Novel TiO$_2$ Based Photocatalyst Utilizing Crystalline Graphene as a Platform

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TiO$_2$, a well-recognized photocatalyst, has been studied extensively over many decades for its potential applications in solar energy conversion, water splitting, environmental pollutant degradation, and water treatment [1]. The reason TiO$_2$ has been studied so intensively is due to the merits of its efficient photocatalytic properties, as well as its high chemical stability, non-toxicity, and low cost. However, there is one major obstacle which hampers the practical application of TiO$_2$. Photo-generated electron-hole pairs of TiO$_2$ have a flash recombination time on the order of 10^{-9} s, while the time of chemical reaction of TiO$_2$ with adsorbed pollutants is in the range of 10^{-8}–10^{-3} s [1]. To overcome the above obstacle, in this present study we used exfoliated highly crystalline few-layer graphene as a platform and electron acceptor for separating the photoexcited electron-hole pairs, with the goal of delaying the recombination and increasing the available photoinduced holes for oxidizing organic pollutants [2].

Crystalline graphene supported TiO$_2$ nanocrystals (NCs) were prepared via a simple chemical process at a temperature of 180°C using titanium (IV) butoxide and expanded graphite as precursors and isoproponal as a solvent, as shown in Fig. 1a. We noted that some of the attached TiO$_2$ NCs were nanocubic with an average size of about 25 nm. A high resolution TEM image (Fig. 1b) shows a typical TiO$_2$ NC is well crystallized with a lattice spacing of 0.35 nm, corresponding to the (101) plane of anatase TiO$_2$. Considering that anatase TiO$_2$ adopts a tetragonal structure with lattice parameters $a = b = 0.377$ nm and $c = 0.950$ nm, the square surface in the crystal structure can be assigned to {001} facets. A SAED pattern (Fig. 1c) shows the diffraction rings that are coincident with anatase TiO$_2$ (101), (004), (220), (105), (211) and (204) from inner to outer, respectively. Fig. 1d shows the XRD patterns of graphene-TiO$_2$ composite. The reflection peaks of pristine exfoliated graphene at 26.4° and 54.5° could be assigned to the (002) and (004) planes of hexagonal graphite. The remaining nine reflection peaks correspond to anatase TiO$_2$ (JCPDS card No.21-1272). EDX revealed the presence of titanium and oxygen in the hybrid (Fig. 1e). Fig. 1f shows a typical Raman spectrum of a graphene-TiO$_2$ sample. The line shape of the 2D band can be analyzed to determine the number of graphene layers. The 2D peak was fitted (Fig. 1f, inset) and then compared with the results of Graf *et al* [3] to identify the graphene is three layer.

Another obstacle which limits the practical application of TiO$_2$ is the difficulty of removal when applying these particles in solution media [4]. To solve this problem, we utilized a two-step deposition process to hybridize graphene with both TiO$_2$ and Fe$_3$O$_4$ NCs, enabling the photocatalyst to be magnetic and can be retrievable by applying external magnetic field. Fig. 2a–c shows the XRD, TEM image and hysteresis loop, respectively. The XRD pattern in Fig. 2a exhibits two extra reflections-- characteristic of (220) and (311) planes from cubic inverse spinel phase Fe$_3$O$_4$ (JCPDS card No. 65-3107)--as compared with XRD pattern of graphene/TiO$_2$ hybrid (Fig. 1d). These results confirmed that the Fe$_3$O$_4$ NCs were deposited on the graphene surface. A low magnification TEM image in Fig. 2b further reveals that particles of a high density are well attached to the graphene substrate. The hysteresis loop (Fig. 2c) suggests that the sample is superparamagnetic with no residual magnetization. The inset photograph demonstrates that the graphene-TiO$_2$&Fe$_3$O$_4$ sample is well redispersed in water as shown in the vial on the left. When a magnetic field is applied (right vial), the suspended graphene agglomerates against the side wall, indicating a strong magnetic response.

References:

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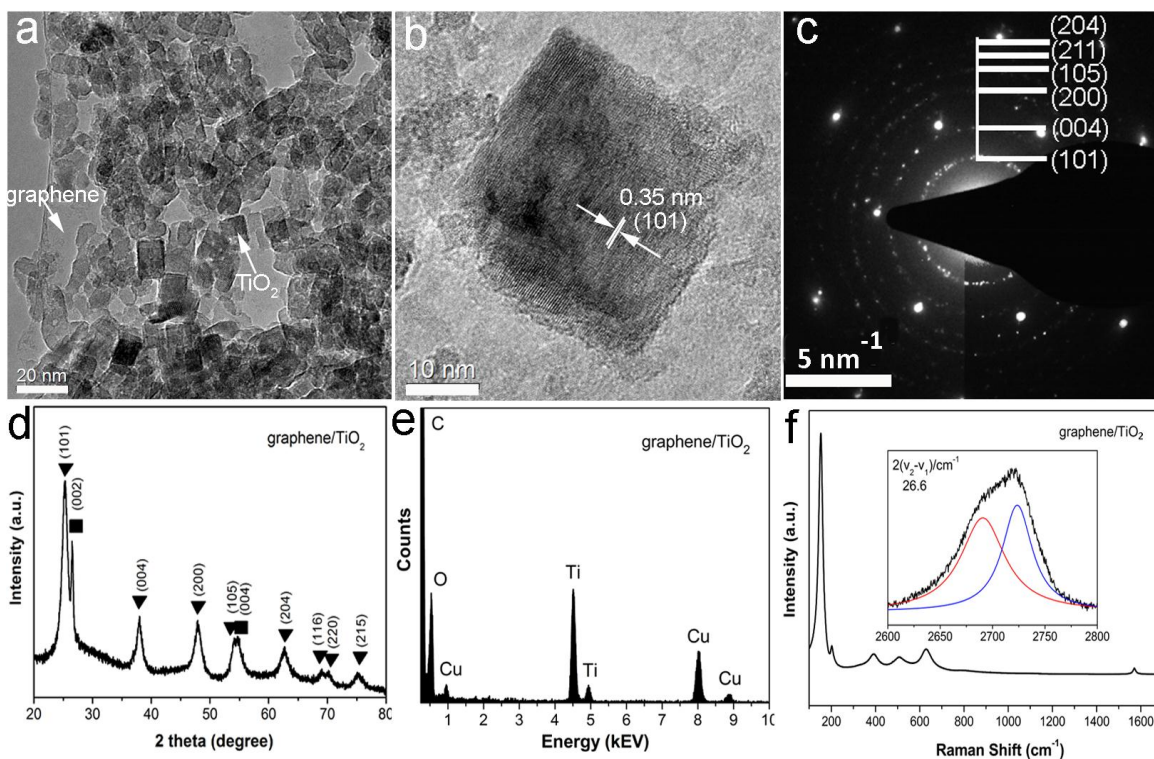
Figure 1. Graphene/TiO_2 hybrids prepared at 180°C. (a) TEM image of samples with reaction times of 12h; (b) HRTEM image of deposited TiO_2 NCs; (c) corresponding SAED pattern; (d) XRD pattern of graphene/TiO2 hybrids; (e) typical EDX pattern of deposited TiO_2 NCs; (f) Raman spectrum of sample with 2D peak fitting (inset).
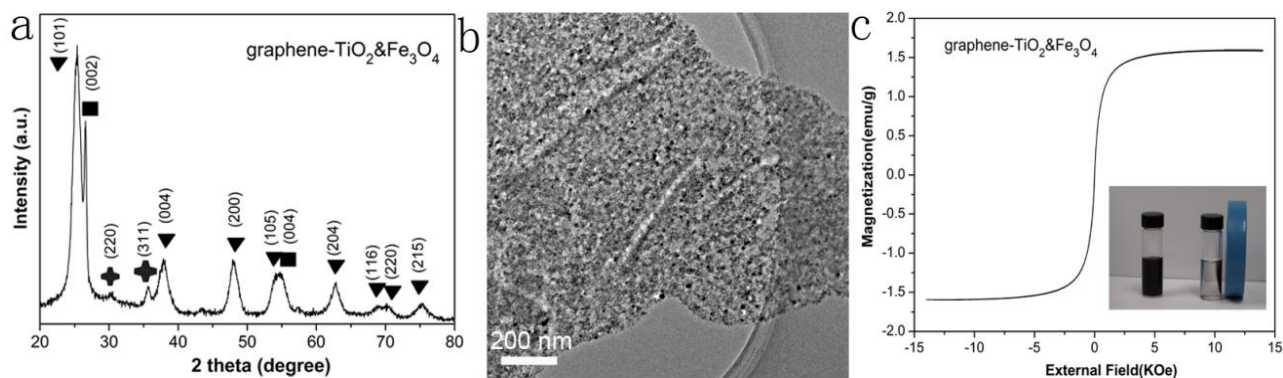
Figure 2. Comprehensive analysis of graphene-TiO_2&Fe_3O_4 composites prepared at 180°C via two-step deposition. (a) XRD pattern of graphene-TiO_2&Fe_3O_4 composites; (b) representative TEM image; (c) typical hysteresis loop of graphene-TiO_2&Fe_3O_4 composites. The inset photograph shows quick response of composite redispersed in water to a magnet.