibit an excitation wavelength-dependency with the fluorescence emission intensity.[36,37]

Therefore, the thermal degradation and oxidation of the carbon bonds in the PMMA species attached to the MGNC surface are strongly correlated with the luminescence emitted over the entire visible range. To investigate this luminescence in more detail, the UV-Vis absorption and photoluminescence (PL) emission spectra of the MGNC-PMMA composites were measured using a UV laser as the excitation source. As shown in Figure 3C, the PMMA and MGNC-PMMA films before irradiation are characterized by lower absorbance values than those obtained with the multiphoton laser irradiated MGNC-PMMA composite films. However, the latter exhibit a significant increase in the absorption intensity in the region between 380 and 600 nm, which indicates the creation of a new electronic band structure with distinctive luminous characteristics for the multiphoton laser irradiated MGNC-PMMA composite films.[34]

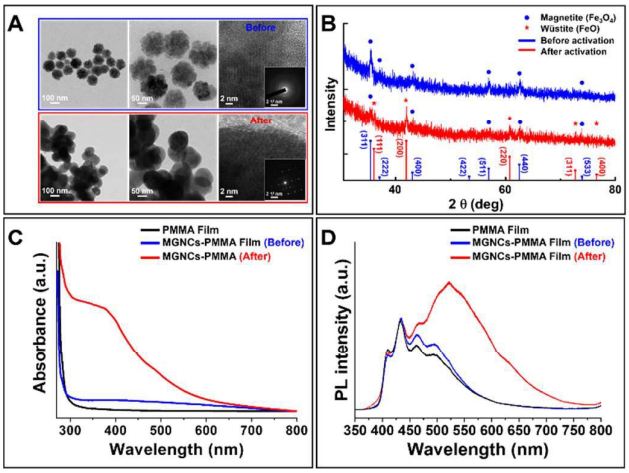

Fig. 3 Structural and optical analysis of the MGNC–PMMA composites before (blue lines) and after (red lines) the laser irradiation. (A) TEM images of the MGNCs. (inset is a selected area electron diffraction pattern from both of MGNCs before and after irradiation) (B) XRD patterns of the MGNC–PMMA composites. The magnetite (JCPDS No. 19-0629) and wüstite (JCPDS No. 46-1312) peak positions are denoted in the bottom part of the figure by the blue and red vertical lines, respectively. (C) UV-Visible absorption spectra of the MGNC–PMMA composites and PMMA film. (D) PL spectra of the MGNC–PMMA composites and PMMA film at the excitation wavelength of 325 nm.

To study the optical properties of the MGNC-PMMA composites, PL experiments were performed in the range between 400 and 800 nm using a 325-nm He-Cd laser. Figure 3D shows the PL spectra for the PMMA and MGNC-PMMA composite films before and after the multiphoton laser irradiation. The MGNC-PMMA composite after irradiation is uniquely characterized by a broad PL peak spreading across the entire visible light region and centered at 520 nm, which is very similar to the one previously reported for carbon-based nanostructures.[33,36] The emission across the entire visible range spectrum can be explained by the formation of conjugated chemical bonds in the polymers under UV irradiation.[38] Thus, this drastic absorption increase in the UV-Vis range (Figure 3C) can result from the formation of structures associated with a new carbon bond state corresponding to the broad PL spectrum. In order to determine whether the luminescence was produced by the modifications in the carbon chains, the conformational changes in the PMMA polymer have to be analyzed.

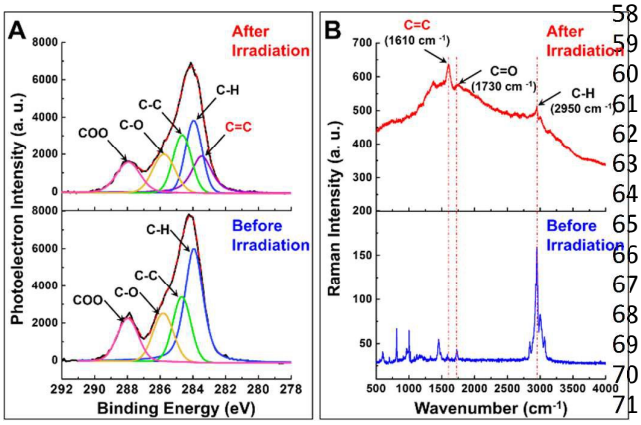

Fig. 4 (A) XPS C 1s spectra of the MGNC−PMMA composites before and after the laser irradiation. (B) Raman spectra of the MGNC−PMMA composites before (blue lines) and after (red lines) the laser irradiation.

To confirm the formation of π-π bonding, XPS spectra of the nanocomposites were obtained before and after the 780 nm multiphoton laser irradiation (Figure 4A). The observed variations in the main C 1s peak centered at a binding energy of 283.46 eV indicate that the intensity of the C=C bond increased after the 780 nm multiphoton laser irradiation, while the intensities of the other carbon components decreased. The obtained XPS results suggest that the photonic reaction of the polymer under the 780 nm multiphoton laser irradiation leads to cleavages of both C-C and C-H bonds with the subsequent formation of C=C bonds from thermal degradation, which in turn result in π-conjugation. Thus, the white-light emission (with a maximum centered at 520 nm) can be attributed to the formation of C=C bonds resulting from the polymer degradation on the surface of the magnetic NPs.

To demonstrate further the carbon bonds of the sample, Raman spectra of the MGNC-PMMA composite were obtained before and after the 780 nm multiphoton laser irradiation (Figure 4B). Supporting the XPS analysis, Raman measurement allows to determine the variation of C=C bonding between both of the MGNC-PMMA composites. Raman signatures exhibit a powerful ability to verify the vibrational symmetric stretch of functional group such as the C = C bond. Moreover, the Raman signatures of PMMA polymer are established well. In figure 4B (lower graph), there are several Raman signatures for the PMMA polymer at 601 cm^{-1} (υ(C–COO), $υ_s$ (C–C–O)), 809 cm^{-1} (υ(C–COO)), 967 cm^{-1} (υ(C–COO)), 995 cm^{-1} (O–CH_3 rock), 1452 cm^{-1} ($δ_a$(C-H) of α-CH_3, $δ_a$(C-H) of O-CH_3), and 2950 cm^{-1} ($ν_s$(C-H) of O-CH_3, $ν_s$(C-H) of α-CH_3, and $ν_a$(CH_2)).[39] Specifically, Raman signatures assigned to C=C bonds and carbonyl functional groups exhibited a substantial variation at 1610 and 1730 cm^{-1}, respectively. A Raman spectrum of irradiated MGNC-PMMA composites shows broad baseline in Figure 4B (upper graph). Because the Raman spectrum was obtained using 532 nm laser as an excitation source, the broad baseline is photoluminescence background from the irradiated sample. Nevertheless, Figure 4B (upper graph) shows the Raman signature at around 1610 cm^{-1}, assigned to the carbon sp^2 bonding, which increases remarkably after the 780 nm multiphoton laser irradiation[40] indicating that the rearrangement of the polyacetylene-like backbone chains (C=C bonding) in π-conjugated polymers promotes the formation of π-π bonding structures, while the conjugated chemical bonding in polymers might produce a white-light emission under UV irradiation.[38] Thus, the formation and rearrangement of the π-conjugated polymer chains are caused by the interaction between the MGNCs and PMMA polymer in the MGNC-PMMA composite irradiated by the 780 nm multiphoton laser (see Electronic Supporting Information, Figure S2).

In this study, we demonstrated that the white-light emission of a MGNC−PMMA composite could be enhanced by multiphoton laser-related interactions. The 780 nm multiphoton laser-irradiated MGNC−PMMA composites emit a bright full-spectrum visible light with a dominant peak at 525 nm, which is associated to the formation of C=C bonds due to the photothermal and photochemical transformations of the polymer. The mechanism of this white-light emission is not yet fully understood; however, the π-conjugation induced by the polymer degradation, as well as the PMMA chain oxidation under the influence of the heat generated due to the photothermal effect of the MGNCs can be suggested.

The MGNCs can widen the scope of applications using the photothermal therapy because they possess excellent heat-generation properties with non-invasive and good penetration characteristics under low-power 780 nm multiphoton laser irradiation. The findings reported in this study suggest that the MGNCs can be potentially used as efficient photothermal agents in the field of cancer therapy. In addition, the generation of white-light by the MGNC−polymer composites can offer new strategies for the preparation of flexible displays and photovoltaic devices.

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